Techno-economic feasibility of producing biodiesel from acidic oil using sulfuric acid and calcium oxide as catalysts

S. N. Gebremariam and J. M. Marchetti*

Faculty of Science and Technology, Norwegian University of Life Sciences, Drøbakveien 31, 1432, Ås, Norway.

* Corresponding author
Email address: Jorge.mario.marchetti@nmbu.no (J. M. Marchetti)
Tel: +47-67231647.

Abstract

Biodiesel is becoming one of the best alternative fuels to substitute conventional diesel fuel for its environmental and fuel benefits. However, its full-fledged substitution to conventional diesel is hindered mainly due to its high cost of production. More than 85% of the production cost is attributed to feedstock cost. This forces to look for alternative feedstock at lower cost, which usually do have higher free fatty acid content. A number of investigations have been done to evaluate the technical and economic efficiency of biodiesel production from such acidic oil. Accordingly, in this study, three alternative production processes using two catalysts have been designed for techno-economic analysis. Sulfuric acid (H_2SO_4) catalyzed Transesterification and Esterification of Acidic oil; Calcium oxide (CaO) Catalyzed Transesterification of Acidic oil; and CaO catalyzed Transesterification with Pre-Esterification of Acidic oil with H_2SO_4.

Super Pro design and Aspen Plus softwares were used to perform the conceptual design and simulation of the different alternatives. The techno-economic competitiveness of three different scenarios were evaluated. The technical parameters were amount and quality of biodiesel and glycerol as well as the amount of biodiesel produced per feedstock used. The economic parameters considered were Total Investment Cost, Operating Cost, Unit Cost of Production, NPV, ROI and Payback time. The CaO catalyzed process could show better economic performances.

Keywords: Biodiesel, Techno-economic analysis, H_2SO_4 catalyzed, CaO Catalyzed

Nomenclature

34	ASTM	American Society for Testing and Materials
35	DG	Di-glyceride
36	DFC	Direct Fixed Cost
37	E	Ethanol
38	FAEE	Fatty Acid Ethyl Ester
39	FFA	Free Fatty Acid
40	G	Glycerol
41	IRR	Internal Rate of Return
42	MG	Mono-glyceride
43	NPV	Net Present Value
44	ROI	Return on Investment
45	TG	Triglyceride

1. Introduction

Biodiesel is a mono alkyl ester of long chain fatty acids. It is a renewable fuel produced from oils and/or fats feedstock such as vegetable oil, animal fat, non-edible plant oil, and waste cooking oil, among others. As a fuel, biodiesel possesses a higher number of benefits than conventional petrol diesel. The most referred benefits are environmental ones such as its biodegradability, non-toxicity, emitting insignificant amount of sulfur, emitting less air pollutants and greenhouse gases other than nitrogen oxides. It also has worth mentioning use benefits as a fuel. These include better lubricity (reduce engine wear) and having higher oxygen content (encourage complete combustion).

The commercial practice to produce biodiesel involves homogeneous alkali catalysis of oil feedstock with free fatty acid content of less than 0.5% [1-3]. The higher the purity of the feedstock (lesser amount of FFA) the more expensive it would be, increasing the production cost to the point of making it a non-competitive alternative. Different investigations have been carried out to find alternative technologies for efficient and affordable production of biodiesel. Among such alternatives, the use of cheaper feedstock, cheaper catalyst and efficient production technologies have been considered. The most widely studied alternatives include heterogeneous and homogeneous acid catalyzed [4-9], heterogeneous alkali catalyzed [10-14], Enzyme catalyzed [15-18] and supercritical [19-22] transesterification reactions. There are also few promising but less studied alternative technologies. These include Nano Catalysts [23-25], Nano Immobilized Enzymes [26-28], Ionic Liquid Catalysts [29-31], and membrane reactors among others [32-34].

The studies so far done on the up supra mentioned biodiesel production technologies include those focusing on finding the optimum reaction conditions [2, 35-38], determining the reaction kinetics [39-44], assessing technical efficiencies and evaluating economic performances [45-49] of selected technological alternatives. The technical and economic studies are usually done together as techno-economic analysis. Such studies are typically based on the stated reaction kinetics and optimum reaction conditions determined for max possible biodiesel yield.

Techno-economic study of biodiesel production technologies enable us to compare both technical and economic efficiencies of alternative technologies so that to choose the better performing option(s). The technical performances are usually determined through energy and material balances of the whole production process. Karmee et al. [47] did a techno-economic

93   study on three alternative technologies; base, acid and enzyme catalyzed transesterification for
94   biodiesel production from waste cooking oil. The technical performances of these alternatives
95   were made to be equal in terms of 100% biodiesel yield based on the optimum reaction
96   conditions. This was then used to compare the cost effectiveness of the technologies. A more
97   distinctive technical comparison was made by Marchetti et al. [50] on three biodiesel production
98   alternatives, where the authors evaluated the technical performances based on material balances.
99   The parameters used to compare the technical performances among the technologies were,
100 biodiesel yield, total glycerol in biodiesel (referring the quality), amount of biodiesel produced
101 per amount of raw materials used (referring performance), and yield of co-product glycerol.

102   In another way, the technological assessment can also be done through evaluating the
103 technical benefits and limitations of the alternatives while attaining a given quantity and/or
104 quality of biodiesel. These can include the number of process steps and the number of equipment
105 required to achieve a given quantity and/or quality. This depicts how complex or how simple the
106 whole production process of the alternative technology might be. Zhang et al. [51] assessed the
107 technological performances of four alternative technologies for biodiesel production from waste
108 cooking oil and vegetable oil. The authors used the size and number of equipment used in each
109 process scenario to evaluate their technical performances and found out that the homogeneous
110 alkali catalyzed process using virgin oil was the least sophisticated option requiring less number
111 of process steps and equipment. They also found out that the acid-catalyzed process using waste
112 cooking oil was less complex (requiring less process steps and less number of equipment) than
113 the alkali-catalyzed process using the same oil character [51].

114   The economic performance evaluations should be done based on the results of the
115 technological assessments. There are a number of economic parameters to test if technically
116 efficient production alternative is cost effective or not, given a specified market scenario.
117 Different researchers used different economic indicators. Zhang et al. [52] used total
118 manufacturing cost, fixed capital cost, after tax rate of return and biodiesel break-even price to
119 evaluate the economic performances of four process alternatives. Total investment cost and
120 manufacturing cost are the most widely used economic parameters to have a clue on which
121 technology option is cost effective. West et al. [53] used after tax rate of return as a parameter in
122 addition to total capital investment and total manufacturing cost. However, it is realistic to
123 consider more economic indicators to get deep insight into the profitability and sustainability of

124 the technological options. Marchetti et al. [50] took a number of economic indicators to compare

125 the economic feasibility of three proposed technological options to produce biodiesel from spent

126 oil with 5% free fatty acid. The main parameters were total capital investment cost, total

127 operating cost, NPV, unit cost of biodiesel, IRR, Gross Margin, and ROI.

128   It is obvious that the uncertain parameters (market variables) associated with biodiesel

129 production could have considerably different effect on the techno-economic feasibility of the

130 production process. Zhang-Chun et al. [54] investigated the effects of some parameters in the

131 techno-economic assessments of biodiesel production. These include capital cost, interest rate,

132 feedstock price, maintenance rate, biodiesel conversion efficiency, glycerol price and operating

133 cost. The global sensitivity analysis done to quantify the contribution of each parameter to Life

134 Cycle Cost and Unit Cost revealed that the feedstock price and the interest rate indicated

135 considerable effects on the techno-economic assessment. In another study, Zhang-Chun et al.

136 [55] also indicated that price of biodiesel, price of feedstock, and cost of operating can

137 considerably affect techno-economic assessment of biodiesel production

138   The studies so far done on techno-economic assessment could cover only a limited type of

139 technological alternatives. This triggers a need to investigate the techno-economic performances

140 of more potential technologies for biodiesel production. Therefore, this study was aimed at

141 assessing and comparing the techno-economic performances of biodiesel production from acidic

142 oil using three process alternatives; H_2SO_4 catalyzed transesterification, CaO catalyzed

143 transesterification, as well as CaO catalyzed transesterification with H_2SO_4 catalyzed pre-

144 esterification.

145   A conceptual simulation of the processes were designed using Super Pro design software

146 from Intelligen, Inc. [56] and Aspen Plus software from Aspentech [57]. Using the process flow

147 sheets, a material balance for the total capacity of 41 thousand tons feedstock per year was done.

148 Accordingly, the technical performances were evaluated in terms of the quantity and quality of

149 biodiesel produced, amount and quality of glycerol produced, and the amount of biodiesel

150 produced per raw material consumed. The economic competitiveness of three different scenarios

151 were compared based on the economic parameters such as Total Investment Cost, Capital

152 Investment Cost, Operating Cost, Unit Production Cost, NPV, ROI, and Gross Margin. The

153 economic effects of change of oil cost and biodiesel selling price were also analyzed using NPV

154 as the main economic indicator.

3

2. Reaction Model

The dominant process in the production of biodiesel is the transesterification of the triglycerides. This reaction takes place in three steps sequentially as shown in Figure 1. There are also some side reactions that could take place, depending on the quality of the feedstock considered and the technology employed. The dominant side reactions that can take place, due to the presence of acidic feedstock, are saponification in the presence of base catalyst and esterification in the presence of an acid catalyst. However, the hydrolysis of triglycerides can also take place depending on the water content of the feedstock as well as the amount of water produced during the esterification reaction.
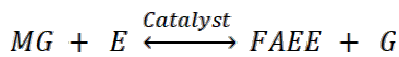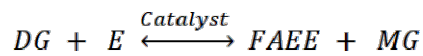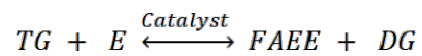
$$TG \ + \ E \ \xrightleftharpoons{Catalyst} \ FAEE \ + \ DG$$

$$DG \ + \ E \ \xrightleftharpoons{Catalyst} \ FAEE \ + \ MG$$

$$MG \ + \ E \ \xrightleftharpoons{Catalyst} \ FAEE \ + \ G$$

Figure 1. The three major reaction steps in catalyzed transesterification of triglycerides with ethanol

In this study, two main catalysts were investigated separately and in combination to find out the most efficient and affordable option(s). Sulfuric acid as homogeneous and calcium oxide as the heterogeneous catalyst. Sulfuric acid was considered because it is the most recommended efficient catalyst for production of biodiesel from feedstock with higher FFA content [58, 59]. Similarly, the CaO catalyst was considered for comparison, because it is the most studied in its catalyzing performance and cheap basic catalyst for biodiesel production, which can be prepared from wastes like eggshell [60, 61]. Ethanol was the alcohol considered in the reactions because it could be produced from renewable resources and it is safe to handle. In all of the study cases, excess ethanol, in terms of molar ratio, was considered in order to favor the forward reaction [35, 62].
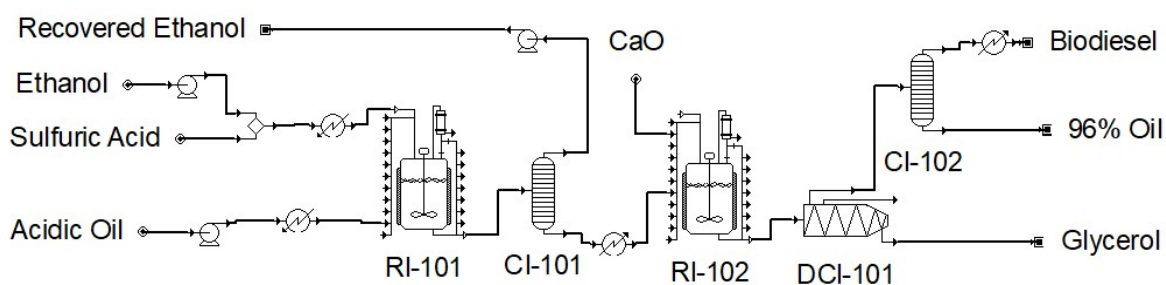
3. Study Models

Three biodiesel production process models based on catalyst options were investigated. Model I: Homogeneous sulfuric acid catalysis; Model II: Heterogeneous calcium oxide catalysis; and Model III: Heterogeneous calcium oxide catalysis with sulfuric acid pre-esterification. The optimum reaction conditions, for all of the process models in this study, were considered from

183 literature [63-65]. All these technological scenarios were considered to be continuous process to
184 fulfill their requirement for industrial scale application. The investigation was made to see the
185 efficient and affordable technological option(s) for production of biodiesel from acidic oil. The
186 oil considered in all of the cases had FFA content of 10% in molar basis. Such feedstock with
187 higher FFA content are cheaper and have potential to reduce the overall production cost. The
188 models presented in this study were based on the simulations done by Super Pro software.
189 However, each technological alternative was redesigned using Aspen Plus software, to
190 substantiate the accuracy of the designs. Aspen Plus provides more choice of physical parameters
191 and methods to select for each specific process considered in the design. And Super Pro design
192 software is also very flexible in executing the economic analysis as it provides easy but detail
193 data entry opportunity. Using the two softwares together would improve the accuracy of the
194 results.

3.1. Model I

196 This model was designed to investigate the production of biodiesel from acidic oil using
197 H_2SO_4 catalyzed transesterification reaction. The process flow diagram is shown in Figure 2.

198 The optimum reaction conditions for the sulfuric acid catalyzed ethanolysis of such acidic
199 oil was taken to be 55°C reaction temperature, 2.1% wt. of catalyst, and 6.1 as molar ratio of
200 alcohol to oil [64]. At these optimum reaction conditions, 97.57% conversion could be achieved
201 in 21 hours [64]. Using these optimum reaction conditions and the rate of oil supply of
202 5177.23kg/h, the required amounts of sulfuric acid catalyst and ethanol were calculated.

Figure 2. Model I - Sulfuric acid catalyzed transesterification of acidic oil

205 Streams of concentrated sulfuric acid (108.72kg/h) and pure ethyl alcohol (1645.7kg/h)
206 were fed into a mixer and then heated up to 55°C. At the same time, acidic oil stream
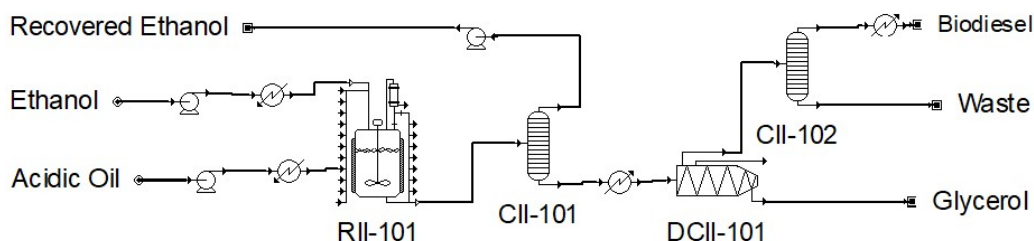
207 (5177.23kg/h) was also pumped through another heater and heated up to 55°C. Both streams

208 were let into the continuous stirred tank reactor (RI-101), where transesterification of the

209 triglyceride and esterification of the FFA were taken place. In this scenario, hydrolysis of the

210 triglyceride was not considered because the water content of the biomass as well as the water

211 formed from esterification was negligible. The product from the reactor was then passed through

212 a short cut distillation column (CI-101) for recovery of the excess ethanol so that it can be reused

213 in the process and considered as credit in the economic calculation. The distillation column was

214 designed to have nine actual stages and 1.6 reflux ratio, beyond which there were no change in

215 the purity of the recovered ethanol. The bottom output from the distillation column, which is

216 mainly composed of ethyl ester, sulfuric acid, water, glycerol and unreacted oil was then cooled

217 down to 25°C and taken to the neutralization reactor (RI-102) so as to neutralize the sulfuric acid

218 with calcium oxide. The required amount of CaO was determined based on the amount of

219 sulfuric acid to be neutralized.

220   After the neutralization, a centrifuge (DCI-101) was employed to separate the biodiesel

221 from the rest of the products. The separated biodiesel was further purified in another distillation

222 column (CI-102). This distillation column was designed to work in vacuum (0.25 bar pressure)

223 so that to lower the temperature below 275°C, because above this temperature biodiesel would

224 be thermally degraded through isomerism, polymerization and pyrolysis [66]. The actual stage of

225 the column was taken to be 6 and its reflux ratio was 1 because increasing the values beyond

226 these could not show significant change in purity of the biodiesel. The bottom output from this

227 distillation column was non-toxic waste, which can be further treated or safely disposed. The

228 bottom product from the centrifuge (DCI-101) was poor quality glycerol byproduct with purity

229 of 76%. The glycerol with such low purity does not have considerable market value. Thus in

230 order to get better quality glycerol (about 96% pure glycerol) for higher market value, further

231 purification might have been considered using another centrifugal decanter. However, this would

232 result in higher equipment purchasing cost and facility dependent costs, making the whole

233 process more expensive.

234 *3.2.*   *Model II*

235   Using this model a simple CaO catalyzed transesterification of acidic oil was studied. The

236 process flow diagram is shown in Figure 3. The designed reactor was a continuous stirred tank

237 reactor packed with CaO catalyst. The optimum reaction conditions considered for best result in

238 CaO catalyzed ethanolysis of acidic oil was taken to be 75°C reaction temperature, 7% wt. CaO

239 catalyst and 9 as molar ratio of ethanol to oil [63]. Accordingly, with these optimum reaction

240 conditions, a maximum conversion of 97.58% could be achieved in 2 hours [63]. The flow rate

241 of the alcohol and the amount of the catalyst required were calculated using the supply rate of the
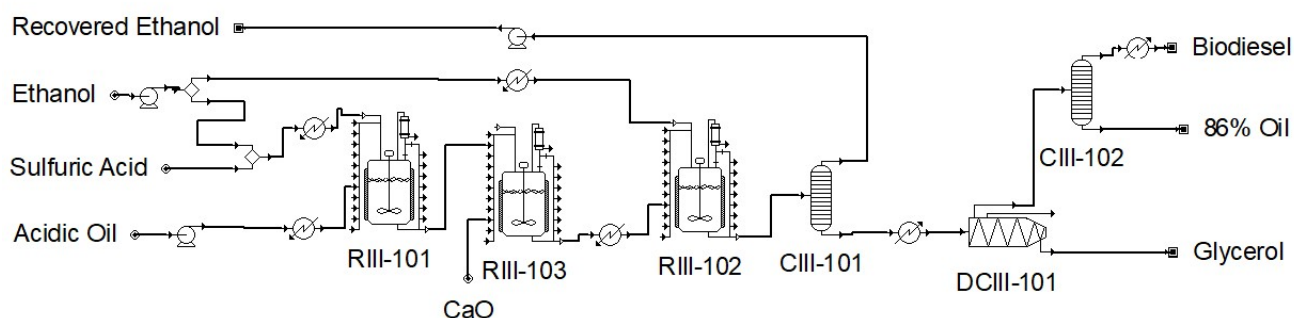
242 oil and the optimum reaction conditions.

243

244 **Figure 3**. Model II - Calcium oxide catalyzed transesterification of acidic oil

245 Acidic oil and ethyl alcohol were separately preheated to 75°C and pumped into the

246 continuous stirred tank reactor (RII-101) at a constant flow rate. In this scenario, due to the

247 presence of considerable amount of FFA in the oil feedstock, saponification of the FFA was

248 considered as the main side reaction. Accordingly, the reaction between some of the CaO

249 catalyst and oleic acid could produce calcium soap (Calcium oleate, $C_{36}H_{66}CaO_4$). The product

250 from the reactor was then let into the short cut distillation column (CII-101) for recovery of the

251 excess ethanol for possible reuse. This distillation column was designed to work at 0.25 bar

252 pressure to avoid thermal degradation of the biodiesel [66] and designed to have 6 actual stages

253 and 1.6 reflux ratio as the maximum values to get the higher purity of the recovered ethanol in

254 the upper output. The bottom output from the distillation column was cooled down to 25°C and

255 taken into a centrifugal decanter (DCII-101) for separation of the biodiesel. Another distillation

256 column (CII-102) was engaged to further purify the biodiesel component from the top output of

257 the centrifugal decanter. The maximum biodiesel purity was attained when the actual stage was 4

258 and reflux ratio was 1.5. The bottom output from the centrifugal decanter (DCII-101) was mainly

259 composed of glycerol with relatively higher percentage of purity (99.8%) than produced from the

260 two other scenarios. Similar results from literature are discussed later in result section. The waste

261 stream from this scenario was non-toxic and mainly composed of calcium soap and unreacted

262 oil, which can be further treated or safely disposed.

7

263   *3.3.   Model III*

264   In this model, the effect of the combination of the two catalysts was investigated. The

265   homogeneous sulfuric acid catalyst for esterification of FFA and the heterogeneous CaO catalyst

266   for transesterification reaction were studied simultaneously in a process following the flowsheet

267   as presented in Figure 4. Two stoichiometric reactors were separately designed. The first reactor

268   (RIII-101) was for pre-esterification of the FFA in the presence of the triglycerides using sulfuric

269   acid catalyst and the other reactor (RIII-102) was for transesterification of the triglycerides using

270   CaO catalyst.

271   The significant reactions considered in the first reactor were esterification reaction between

272   the alcohol and the FFA to produce water and ethyl ester as well as the transesterification

273   reaction, as a side reaction, between the triglyceride and the alcohol to produce ethyl ester and

274   glycerol. The optimum reaction conditions in the first reactor were taken to be 55°C temperature,

275   2.26% wt. sulfuric acid, and 6.1 ethanol to oil molar ratio [65]. With these optimum reaction

276   conditions, a 96% FFA conversion and around 30% conversion of the triglyceride could be

277   achieved in 4 hours [65]. Similarly, the optimum reaction conditions required to achieve best

278   result in CaO catalyzed ethanolysis process in the second reactor were taken to be 75°C

279   temperature, 9 ethanol to oil molar ratio and 7% wt. CaO catalyst [63]. At these optimum

280   reaction conditions, a maximum conversion of 97.58% could be achieved within 2 hours [63].

281   Accordingly, the amount of sulfuric acid catalyst and ethanol were calculated based on these

282   stated optimum reaction conditions and the oil supply rate of 5177.23 Kg/h.

283

284   **Figure 4**. Model III - Calcium oxide catalyzed transesterification with sulfuric acid catalyzed pre-
285   esterification of acidic oil

286   The proportion of the alcohol for pre-esterification reaction (1646kg/h) was mixed with

287   sulfuric acid (117kg/h) in a simple mixer. The mixture was then heated up to 55°C and let into

8

288   the first stirred tank reactor (RIII-101). Simultaneously, the alcohol proportion for

289   transesterification reaction (1639kg/h) was also heated up to 75°C and let into the second

290   continuous stirred tank reactor (RIII-102). The second reactor was a fixed bed reactor packed

291   with CaO catalyst in which transesterification of the triglyceride was taken place to produce

292   more biodiesel. In this scenario, hydrolysis of the triglyceride, in the first reactor, was not

293   considered for that the water content of the biomass as well as the water formed from

294   esterification was negligible. In addition, the occurrence of saponification reaction in the second

295   reactor was also neglected because almost all FFA were supposed to be consumed in the first

296   reactor during esterification reaction.

297   The product from the esterification process, mainly composed of unreacted triglyceride,

298   ethanol, sulfuric acid, FAEE and water, was directly taken into the neutralization reactor (RIII-

299   103) to neutralize the sulfuric acid so that to avoid calcium salt formation and consumption of

300   the catalyst in the second reactor. CaO was used to neutralize the sulfuric acid, as it can easily be

301   prepared from wastes like eggshell with less expense. The outlet from the neutralization process

302   was directly let into the second reactor (RIII-102) where CaO catalyzed transesterification

303   reaction dominantly took place to produce more FAEE. The product from the transesterification

304   reactor was let into a short cut distillation column (CIII-101) for recovery of excess ethanol for

305   possible reuse. This distillation column had 1.5 reflux ratio and 3 actual stages for maximum

306   possible purity of recovered ethanol. The bottom product from the distillation column then fed

307   into centrifugal decanter (DCIII-101) for separation of the biodiesel component from the rest of

308   the product. The separated biodiesel from the top output of the decanter was further purified in

309   another distillation column (CIII-102). This distillation column was designed with 7 actual stages

310   and 0.3 reflux ratio at which the maximum possible biodiesel purity could be achieved. The

311   bottom product from this distillation column was mainly composed of 86% unreacted oil

312   (123kg/h), which could be reused with minor treatment. The bottom product from the centrifugal

313   decanter (DCIII-101) was glycerol with 76% purity. Since glycerol with this purity could not get

314   higher value in the market, further purification might have been considered like in the case of

315   model I. Nevertheless, this would, otherwise incur additional cost into the process to make it

316   more expensive.

317   In all of the three models, storage tanks for both raw materials and products were not

318   included in the designs assuming that the raw materials would be consumed and the products

319 would immediately be used without storage. The waste streams in all of the models were non-
320 toxic and could safely and easily be treated or disposed, or otherwise be reused. For instance, if
321 the glycerol byproducts from Models I and III were to be further purified, calcium sulfate (with
322 more than 86% purity) would be another valuable byproduct. Calcium sulfate, in its direct
323 application, as uncalcined gypsum, can be used as a soil conditioner. If it is further purified and
324 calcined, it can also be used to make tiles and wallboard among others.

4. Results and Discussion

326 The models designed were mainly for techno-economic study of production of biodiesel
327 from acidic oil with 10% FFA content on molar basis. These could be used to identify the better
328 option(s) in terms of technical efficiency and affordability. The technical efficiency was assessed
329 based on the quality and quantity of products through material balance and the affordability was
330 assessed based on the total investment, operating cost, ROI, Gross Margin, and NPV. The results
331 of the study are more explained in the following sections.

4.1. Process descriptions and technical performances

333 The process in the models were designed using commercial software called Super Pro
334 design from Intelligen Inc. [56] as well as Aspen Plus from Aspentech [57]. Each model was
335 designed to accommodate a capacity of 41 thousand tons of acidic oil per year. In all of the three
336 models, the reaction condition was isothermal at required optimum reaction temperatures taken
337 for each reaction type according to literature [63-65]. The allocation of the catalysts and alcohol
338 amounts were based on their relative optimum amounts with respect to the proportion of the
339 feedstock considered in each reaction type recommended to get the maximum conversion. More
340 amount of CaO was considered in Model II, where both transesterification and saponification
341 reactions were supposed to take place. Eventually, the least amount of CaO catalyst was
342 allocated for Model III for that only transesterification reaction needed the catalyst. In terms of
343 the overall catalyst amount, Model I required the least catalyst amount, because only sulfuric
344 acid catalyst with 2.1% wt. was considered. In addition, the calculation of the amount of alcohol
345 required were based on the type of reaction as to whether esterification, transesterification or
346 both, since the optimum molar ratio required is dependent on the reaction type.

347 All the models guaranteed a potential to produce biodiesel with required quality. It was
348 possible to get more than 99% pure biodiesel in all of the process models studied. These results

349 were in agreement with similar studies in literature [67-69]. Table 1 indicated some significant
350 technical aspects of the three process models for comparison.

Table 1. Technical aspects of the process models studied			
	Model I	Model II	Model III
Capacity (Thousands ton/year)	41	41	41
Process Temperature (°C)	55	75	55&75[a]
Input stream (Kg/h)			
Oil feedstock	5177.23	5177.23	5177.23
Alcohol	1646	2341	3285
Sulfuric Acid	109	-	117
Output Streams			
Biodiesel (kg/h)	5187	5132	5308
Glycerol in biodiesel (wt. %)	0.06	0.0014	0.07
Performance[b]	1	0.99	1.03
Glycerol (kg/h)	500	505	501
Glycerol Purity (%)	76	99.8	76
Ethanol recovered (%)	52	67.5	76

351 *[a] 55°C was in reactor number one and 75°C was in reactor number two*
352 *[b] amount of biodiesel produced per amount of feedstock used*

353   Model III gave the higher amount of biodiesel whereas model II provided the least amount.
354 This was because in Model II considerable amount of the FFA was consumed by saponification
355 reaction, which could otherwise be converted into FAEE. In Model III, the pre-esterification
356 reaction could provide additional FAEE, increasing the amount of biodiesel produced throughout
357 the whole process. Model II showed the minimum performance by producing 0.99 metric ton of
358 biodiesel for each metric ton of oil feedstock used, but it could still be taken as standard
359 achievement. In all of the models, the use of distillation column for biodiesel purification could
360 help to get high quality product to meet the ASTM standards. For instance, the higher percentage
361 of glycerol was about 0.07 in the biodiesel from Model III, which was still far below the
362 maximum allowable amount (0.24% wt.) according to the ASTM standard [70]. Higher amount
363 (505kg/h) and better quality (99%) of glycerol was attained in Model II. This was mainly
364 because the catalyst was heterogeneous (with higher density difference) making the separation
365 process very effective to get high amount and high quality glycerol [9, 71]. This result was in
366 agreement with some results from literature [13, 72].

367

368

369   ### *4.2. Economic Assessment*

370   The capital, operating, equipment, raw material, utilities and labor costs were estimated
371   based on literature and market price from different suppliers in Ethiopia. The purchasing cost
372   (delivered cost) of equipment were estimated based on Peters and Timmerhaus method [73]
373   using the latest Chemical Engineering Plant Cost Index of 591.335 [74]. While calculating the
374   equipment costs using this method, the cost of associated utilities, as well as installation and
375   instrumentation costs were not included but the calculations of these cost categories are indicated
376   under section 4.2.1. The list and cost of equipment for each model are shown in Table 2.

Table 2. List and cost of equipment involved in designing the three process models			
Equipment	Equipment Cost for each Model (US$)		
	Model I	Model II	Model III
Stirred tank reactor(s)	628,562	165,000	477,000
Distillation columns	82,000	79,000	54,000
Decanter Centrifuge(s)	102,000	102,000	102,000
Heat exchangers	42,000	21,000	42,000
Pumps	6,000	6,000	6,000
Unlisted equipment	215,000	95,000	179,000
Total Equipment cost	1,077,000	476,000	897,000

377

378   ### *4.2.1. Capital Costs*

379   In addition to the equipment purchasing cost, total capital investment cost includes working
380   capital and startup & validation costs as well as direct and indirect expenses associated with
381   instrumentation, insulation, piping, electrical facilities, auxiliary facilities and construction
382   overheads, among others. The calculation of the direct and indirect expenses were based on
383   percentage allocation on total purchasing cost of equipment as shown in Table 3.

384

385

386

Table 3. Direct plant cost categories and their percentage allocations with equipment cost [47]	
Cost category	% allocation with equipment cost
Piping	20
Instrumentation	10
Electrical	15
Insulation	3
Building	15
Yard improvement	10
Auxiliary facilities	25
Unlisted equipment	20

387   Startup & validation cost for each scenario was taken to be 5% of the DFC. The two
388   common indirect plant costs considered in the designs were engineering cost (25% of DFC) and
389   construction cost (35% of DFC). Table 4 indicates capital cost categories and total capital
390   investment cost for each Model for comparison.

Table 4. Total capital investment cost for each model for comparison (thousand US$)			
Capital cost category	Model I	Model II	Model III
Direct Fixed Capital Cost	4,437	1,963	3,715
Working Capital	3,064	2,765	3,078
Startup & Validation Cost	222	98	186
Total Capital Investment Cost	7,723	4,827	6,978

391   As shown in Table 4, the most expensive alternative was Model I. In this alternative, the
392   dominant reaction was the acid catalyzed transesterification reaction. Acid catalyzed
393   transesterification is very slow reaction [75, 76] and due to this it requires larger volume to attain
394   equivalent production rate with its counterparts, such as alkali catalyzed transesterification.
395   Therefore, in this scenario, Model I required a larger volume reactor in order to attain
396   comparable production rate with the two other models. Such larger reactor volume resulted in
397   higher equipment purchasing cost, higher facility dependent costs as well as very high amount of
398   utilities required to run the process. Model II was the cheapest alternative. The dominant reaction
399   in this model was the CaO catalyzed transesterification reaction. This reaction is relatively fast, it
400   only takes 2 hours to attain more than 97% conversion [63], favoring the alternative to have
401   relatively smaller reactor volume. In addition, the use of CaO heterogeneous catalyst enabled to
402   have less process steps required to attain a comparable production amount and quality with

403 respect to the two other models. Model II, had total investment cost of 4.8 million US$, which
404 was 31% less than that of Model III and 37% less than that of Model I. In all of the Models, the
405 materials of construction for the reactors were stainless steel with 345kpa pressure.

406 *4.2.2. Operating costs*

407 The calculation of the operating costs included estimation of raw materials cost, facility
408 dependent cost, labor dependent costs, costs associated with laboratory & quality control,
409 utilities costs and some miscellaneous costs.

410 The raw materials, utilities and labor costs were taken based on current market prices from
411 different sources in Ethiopia, since this study envisioned possible development of biodiesel
412 production plant in Ethiopia using Jatropha oil as feedstock. The cost of raw materials (delivered
413 costs), utilities and labors considered in the process designs are indicated in Table 5. The oil
414 feedstock used in all of the three models had FFA content of 10% of the oil on molar basis.
415 According to some literatures, the cost of such feedstock can be put in a range of 478 -
416 684US$/ton [77, 78]. For this study the average value, 580US$/ton or 0.58US$/Kg was taken as
417 the cost of the acidic oil feedstock in all three designs.

Table 5. Cost of raw materials, utilities and labor considered in the three process models

Raw Material	
Oil	0.58 US$/Kg
Alcohol	0.30 US$/Kg
Sulfuric Acid	0.4 US$/Kg
CaO	0.12 US$/Kg
Utilities	
Electricity	0.09 US$/KW-h
Steam	12 US$/MT
Chilled water	0.4 US$/MT
Labor (Basic rate)	
Operator	10 US$/h
Reactor Operator	15 US$/h
Supervisor	20 US$/h

418 Labor cost calculation was based on the basic rate estimated for each labor category. The
419 estimation of the basic rate was done using the current wage indicator in Ethiopia [79] as
420 minimum starting scale and by scaling up these payments to certain label to match international
421 standards. The utilities considered in these processes models were steam, chilled water and
422 electricity.

Table 6 displays the operating cost categories with their calculated amount for all models. Cost of materials include cost of oil, catalysts, and alcohol. Model III showed higher amount of material cost than the other two. This was due to a higher amount of alcohol and two catalysts, sulfuric acid and CaO, used in the two separate processes. The facility dependent and utility costs were very high in Model I mainly due to larger volume of the reactor. The facility dependent cost included cost for maintenance, depreciation, insurance, local tax and factory expenses.

Table 6. Operating cost categories and their calculated values for each model

Operating Cost category	Operating cost amount in US$		
	Model I	Model II	Model III
Materials	28,095,704	29,373,303	32,029,315
Facility dependent	2,371,419	981,693	1,858,907
Labor dependent	813,214	513,951	904,294
Laboratory	243,964	154,185	271,288
Utilities	4,792,603	531,308	921,461
Miscellaneous	110,000	110,000	110,000
Total annual operating cost	36,426,905	31,664,441	36,095,266
% of Raw Material Cost	*77*	*93*	*89*
% of Facility Dependent Cost	*7*	*3*	*5*
% of Utilities Cost	*13*	*2*	*3*

The economic competitiveness of the models were evaluated based on the same assumptions for all the process. The process lifetime in all the models was considered to be 15 years with all the process plants operating in their full capacity. All the projects were supposed to be funded by own finance without any loan. It was also assumed that all the equipment depreciate throughout the lifetime of the project. Local tax was taken as 35% of the DFC and insurance was 2% of the DFC. The local tax amount was determined based on the possible tax allocations (such as corporate income tax and turnover tax) for such kind of investment in Ethiopia [80]. The calculation of the labor cost was using the detailed rate, where the basic rate was multiplied by the sum of the benefit, supervision, supplies and administration rates. The percent of work time devoted to process-related activities, which was used to estimate the labor time, was taken to be 70% in all of the models considering that they are continuous processes.

441 Based on the same optimum market values of inputs for the three Models, their economic
442 performance was evaluated and shown in Table 7 for comparison.

Table 7. Economic performances of the models studied			
	Model I	**Model II**	**Model III**
Feedstock Capacity (kg/year)	41,003,662	41,003,662	41,003,662
Annual Biodiesel Production (kg/year)	41,115,414	40,644,750	42,115,566
Total Investment cost (US$)	7,723,101	4,827,041	6,978,211
Annual operating cost (US$)	36,426,905	31,664,441	36,095,266
Total Annual Revenue (US$)	34,342,293	33,305,116	33,187,279
Unit Production Cost (US$/kg)	0.8860	0.7791	0.8571
Net Unit Production Cost (US$/kg)	0.8034	0.6867	0.7240
Unit Production Revenue (US$/kg)	0.8353	0.8194	0.7880
Gross Margin (%)	3.81	16.19	8.12
Return Over Investment, ROI (%)	15.63	75.09	28.36
Payback Time (year)	6.4	1.33	3.53
Net Present Value at 7% (US$)	-19,345,239	7,051,638	-30,424,382

443 The unit production cost variation among the studied Models was considerable, with
444 maximum variation of 0.11US$/kg. Moreover, these calculated unit production cost values were
445 more or less in agreement with some similar studies done using different catalyst technologies
446 and feedstock types [46, 47, 81]. For instance the unit production costs calculated by Karmee et
447 al. [47] using three catalyst technologies (base, acid and lipase) to produce biodiesel from waste
448 cooking oil were in a range of 0.75 US$/kg up to 1.048US$/kg. In our study, the maximum unit
449 cost of production was 0.886US$/kg in Model I and the minimum was 0.779US$/kg in Model II.

450 As shown in Table 7, Model I took longer time to payback the investment and had the
451 second minimum NPV at 7% interest rate. It was also more expensive to produce biodiesel using
452 Model I and Model III than Model II. Model II found to be the better alternative in terms of
453 economic performances. Even though the amount of biodiesel produced was the least, Model II
454 showed positive NPV at 7% interest, higher ROI and minimum payback time. However, Model I
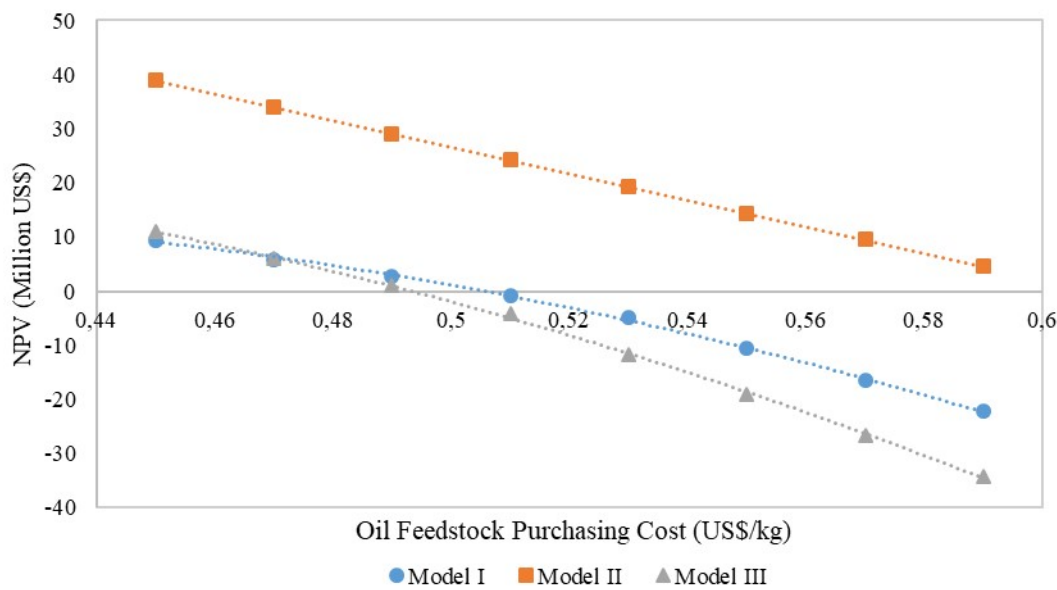
455 and III had poor economic performances, which could be indicated by negative NPV for the
456 same optimum market values of inputs and outputs applied for the three Models.

457 ### *4.3. Sensitivity analysis*

458 There was a wider gap in economic performances among the Models studied. This in turn
459 invited to further investigate the sensitivity of the technologies towards the possible fluctuation
460 of market values of the input and output variables. Because, the economic feasibility of such
461 technologies are always compromised by the market prices of inputs and outputs, such as price
462 of biodiesel, price of feedstock, as well as operation cost [55]. This demands a systematic
463 investigation of how these market variables affect the feasibility of the business. With this
464 respect, the effect of two main market variables (oil cost and biodiesel price) were tested to
465 investigate how the economic feasibility of process alternatives could be affected by change of
466 cost of these market variables. The economic parameter used to test the effect of the market
467 variables was the NPV. It denotes the present value of net cash inflows generated by a project
468 minus the initial investment on the project. It is one of the most meaningful measures of capital
469 budgeting in a project because it considers time value of money.

470 ### *4.3.1. Effect of change of oil purchasing cost on NPV*

471 The first sensitivity analysis was done on the purchasing cost of oil feedstock. Oil feedstock
472 took the higher share of the material cost and thus the total operating cost. This implied that the
473 fluctuation of the cost of oil feedstock could affect the biodiesel production business. To test how
474 NPV changes with change in cost of feedstock, a feedstock price range of 0.45 up to 0.59US$/kg
475 was taken. Figure 5 shows the effect of change of oil feedstock purchasing cost on NPV among
476 the models.
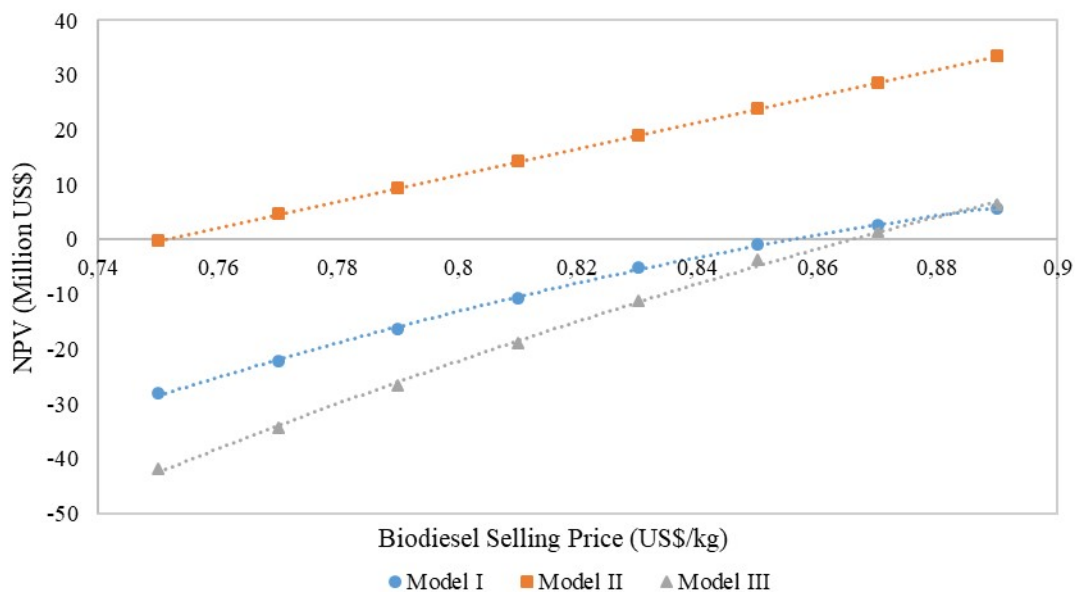
Figure 5. Effect of change of oil cost on NPV for Model I (●), Model II (■) & Model III (▲)

The percentage share of cost of oil feedstock from total raw material cost was 85% for Model I, 81% for Model II and 74% for Model III. As shown in Figure 5, the tendency of change of NPV with oil feedstock purchasing cost was the same for Model I and II, with a little change for Model III in this regard. In addition, among the three models, Model III showed more sensitivity to the change in oil feedstock cost, particularly above 0.480US$/kg. For instance, a 0.02US$/kg change in oil feedstock cost would result a decrease in NPV of 7.5 Million US$ for Model III and 5.8 Million US$ for Model I. In Model III, oil feedstock price above 0.490US$/kg would make the business unprofitable. For Model I, the maximum oil cost that could still make the business profitable was 0.509US$/kg. Accordingly, Models I and III were the least dependable alternatives for sustainable production of biodiesel. However, Model II showed more tolerance to fluctuation of oil cost, enabling to accommodate relatively expensive feedstock, up to 0.590US$/kg, and make the business profitable with positive NPV.

4.3.2. Effect of change of biodiesel selling price on NPV

The other market variable considered for sensitivity analysis was the biodiesel selling price. As biodiesel is the main product stream for all the processes, its selling price could have strong effect on the profitability of the businesses. For this study a selling price range of 0.75 up to 0.87 US$/kg of biodiesel was taken into consideration. Figure 6 shows the effect of change of biodiesel selling price on NPV among the three models.

Figure 6. Effect of change of biodiesel selling price on NPV for Model I (●), Model II (■) & Model III (▲)

As shown in figure 6, Models I and II had the same tendency in change of NPV due to change in biodiesel selling price. Whereas, Model III had a little difference in tendency of change of NPV, indicating higher change, particularly below 0.870US$/kg of biodiesel price. Because of this, Model III was the most sensitive to a decrease in the selling price of biodiesel. The minimum price, below which the business would be unprofitable, was 0.865US$/kg for Model III and 0.853US$/kg for Model I. Model II had more tolerance to market fluctuation of the selling price of biodiesel up to the minimum value of 0.754US$/kg.

5. Conclusion

The techno-economic analysis of biodiesel production from acidic oil was carried out for three production technologies using two catalyst types. The technical performances of the three technologies were compared in terms of the amount and quality of biodiesel, amount and purity of glycerol produced as well as the amount of biodiesel produced per amount of raw materials consumed. Accordingly, it was possible to get higher amount of biodiesel produced using Model III. Model II produced the least amount of biodiesel. At optimum production conditions, the biodiesel yield variation among the models could get up to 176 kg/hr. Model III showed the maximum performance by producing 1.03 metric ton of biodiesel for each metric ton of oil feedstock used. The purity of the biodiesel produced from all technological alternatives studied

was in line with the quality requirement of ASTM in terms of percentage of total glycerol. Model II could produce high quality glycerol, as it used heterogeneous catalyst. Whereas, in Models I and III, the quality of glycerol produced was less due to the presence of $CaSO_4$ as a product of catalyst neutralization reactions in the two Models. The presence of $CaSO_4$ could make the separation inefficient resulting in poor quality of the glycerol. Model I produced less amount of glycerol compared to the other two models.

The economic performances of the three alternatives were assessed in terms of the total investment cost, total operating cost, unit production cost, ROI, Gross Margin, payback time and NPV. Accordingly, compared to the two other models, Model II was the superior alternative scoring better results in all of the parameters. It showed lower unit production cost, shorter payback time, and larger amount of NPV at 7% interest rate, to mention some.

The effect of change of oil feedstock cost and biodiesel selling price on NPV was analyzed for the three models and the results were compared. It was clearly indicated that Model II was more tolerant than the two models for market fluctuations of purchasing cost of oil feedstock and selling price of biodiesel.

Disclaimer

The authors do not have responsibility for a decision made based on the results of these process designs. The process designs indicated in this work are solely for research purposes. For specific applications, please contact the authors to get information about the limitations and scope of the process designs.

Acknowledgements

Conflict of Interest

All authors declare no conflicts of interest in this paper.

544 **Reference**

545 [1] Keera ST, El Sabagh SM, Taman AR. Transesterification of vegetable oil to biodiesel fuel

546 using alkaline catalyst. Fuel. 2011;90:42-7.

547 [2] Fadhil AB, Ali LH. Alkaline-catalyzed transesterification of Silurus triostegus Heckel fish

548 oil: Optimization of transesterification parameters. Renewable Energy. 2013;60:481-8.

549 [3] Leung D, Guo Y. Transesterification of neat and used frying oil: optimization for biodiesel

550 production. Fuel Proces Techno. 2006;87:883-90.

551 [4] Miao X, Li R, Yao H. Effective acid-catalyzed transesterification for biodiesel production.

552 Energ Conver and Manage. 2009;50:2680-4.

553 [5] Soriano Jr NU, Venditti R, Argyropoulos DS. Biodiesel synthesis via homogeneous Lewis

554 acid-catalyzed transesterification. Fuel. 2009;88:560-5.

555 [6] Guan G, Kusakabe K, Sakurai N, Moriyama K. Transesterification of vegetable oil to

556 biodiesel fuel using acid catalysts in the presence of dimethyl ether. Fuel. 2009;88:81-6.

557 [7] Kulkarni MG, Gopinath R, Meher LC, Dalai AK. Solid acid catalyzed biodiesel production

558 by simultaneous esterification and transesterification. Green Chemistry. 2006;8:1056-62.

559 [8] Lam MK, Lee KT, Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis for

560 transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review.

561 Biotechnology Advances. 2010;28:500-18.

562 [9] Semwal S, Arora AK, Badoni RP, Tuli DK. Biodiesel production using heterogeneous

563 catalysts. Bioresour Technol. 2011;102:2151-61.

564 [10] Kouzu M, Yamanaka S-y, Hidaka J-s, Tsunomori M. Heterogeneous catalysis of calcium

565 oxide used for transesterification of soybean oil with refluxing methanol. Applied Catalysis A:

566 General. 2009;355:94-9.

567 [11] Kouzu M, Tsunomori M, Yamanaka S, Hidaka J. Solid base catalysis of calcium oxide for a

568 reaction to convert vegetable oil into biodiesel. Advanced Powder Technology. 2010;21:488-94.

569 [12] Reyero I, Arzamendi G, Gandía LM. Heterogenization of the biodiesel synthesis catalysis:

570 CaO and novel calcium compounds as transesterification catalysts. Chemical Engineering

571 Research and Design. 2014;92:1519-30.

572 [13] Bournay L, Casanave D, Delfort B, Hillion G, Chodorge JA. New heterogeneous process

573 for biodiesel production: A way to improve the quality and the value of the crude glycerin

574 produced by biodiesel plants. Catalysis Today. 2005;106:190-2.

[14] Avhad MR, Marchetti JM. Innovation in solid heterogeneous catalysis for the generation of economically viable and ecofriendly biodiesel: A review. Catalysis Reviews. 2016;58:157-208.

[15] Li L, Du W, Liu D, Wang L, Li Z. Lipase-catalyzed transesterification of rapeseed oils for biodiesel production with a novel organic solvent as the reaction medium. Journal of Molecular Catalysis B: Enzymatic. 2006;43:58-62.

[16] Ranganathan SV, Narasimhan SL, Muthukumar K. An overview of enzymatic production of biodiesel. Bioresou techno. 2008;99:3975-81.

[17] Ha SH, Lan MN, Lee SH, Hwang SM, Koo Y-M. Lipase-catalyzed biodiesel production from soybean oil in ionic liquids. Enzy and Microbi Technol. 2007;41:480-3.

[18] Gog A, Roman M, Toşa M, Paizs C, Irimie FD. Biodiesel production using enzymatic transesterification – Current state and perspectives. Renewa Energy. 2012;39:10-6.

[19] Kiss FE, Micic RD, Tomić MD, Nikolić-Djorić EB, Simikić MĐ. Supercritical transesterification: Impact of different types of alcohol on biodiesel yield and LCA results. The J of Supercriti Fluids. 2014;86:23-32.

[20] Santana A, Maçaira J, Larrayoz MA. Continuous production of biodiesel using supercritical fluids: A comparative study between methanol and ethanol. Fuel Proces Technol. 2012;102:110-5.

[21] Micic RD, Tomić MD, Kiss FE, Nikolić-Djorić EB, Simikić MĐ. Influence of reaction conditions and type of alcohol on biodiesel yields and process economics of supercritical transesterification. Energ Conver and Manage. 2014;86:717-26.

[22] Shin H-Y, Lee S-H, Ryu J-H, Bae S-Y. Biodiesel production from waste lard using supercritical methanol. The J of Supercriti Fluids. 2012;61:134-8.

[23] Tahvildari K, Anaraki YN, Fazaeli R, Mirpanji S, Delrish E. The study of CaO and MgO heterogenic nano-catalyst coupling on transesterification reaction efficacy in the production of biodiesel from recycled cooking oil. J Environ Health Sci Eng. 2015;13:73.

[24] Sidra Hashmi SG, Tariq Mahmood3, Umar Nawaz, Hadayatullah Farooqi. Biodiesel Production by using CaO-Al2O3 Nano Catalyst. Intl J of Engng Resear & Sci (IJOER). 2016;2:2395-6992.

[25] Gupta J, Agarwal M. Preparation and characterizaton of CaO nanoparticle for biodiesel production. 2nd International Conference on Emerging Technologies. American Institute of Physics, Jaipur, 302017, India, 2016. p. 020066.

22

[26] Verma ML, Puri M, Barrow CJ. Recent trends in nanomaterials immobilised enzymes for biofuel production. Critical Reviews in Biotechnology. 2016;36:108-19.

[27] Xie W, Ma N. Enzymatic transesterification of soybean oil by using immobilized lipase on magnetic nano-particles. Biomass and Bioenergy. 2010;34:890-6.

[28] Mehrasbi MR, Mohammadi J, Peyda M, Mohammadi M. Covalent immobilization of Candida antarctica lipase on core-shell magnetic nanoparticles for production of biodiesel from waste cooking oil. Renewable Energy. 2017;101:593-602.

[29] Fan P, Xing S, Wang J, Fu J, Yang L, Yang G, et al. Sulfonated imidazolium ionic liquid-catalyzed transesterification for biodiesel synthesis. Fuel. 2017;188:483-8.

[30] Ishak ZI, Sairi NA, Alias Y, Aroua MKT, Yusoff R. A review of ionic liquids as catalysts for transesterification reactions of biodiesel and glycerol carbonate production. Catalysis Reviews. 2017;59:44-93.

[31] Ren Q, Zuo T, Pan J, Chen C, Li W. Preparation of Biodiesel from Soybean Catalyzed by Basic Ionic Liquids [Hnmm]OH. Materials. 2014;7:8012-23.

[32] Dube MA, Tremblay AY, Liu J. Biodiesel production using a membrane reactor. Bioresour Technol. 2007;98:639-47.

[33] Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. Membrane biodiesel production and refining technology: A critical review. Renewable and Sustainable Energy Reviews. 2011;15:5051-62.

[34] Baroutian S, Aroua MK, Raman AA, Sulaiman NM. A packed bed membrane reactor for production of biodiesel using activated carbon supported catalyst. Bioresour Technol. 2011;102:1095-102.

[35] Farag HA, El-Maghraby A, Taha NA. Optimization of factors affecting esterification of mixed oil with high percentage of free fatty acid. Fuel Proces Technolo. 2011;92:507-10.

[36] Uzun BB, Kılıç M, Özbay N, Pütün AE, Pütün E. Biodiesel production from waste frying oils: Optimization of reaction parameters and determination of fuel properties. Energy. 2012;44:347-51.

[37] Meher L, Dharmagadda VS, Naik S. Optimization of alkali-catalyzed transesterification of Pongamia pinnata oil for production of biodiesel. Bioresou techno. 2006;97:1392-7.

[38] Patil PD, Deng S. Optimization of biodiesel production from edible and non-edible vegetable oils. Fuel. 2009;88:1302-6.

637 [39] Miladinović MR, Krstić JB, Tasić MB, Stamenković OS, Veljković VB. A kinetic study of

638 quicklime-catalyzed sunflower oil methanolysis. Chemical Engineering Research and Design.

639 2014;92:1740-52.

640 [40] Velickovic A, Avramovic J, Stamenkovic O, Veljkovic V. Kinetics of the sunflower oil

641 ethanolysis using CaO as catalyst. Chemical Industry and Chemical Engineering Quarterly.

642 2016;22:409-18.

643 [41] Avhad M, Sánchez M, Bouaid A, Martínez M, Aracil J, Marchetti J. Modeling chemical

644 kinetics of avocado oil ethanolysis catalyzed by solid glycerol-enriched calcium oxide. Energy

645 Conversion and Management. 2016;126:1168-77.

646 [42] Ong LK, Kurniawan A, Suwandi AC, Lin CX, Zhao XS, Ismadji S. Transesterification of

647 leather tanning waste to biodiesel at supercritical condition: Kinetics and thermodynamics

648 studies. The J of Supercriti Fluids. 2013;75:11-20.

649 [43] Kusdiana D, Saka S. Kinetics of transesterification in rapeseed oil to biodiesel fuel as

650 treated in supercritical methanol. Fuel. 2001;80:693-8.

651 [44] Sánchez M, Marchetti JM, El Boulifi N, Aracil J, Martínez M. Kinetics of Jojoba oil

652 methanolysis using a waste from fish industry as catalyst. Chemical Engineering Journal.

653 2015;262:640-7.

654 [45] El-Galad MI, El-Khatib KM, Zaher FA. Economic feasibility study of biodiesel production

655 by direct esterification of fatty acids from the oil and soap industrial sector. Egyptian Journal of

656 Petroleum. 2015;24:455-60.

657 [46] Apostolakou AA, Kookos IK, Marazioti C, Angelopoulos KC. Techno-economic analysis of

658 a biodiesel production process from vegetable oils. Fuel Proces Technol. 2009;90:1023-31.

659 [47] Karmee SK, Patria RD, Lin CSK. Techno-economic evaluation of biodiesel production

660 from waste cooking oil—a case study of Hong Kong. Intl j of molecul scienc. 2015;16:4362-71.

661 [48] Jegannathan KR, Eng-Seng C, Ravindra P. Economic assessment of biodiesel production:

662 Comparison of alkali and biocatalyst processes. Renew Sust Energ Rev 2011;15:745-51.

663 [49] Olkiewicz M, Torres CM, Jiménez L, Font J, Bengoa C. Scale-up and economic analysis of

664 biodiesel production from municipal primary sewage sludge. Bioresourc technol. 2016;214:122-

665 31.

666 [50] Marchetti J, Miguel V, Errazu A. Techno-economic study of different alternatives for

667 biodiesel production. Fuel Proces Techno. 2008;89:740-8.

668 [51] Zhang Y, Dube M, McLean D, Kates M. Biodiesel production from waste cooking oil: 1.
669 Process design and technological assessment. Bioresou techno. 2003;89:1-16.

670 [52] Zhang Y, Dube M, McLean D, Kates M. Biodiesel production from waste cooking oil: 2.
671 Economic assessment and sensitivity analysis. Bioresourc technol. 2003;90:229-40.

672 [53] West AH, Posarac D, Ellis N. Assessment of four biodiesel production processes using
673 HYSYS.Plant. Bioresourc Technol. 2008;99:6587-601.

674 [54] Zhang-Chun Tang LZ, Liu Zhiwen, Xiao Ningcong. Uncertainty analysis and global
675 sensitivity analysis of techno-economic assessments for biodiesel production. Bioresour Technol.
676 2015;175:502-8.

677 [55] Zhang-Chun Tang YX, Qi Xue and Jie Liu. A Non-Probabilistic Solution for Uncertainty
678 and Sensitivity Analysis on Techno-Economic Assessments of Biodiesel Production with
679 Interval Uncertainties. Energies. 2018;11.

680 [56] Intelligen I. SuperPro Designer®. 1996.

681 [57] Aspentech. Aspen Plus®. 2018.

682 [58] Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. The effects of catalysts in
683 biodiesel production: A review. J of Industal and Enging Chemis. 2013;19:14-26.

684 [59] Avhad MR, Marchetti JM. A review on recent advancement in catalytic materials for
685 biodiesel production. Renew Sust Energ Rev 2015;50:696-718.

686 [60] Boey P-L, Maniam GP, Hamid SA. Performance of calcium oxide as a heterogeneous
687 catalyst in biodiesel production: A review. Chemi Enging J. 2011;168:15-22.

688 [61] Marinković DM, Stanković MV, Veličković AV, Avramović JM, Miladinović MR,
689 Stamenković OO, et al. Calcium oxide as a promising heterogeneous catalyst for biodiesel
690 production: Current state and perspectives. Renewable and Sustainable Energy Reviews.
691 2016;56:1387-408.

692 [62] Leung DYC, Guo Y. Transesterification of neat and used frying oil: Optimization for
693 biodiesel production. Fuel Processing Technology. 2006;87:883-90.

694 [63] Avhad MR, Sánchez M, Bouaid A, Martínez M, Aracil J, Marchetti JM. Modeling chemical
695 kinetics of avocado oil ethanolysis catalyzed by solid glycerol-enriched calcium oxide. Energ
696 Conver and Manage. 2016;126:1168-77.

697   [64] Marchetti JM, Pedernera MN, Schbib NS. Production of biodiesel from acid oil using

698   sulfuric acid as catalyst: kinetics study. International Journal of Low-Carbon Technologies.

699   2010;6:38-43.

700   [65] Marchetti J, Errazu A. Esterification of free fatty acids using sulfuric acid as catalyst in the

701   presence of triglycerides. Biomass and Bioenergy. 2008;32:892-5.

702   [66] Lin R, Zhu Y, Tavlarides LL. Mechanism and kinetics of thermal decomposition of

703   biodiesel fuel. Fuel. 2013;106:593-604.

704   [67] Refaat AA. Biodiesel production using solid metal oxide catalysts. Int J Environ Sci Tech.

705   2011;8:203-21.

706   [68] Santana GCS, Martins PF, de Lima da Silva N, Batistella CB, Maciel Filho R, Wolf Maciel

707   MR. Simulation and cost estimate for biodiesel production using castor oil. Chem Enging Resear

708   and Design. 2010;88:626-32.

709   [69] Wang Y, Pengzhan Liu SO, Zhang Z. Preparation of biodiesel from waste cooking oil via

710   two-step catalyzed process. Energy Conversion and Management. 2007;48:184-8.

711   [70] Guide DT. Biodiesel Standards & Properties. 2009.

712   [71] Lee JS, Saka S. Biodiesel production by heterogeneous catalysts and supercritical

713   technologies. Bioresour Technol. 2010;101:7191-200.

714   [72] Zabeti M, Daud WMAW, Aroua MK. Biodiesel production using alumina-supported

715   calcium oxide: An optimization study. Fuel Processing Technology. 2010;91:243-8.

716   [73] Peters MS, Timmerhaus KD, West RE, Timmerhaus K, West R. Plant design and

717   economics for chemical engineers. McGraw-Hill New York1991.

718   [74] Engineering C. The Chemical Engineering Plant Cost Index. 2018.

719   [75] M. Canakci JVG. Biodiesel production from oils and fats with high free fatty acids.

720   Transactions of the ASAE 2003;44(6):1429-36.

721   [76] Michael J. Goff NSB, Shailesh Lopes, William R. Sutterlin, and Galen J. Suppes. Acid

722   Catalyzed alcoholysis of soybean oil. J Am Oil Chem Soc 2004;81:415-20.

723   [77] Kumar A, Sharma S. Potential non-edible oil resources as biodiesel feedstock: An Indian

724   perspective. Renewable and Sustainable Energy Reviews. 2011;15:1791-800.

725   [78] Gui MM, Lee KT, Bhatia S. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as

726   biodiesel feedstock. Energy. 2008;33:1646-53.

727   [79] Wage Indicator Foundation. Salary Scale in Ethiopian Public Sector. 2018.

728   [80] Ethiopian Investment Commission. *Incentives, Taxation, and Other Procedures*. 2018.

729   [81] Santander C, Robles PA, Cisternas LA, Rivas M. Technical–economic feasibility study of

730   the installation of biodiesel from microalgae crops in the Atacama Desert of Chile. Fuel

731   Processing Technology. 2014;125:267-76.

732

733