Biodiesel production through sulfuric acid catalyzed transesterification of acidic oil: Techno economic feasibility of different process alternatives

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

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

* Corresponding author.

 ${\it Email address:} \ \underline{{\it Jorge.mario.marchetti@nmbu.no}} \ (J.\ M.\ Marchetti)$

Tel: +47-67231647.

1011 Abstract

Biodiesel is renewable fuel produced from fats and oils. When compared to conventional diesel fuel, it has considerable environmental benefits. However, its extensive use is hindered by high cost of production, mainly due to cost of feedstock. Among the different biodiesel production routes, acid catalyzed transesterification enables to use feedstock with higher free fatty acid content (cheaper feedstock). The absence of soap formation while using acid as a catalyst also simplifies the downstream separation and purification processes. In this study, a homogeneous sulfuric acid catalyzed transesterification of acidic oil is designed into four process scenarios based on four different downstream process routes.

The conceptual design and simulation of these process alternatives have been carried out using Super Pro and Aspen Plus software. These process models were used to evaluate the techno economic competitiveness of the four different scenarios. In the four process scenarios, all reactors for biodiesel production have been designed to have the same reaction conditions and the same amount of oil feedstock input. The difference of the scenarios was only on the arrangements and type of downstream process equipment required to get fuel grade biodiesel. The technical performances have been evaluated based on quality and quantity of products as well as the amount of biodiesel produced per feedstock consumed. The specific economic parameters considered were Unit Production Cost, NPV, IRR (after tax), and Payback time. The process scenario with ethanol recovery after catalyst neutralization and glycerol separation using decanting just before biodiesel purification has better technical and economic performances. Whereas the double reactor scenario shows much better technical performances with very low economic feasibility.

Keywords: Biodiesel, sulfuric acid catalyst, techno economics, sensitivity analysis

- 36 Nomenclature
- 37 ASTM American Society of Testing and Materials
- 38 CSTR Continuous Stirred Tank Reactor
- 39 DG Di-glyceride
- 40 DFC Direct Fixed Cost
- 41 E Ethanol
- 42 FAEE Fatty Acid Ethyl Ester
- 43 FFA Free Fatty Acid
- 44 G Glycerol
- 45 GHG Greenhouse Gas
- 46 IRR Internal Rate of Return
- 47 MG Mono-glyceride
- 48 NPV Net Present Value
- 49 PC Purchasing Cost
- 50 PCUE Purchasing Cost of Unlisted Equipment
- 51 ROI Return on Investment
- 52 TLC Total Labor Cost
- 53 TG Triglyceride

55

56

57

58

59

60

61

62

63

64

1. Introduction

The world energy demand is skyrocketing mainly due to economic growth and population expansion [1]. Such high demand together with the negative global environmental impacts of using fossil fuel for generations brings a question on dependability of the fossil fuel for sustainable economic growth. As a way out, the world is tending to depend more on renewables to secure the energy supply for extensive demands because of economic growth, improved standard of living and population expansion [2, 3]. Among the promising renewable energy resources for substitution of fossil fuels are biofuels [4]. Biodiesel is one of these biofuels with significant advantages over its counterpart fossil diesel. It is produced from renewable resources like edible and non-edible oils, animal fats, and waste cooking oil. When compared to fossil diesel production, the process technologies usually employed to produce biodiesel are simpler and can easily be implemented in decentralized manner from small scale to large scale levels. The other major advantages are associated with its environmental and ecological benefits compared to the fossil diesel. It is biodegradable, non-toxic and free from sulfur and aromatics [5]. Combustion of biodiesel for energy releases less GHG, less air pollutants, and less particulate matters compared to the conventional fossil diesel, because it has relatively high amount of oxygen required for complete combustion of the fuel [6].

Biodiesel is a mono alkyl ester of long chain fatty acids produced mainly through the process of transesterification reaction. There are a number of possible process alternatives to accomplish transesterification reaction. Transesterification might be catalyzed or non-catalyzed. The catalyzed options are heterogeneous and homogeneous acid catalyzed, heterogeneous and homogeneous alkali catalyzed, and enzyme catalyzed transesterification reactions. The non-catalyzed option is usually supercritical methanol transesterification reaction taking place at higher pressure and temperature.

Depending on the characteristics of the feedstock used for biodiesel production, each method has its own advantages and disadvantages. However, the commercially known technological route for biodiesel production is the homogeneous alkali catalyzed alternative [7-10]. This technology requires a feedstock with minimum FFA content, less than 0.5% [7, 11, 12]. Such oil feedstock are high quality oil like edible oil, which are usually expensive for biodiesel production.

The cost of biodiesel feedstock usually took the higher percentage share of the total manufacturing cost, affecting the unit cost of biodiesel production. In most cases, this cost share

is greater than 80% [13, 14]. Consequently, the unit cost of biodiesel production can directly be reduced while using the least cost feedstock alternatives [15, 16]. Technically possible options to produce fuel grade biodiesel from such low quality feedstock types are acid catalyzed, enzyme catalyzed and supercritical transesterification routes [17-19]. Among them, supercritical route could give the least cost of materials as there is no any catalyst considered in the process. However, its higher pressure and temperature requirements result in bigger utility cost, making the alternative expensive [20, 21]. The other alternative, enzyme catalyzed technology, is usually taken as a better choice for production of fuel grade biodiesel from low value feedstock [19]. However, the expensiveness of the catalyst is mentioned as the main drawback to use this option at industrial scale for production of biodiesel in economically competitive manner with that of fossil diesel [22].

One of the most viable options to produce biodiesel from low cost feedstock is the acid catalyzed transesterification reaction [23, 24]. This is mainly because there is no additional pretreatment step required to reduce FFA, and the product separation and purification can be done with simple process steps as there is no soap formation [25, 26]. Among the different possible types of acid catalysts for biodiesel production, sulfuric acid is the most studied one. It can catalyze the transesterification reaction at atmospheric pressure and relatively medium temperature range, from 55°C up to 88°C [27-29].

The study done by Michael et al. [29] evaluated alcoholysis of soybean oil using sulfuric, hydrochloric, formic, acetic, and nitric acids at different loading rates and found out that the sulfuric acid catalyst was the most effective. Their result showed that at 100°C reaction temperature, 99% conversion of TG in soybean oil could be achieved in 8 h, when 0.5% sulfuric acid catalyst, and nine times methanol stoichiometry are used [29].

Farag et al. [30] studied the factors affecting production of methyl ester from mixed oil formed from 50% sunflower and 50% soybean oil using sulfuric acid as the catalyst. They found out that the optimum reaction conditions for the best conversion efficiency of 96.6%, was 6:1 molar ratio of methanol to oil, 60°C reaction temperature and, 2.5% wt. of H₂SO₄ with respect to the oil feedstock [30].

In another study, Marchetti et al. [31], indicated that a conversion of 96% of acidic oil, with 10.684 % FFA content, could be reached with an optimum reaction conditions of sulfuric acid amount of 2.5%, ethanol molar ratio of 6.1:1 and reaction temperature of 55°C. However, while using sulfuric acid as a catalyst, excess amount of alcohol is usually recommended to get higher final conversion percentage [9, 32, 33].

The maximum conversion in an optimized transesterification reaction catalyzed by sulfuric acid could reach up to 96% - 99% [27, 30, 33]. Practically there are two main reactions taking place when acidic catalyst like sulfuric acid is used to catalyze the biodiesel production process using oil with higher FFA content. These are transesterification and esterification reactions. Transesterification is a reversible reaction between one mole of the triglyceride of the oil and three moles of alcohol in the presence of the catalyst to produce one mole of glycerol and three moles of ester. This happens in three consecutive reaction steps as depicted in Figure 1. Esterification reaction takes place when one mole of FFA reacts with one mole of alcohol to produce one mole of ester and one mole of water as shown in Figure 2.

141
$$TG + E \xrightarrow{Catalyst} FAEE + DG$$
142
$$DG + E \xrightarrow{Catalyst} FAEE + MG$$
143
$$MG + E \xrightarrow{Catalyst} FAEE + G$$
144 **Figure 1**. Steps in transesterification reaction

132

133

134

135

136

137

138

139

140

147

148

149

150

151

152

153

154

155

156

157

158

159

160

161

162

Figure 1. Steps in transesterification reaction

145
$$FFA + E \xrightarrow{Catalyst} FAEE + WATER$$
146 Figure 2. Esterification reaction

However, there might also be hydrolysis, depending on the amount of water in the feedstock and the amount of water formed during esterification.

A number of studies have been done to show how sulfuric acid catalyzed process is cost effective for biodiesel production from feedstock with high free fatty acid content [9, 15, 34]. Karmee et al. [15] compared the techno-economic performances of acid, base and enzyme catalysts for the production of fuel grade biodiesel from waste cooking oil. They found out that, the acid catalyst technology was the cost effective option by indicating better IRR compared to the two other options [15]. In another study Zhang et al. [34] compared the economic performances of producing biodiesel from waste cooking oil using alkali catalyzed and acid catalyzed processes and found out that the sulfuric acid catalyzed process was the most economically feasible alternative.

The techno-economic feasibility of the whole process of biodiesel production through sulfuric acid catalyzed transesterification can be further improved by using the most cost effective arrangement of equipment and selection of operation units for the major process steps. In this respect, there are a number of possible arrangement of alternative equipment for separation of the biodiesel from the glycerol as well as for purification of both the biodiesel product and the glycerol byproduct. Accordingly, this study is specifically targeted to sort out the most cost effective, technically efficient and economically sustainable biodiesel production route using sulfuric acid as homogeneous catalyst. To do so four different scenarios of sulfuric acid catalyzed biodiesel production processes have been simulated based on four different arrangement of operation units for major downstream processes. Eventually, the technical performances of the scenarios have been compared in terms of the amount and quality of biodiesel and glycerol produced as well as the amount of product produced per unit of feedstock consumed. The economic evaluations, among the four scenarios, were also done based on total investment cost, unit cost of biodiesel production, IRR, NPV and payback time. The economic sustainability of the alternatives has been tested through sensitivity analysis over selected market variables. The sensitivity analysis was done to investigate how NPV and Payback time could be affected by change in market values of biodiesel selling price and oil purchasing cost so that to identify the most tolerant alternative to the global market fluctuations of the variables.

2. Process Descriptions and Methods

This study has been done on four process alternatives to produce biodiesel from acidic oil using homogeneous sulfuric acid as a catalyst. In all of the scenarios, since the amount of water in the biomass and amount of water produced during esterification is insignificant, hydrolysis has been neglected and the only dominant reactions considered are transesterification and esterification. Continuous stirred tank reactor is considered as the main reactor in all of the scenarios, for which the reaction temperature is set to be 55°C. This is the optimum temperature for better biodiesel production from acidic oil using sulfuric acid catalyst [30, 31, 35].

2.1. Specifications of raw materials

The raw materials used in all process scenarios are the same in amount and quality. These include acidic oil feedstock, sulfuric acid catalyst, ethanol and calcium oxide. The oil feedstock is with 10% FFA content. This could represent most of second generation oil feedstock types from non-edible plants [36, 37], which can have up to 14% FFA. The alcohol considered in the process designs is ethanol, which can be produced from renewable resources and which is also less toxic and safe to use. In all of the process scenarios, the ethanol is taken to be in 6.1:1 molar ratio with the oil feedstock amount to encourage the forward reaction and get more conversion [30, 31, 35]. The acid catalyst used is sulfuric acid, with up to 98% concentration, as it is the most studied and effective acidic catalyst available for biodiesel production [23, 38]. The relative optimum amount of sulfuric acid catalyst taken in all the processes is 2.1% wt. of the oil feedstock [35]. The calcium oxide is included to totally neutralize the catalyst after the

transesterification reaction. Calcium oxide is selected because it can be cheaply produced from waste materials like eggshells, mud scrap shells, and cockleshells among others. Eventually, the amount of each raw material has been determined based on their optimum allocations with respect to oil feedstock amount required for maximum conversion.

2.2. Design assumptions

196

197

198

199

200

201

202

203

204

205

217

218

219

220

222

223

224

The major assumptions considered for reasonable designing of the process scenarios are as follows:

- Oil feedstock capacities in all the scenarios are the same and equal to 41 million kg per year.
- The oil feedstock is assumed to be 100% free from solid particle.
- Oil feedstock input is assumed to be supplied throughout the whole year.
- Working hours per year is taken to be 7920 (330 working days per year).
- Pressure drop in all the process equipment is neglected.
- Moisture content of the feedstock is assumed to be very low and the water formed during esterification reaction is also considered negligible. Thus, the hydrolysis process is not considered in all of the scenarios.
- Transesterification and esterification are the only dominant reactions considered in all of the scenarios.
- Triolien represents the acidic oil with oil density of 907.8 kg/m³, oleic acid represents the fatty acid with density of 895 kg/m³ and ethyloleate represents biodiesel with density of 873.9 kg/m³.
 - As the property package for calculation of activity coefficient of the liquid phase in the simulations, the non-random two liquid (NRTL) thermodynamic model is selected due to the presence of polar compounds such as ethanol and glycerol in the process.
 - Life time of the project is assumed to be 15 years
- The whole production processes are assumed to be run by own money without loan

2.3. Process alternative scenarios

Four possible process scenarios have been designed to investigate their techno economic feasibility so as to identify the most cost effective, technically efficient and economically reliable

option(s) in producing biodiesel from low value oil feedstock using sulfuric acid as a catalyst. The scenarios are designed based on the various possible configurations of the six main downstream processes. These six main downstream processes are separation of biodiesel and glycerol, biodiesel purification, glycerol purification, excess ethanol recovery, catalyst neutralization, and separation of calcium sulfate. A number of possible unit procedures with different equipment types can be used to accomplish the six major downstream processes for production of fuel grade biodiesel. Accordingly, the four scenarios are designed by configuring technically viable as well as least cost equipment options as much as possible. The four process scenarios with their unit procedures and equipment types used for each process step are shown in Table 1.

Table 1. Process scenarios with required equipment for each process step							
Process		Scenarios with unit proce	dures and equipment in each st	tep			
steps	Scenario - I	Scenario - II	Scenario - III	Scenario - IV			
1	Reaction	Reaction	Reaction	Reaction			
1	(CSTR - Single)	(CSTR - Single)	(CSTR - double)	(CSTR - Single)			
2	Ethanol recovery	Catalyst neutralization	Catalyst neutralization	Catalyst neutralization			
2	(Distillation)	(Distillation) (CSTR) (CSTR)		(CSTR)			
2	Catalyst	CaSO ₄ separation	CaSO ₄ separation	CaSO ₄ separation			
3	neutralization (CSTR)	(Centrifuge)	(Centrifuge)	(Centrifuge)			
4	CaSO ₄ separation	Ethanol recovery	Ethanol recovery	Ethanol recovery			
4	(Centrifuge)	(Distillation)	(Distillation)	(Distillation)			
-	Glycerol separation	Glycerol separation	Glycerol separation	Biodiesel and glycerol			
5	(Decanter)	(Decanter)	(Decanter)	purification (Distillation)			
	Biodiesel purification	Biodiesel purification	Biodiesel purification	Biodiesel and Glycerol			
6	(Distillation)	(Distillation)	(Distillation)	separation (Decanter)			

Each process has been designed with a capacity of 41 million kg feedstock per year. Acidic oil with 10% FFA content is heated up to 55°C and feed into the continuous stirred tank reactor at a rate of 5177.23 kg/h. At the same time, ethanol (1645.69 kg/h) and sulfuric acid catalyst (108.7kg/h) are mixed in a simple two-way mixer, heated up to 55°C and pumped into the continuous stirred tank reactor. The reaction condition in the stirred tank reactor is set to be isothermal at 55°C and 1.013 bar pressure. The isothermal condition could be achieved using steam as heat transfer agent. The rate at which the product leaves the reactor is in such a way to attain 21h residence time in the reactor. Because at the given reaction conditions (55°C temperature, 2.1 % wt. catalyst & 6.1:1 molar ratio of the alcohol to oil) the conversion could reach at about 97.57% in 21h [35]. All reaction conditions and everything else are made the same for all scenarios until this point

The product from the reactor is then passed through the different downstream configurations to get fuel grade biodiesel. In all of the scenarios, the calcium sulfate salt formed during the neutralization of the acidic catalyst is removed using centrifugal decanter just after neutralization reactor. The excess ethanol is recovered using distillation column in all of the scenarios. In scenarios II, III & IV, the excess ethanol is recovered just after the salt is removed. However, in scenario I the excess ethanol recovery is done before the catalyst is neutralized. In scenario III, the reaction is carried out in two consecutive CSTR where there is a decanter in between them to separate the glycerol part after the first reactor. This double reactor configuration is the main difference between scenario II and III. In scenario IV, the separation of biodiesel from the glycerol is considered at the end after the unreacted oil is separated using distillation column. Whereas in scenarios I, II & III the final step is purification of the biodiesel using distillation column. This is very effective in separating the biodiesel from the unreacted oil remaining in the product. The other similar situation in all scenarios is neutralization of the acid catalyst. This is done by using CaO in a CSTR just after the main reactor(s) for biodiesel production in scenarios II, III & IV, whereas in scenario I, neutralization of the catalyst is considered after the excess ethanol is recovered.

246

247

248

249

250

251

252

253

254

255

256

257

258

259

260

261

262

263

264

265

266

267

268

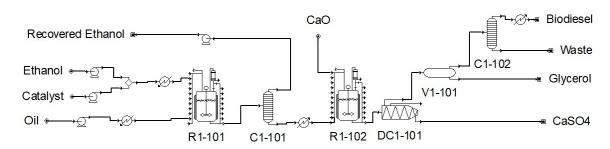
269

270

271

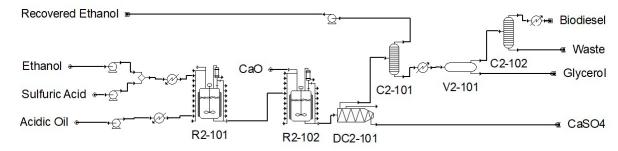
272273

The process flow sheets shown in this study are performed using Super Pro design software from Intellegin Inc.[39]. In order to verify their correctness, each process model has also been redesigned using Aspen Plus software from Aspentech [40]. This is because Aspen Plus has a broader choice in physical parameters and physical property methods to select for each specific process taken in the design. This would help to increase the viability of the results. Figure 3 up to Figure 6 show the designed process flow sheets for each scenario.



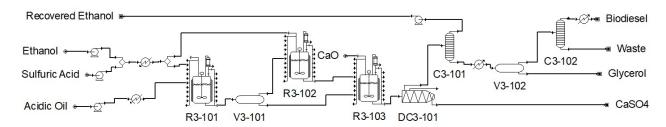
Time Ref: h		Acidic Oil	Biodiesel	CaO	CaSO4	Ethanol	Glycerol	Recovered ethanol	Sulfuric Acid	Waste
Туре		Raw Material	Revenue	Raw Material	Revenue	Raw Material	Revenue	Credit	Raw Material	
Total Mass Flow	kg	5177.2300	5151.3815	62.1700	155.8011	1645.6900	526.9222	866.4676	108.7200	293.3269
Temperature	°C	25.0	25.0	25.0	32.8	25.0	32.8	47.3	25.0	219.3
Pressure	bar	1.013	0.250	1.013	1.013	1.013	1.013	3.750	1.013	0.250

Figure 3: Scenario I: R1-101 CSTR for biodiesel production, C1-101 shortcut distillation column for ethanol recovery, R1-102 CSTR for catalyst neutralization, DC1-101 centrifuge decanter for CaSO₄ separation, V1-101 decanting tank for glycerol separation and C1-102 shortcut distillation column for biodiesel purification



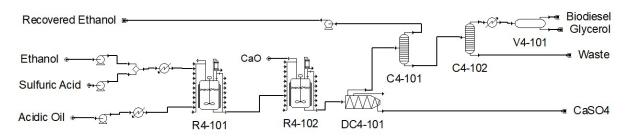
Time Ref: h		Acidic Oil	Biodiesel	CaO	CaSO4	Ethanol	Glycerol	Recovered Ethanol	Sulfuric Acid	Waste
Туре		Raw Material	Revenue	Raw Material	Revenue	Raw Material	Revenue	Credit	Raw Material	
Total Mass Flow	kg	5177.2300	5282.1413	62.1700	155.7168	1645.6900	506.6240	885.9599	108.7200	163.4574
Temperature	°C	25.0	25.0	25.0	61.6	25.0	25.0	48.3	25.0	160.7
Pressure	bar	1.013	0.250	1.013	1.013	1.013	0.250	3.750	1.013	0.250

Figure 4: Scenario II: R2-101 CSTR for biodiesel production, R2-102 CSTR for catalyst neutralization, DC2-101 centrifuge decanter for CaSO₄ separation, C2-101 shortcut distillation column for ethanol recovery, V2-101 decanting tank for glycerol separation and C2-102 shortcut distillation column for biodiesel purification



Time Ref: h		Acidic Oil	Biodiesel	CaO	CaSO4	Ethanol	Glycerol	Recovered Ethanol	Sulfuric Acid	Waste
Туре		Raw Material	Revenue	Raw Material	Revenue	Raw Material	Revenue	Credit	Raw Material	
Total Mass Flow	kg	5177.2300	5354.4722	62.1700	155.3394	1645.6900	513.0250	877.0671	108.7200	93.9966
Temperature	°C	25.0	25.0	25.0	61.5	25.0	25.0	48.3	25.0	179.2
Pressure	bar	1.013	0.250	1.013	1.013	1.013	0.250	3.750	1.013	0.250

Figure 5: Scenario III: R3-101 first CSTR for biodiesel production, V3-101 first decanter for glycerol separation, R3-102 second CSTR for additional biodiesel production, R3-103 CSTR for catalyst neutralization, DC3-101 centrifuge decanter for CaSO₄ separation, C3-101 shortcut distillation column for ethanol recovery, V3-102 second decanting tank for glycerol separation and C3-102 shortcut distillation column for biodiesel purification



Time Ref: h		Acidic Oil	biodiesel	CaO	CaSO4	Ethanol	Glycerol	Recovered Ethanol	Sulfuric acid	Waste
Туре		Raw Material	Revenue	Raw Material	Revenue	Raw Material	Revenue	Credit	Raw Material	
Total Mass Flow	kg	5177.2300	5012.8942	62.1700	155.4479	1645.6900	507.3237	885.9159	108.7200	432.3176
Temperature	°C	25.0	25.0	25.0	57.6	25.0	25.0	48.3	25.0	234.3
Pressure	bar	1.013	0.250	1.013	1.013	1.013	0.250	3.750	1.013	0.250

Figure 6: Scenario IV: R4-101 CSTR for biodiesel production, R4-102 CSTR for catalyst neutralization, DC4-101 centrifuge decanter for CaSO₄ separation, C4-101 shortcut distillation column for ethanol recovery, C4-102 short cut distillation column for biodiesel purification and V4-101 decanting tank for glycerol separation

2.4. Economic Assessment

The economic performance evaluation of the studied process scenarios has been done considering latest and estimated costs of raw materials, labor, utilities and equipment as well as associated costs of equipment installation, auxiliary facilities and depreciation cost among others. The oil feedstock considered in these processes is the cheapest from non-edible oil plants, and estimated to cost in a range of 478 - 684US\$/ton [41, 42]. We take the lower value 478US\$/ton to be the estimated cost of oil feedstock. The cost of other raw materials such as catalyst, ethanol and calcium oxide are based on latest market prices from different suppliers in Ethiopia and relevant literatures [43, 44]. The labor cost is estimated based on the current wage indicator in Ethiopia [45], which is then extrapolated to scale it up to some amount. The calculation of the labor cost is based on detailed estimate using the basic rate allocated for each labor category. The other cost category included in the annual operating cost calculations is cost of utilities. The utilities considered in all of the studied scenarios are cooling water, steam, steam high and electricity, for which the cost estimations are entirely based on current market prices in Ethiopia and relevant literatures [46, 47]. Table 2 shows estimated costs of raw materials, utilities and labor considered in the process alternatives.

Table 2 . Estimated costs of raw materials,								
utilities and labor considered in all process								
scenarios								
Raw Material								
Oil	0.478 US\$/kg							
Ethanol	0.300 US\$/kg							
Sulfuric Acid	0.275 US\$/kg							
CaO	0.120 US\$/kg							
Utilities								
Electricity	0.021 US\$/KW-h							
Steam	6 US\$/MT							
Steam high	10 US\$/MT							
Cooling water	0.025 US\$/MT							
Labor (Basic rate)								
Operator	10 US\$/h							
Reactor Operator	15 US\$/h							
Supervisor	15 US\$/h							

The purchasing cost of each equipment designed in each process scenario is estimated using Peter and Timmerhaus method [48], where Chemical Engineering plant cost index of 591.335 for January 2018 is used [49]. This index denotes changes in the value of money due to inflation and deflation so that it helps to estimate the average cost of each equipment for the year 2018 based on previous year costs. The other components of the capital investment cost, such as installation,

piping, electricity, instrumentation, and yard improvement are estimated based on the percentage allocation of the equipment purchasing cost for each cost item as shown in Table 3.

Table 3. Direct plant cost categories and their percentage							
allocations with equipment cost [15]							
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						

The cost estimation interface in the Super Pro design software gives options to allocate estimated percentage share of such cost categories as well as other associated costs like maintenance cost, depreciation, insurance and tax, during designing the processes. The percentage allocation of these type of costs are indicated in Table 4.

Table 4. Cost estimation methods for components of capital								
investment and operating costs [50]								
Cost items	Estimation methods							
Capital Investment Cost Categories								
Installation cost (for each equipment)	0.2 X PC							
Maintenance cost (for each equipment)	0.1 X PC							
Purchasing cost of unlisted equipment (PCUE)	0.2 X PC							
Installation cost of unlisted equipment	0.5 X PCUE							
Operating Cost Categories								
Insurance	2 X DFC							
Local Tax	15 X DFC							
Factory expense	5 X DFC							
Laboratory and quality control	30 X TLC							

3. Results

Having optimized process conditions and determined equipment sizes, the material and energy balances of the four process alternatives have been carried out. Based on the results of the material and energy balances of each scenario as well as market values of input materials, labor and utilities the techno economics of the processes have been analyzed and presented as follows.

3.1. Technical performances

329

330

331

332

333

334

335

336

337

338

339

340

341

342

343

344

345

346

347

348

349

350

351

352

353

354

355

356

357

358

359

360

361

362

All four process scenarios are found to be technically feasible ways to produce biodiesel at required quality in accordance with ASTM standards. The technical performance results, such as biodiesel purity, glycerol purity and amount of biodiesel and glycerol produced per amount of feedstock used, are in agreement with those reported in other studies [15, 51]. However, there is still a comparable difference among the scenarios in terms of these technical performances. For instance, scenarios II & III show better performance regarding the amount of biodiesel produced per amount of feedstock consumed. For scenario III, this is due to the double reactor configuration designed to improve the overall conversion of the oil into biodiesel. Whereas for scenario II, the higher performance might be due to arrangement of the downstream processes, where ethanol recovery is done after catalyst neutralization as well as biodiesel purification is done using distillation just after the glycerol separation by decanting. Such process arrangement helps to minimize the amount of biodiesel lost during biodiesel purification and waste separation through distillation. In contrary, the least performance is recorded in scenario IV, where, during separating the unreacted oil from the biodiesel in the second distillation process, considerable amount of the biodiesel could also be removed together with the unreacted oil. This might be due to the higher temperature of the reboiler required to separate the mixture of biodiesel and glycerol from the unreacted oil. Accordingly, the difference in amount of biodiesel produced among the scenarios could range up to 341 kg/h. This value specially indicates the product difference between scenario II and IV. In all of the scenarios, the biodiesel purity achieved is about 99.99 %. This is mainly because of the fractional distillation employed to further purify the biodiesel after different arrangement of glycerol and calcium sulfate separation processes. As the main byproduct, glycerol could also be obtained at higher quality because a number of separation processes are employed in each scenario. Apparently, the higher glycerol product is recorded in scenario III, where two consecutive reactors are designed for higher conversion percentages. The purity of ethanol recovered in each scenario is the same. However, the amount recovered in scenario III is slightly less than the rest because a little more is consumed due to the second reactor.

The other crucial point that might improve the productivity of the whole production process is considering the production of more valuable byproducts for additional income generation. With this respect, a good quality calcium sulfate could be produced from all the scenarios with almost the same quantity. In all of the scenarios the separation of the calcium sulfate is done using centrifugal decanter as it is efficient in separating the solid calcium sulfate from the rest of the components. This is done just after the acid catalyst is neutralized so that to avoid the

interference of the solid calcium sulfate to the liquid flow downstream afterwards. Calcium sulfate, as the second byproduct, can be used as a soil conditioner and if further calcined at required temperature, it can also be used in making tiles, wallboard, and various plasters among others [52]. Table 5 shows summary of technical performances of the studied process scenarios.

Table 5. Summary of technical performances of the process scenarios								
Technical performance indicators	Process scen	Process scenarios with respective technical performances						
reclinical performance maleators	Scenario I	Scenario II	Scenario III	Scenario IV				
Annual Biodiesel production (kg/year)	40,798,942	41,834,559	42,407,420	39,702,122				
Annual Glycerol production (kg/year)	4,018,719	4,018,719	4,067,549	4,018,719				
Annual CaSO ₄ production (kg/year)	1,195,301	1,195,301	1,195,301	1,195,301				
Biodiesel purity (%)	99.998	99.990	99.990	99.990				
Glycerol purity (%)	96.20	99.98	99.95	99.86				
CaSO ₄ purity (%)	97	97	97	97				
Biodiesel produced per oil feedstock consumed (wt./wt.)	0.995	1	1	0.968				

3.2. Economic performances

Having determined plant size, optimized reaction conditions and estimated costs for goods and services, it has been possible to compare the performances of the process alternatives in terms of some selected economic parameters. The economic parameters used for comparison are total investment cost, total annual operating cost, unit production cost, payback time, NPV, ROI, and after tax IRR. Summary of the economic performances of the alternative process scenarios is indicated in Table 6.

Table 6. Summary of the economic performances of the studied process scenarios								
Economic performance indicators	Scenario - I	Scenario - II	Scenario - III	Scenario - IV				
Total capital investment cost (US\$)	22,359,405	21,865,163	31,542,376	21,869,629				
Total equipment purchasing cost (US\$)	4,372,471	4,346,531	6,477,990	4,271,634				
Direct Fixed Capital (US\$)	18,021,578	17,521,523	26,699,684	17,605,966				
Working Capital (US\$)	3,436,748	3,467,564	3,507,708	3,383,365				
Total Annual operating cost (US\$)	44,081,688	44,262,764	47,811,814	43,353,794				
Total annual raw material cost (US\$)	23,805,788	23,805,788	23,805,788	23,805,788				
Labor dependent cost (US\$)	469,543	475,200	627,943	463,886				
Facility dependent cost (US\$)	6,026,595	5,867,002	8,928,640	5,887,610				
Laboratory, Quality Control & Analysis (US\$)	140,863	142,560	188,383	139,166				
Utility cost (US\$)	13,528,900	13,862,214	14,151,061	12,967,345				
Annual revenue from Biodiesel (US\$/year)	46,917,850	48,090,537	48,752,243	45,641,805				
Annual revenue from Glycerol (US\$/year)	417,323	417,323	422,206	417,323				
Annual revenue from CaSO ₄ (US\$/year)	153,173	153,173	153,173	153,173				
Total Annual Revenue (US\$/year)	47,488,346	48,661,033	49,327,622	46,212,301				
Unit production cost (US\$/kg biodiesel)	1.0805	1.0580	1.1274	1.0920				
NPV at 7% (US\$)	4,268,069	8,761,177	-7,556,647	3,076,566				
ROI (%)	19.02	22.19	12.47	18.01				
After tax IRR (%)	9.92	12.73	2.89	9.14				
Gross Margin (%)	8.92	10.92	4.72	8.17				
Payback time in years	5.26	4.51	8.02	5.55				

As shown in Table 6, scenario III is the most expensive alternative. This is mainly because of the double reactor scenario, which is supposed to improve the oil conversion efficiency and get more biodiesel produced. Because as the number of equipment increased, there would be associated increase in the total equipment cost, labor cost and utility cost. Even though this double reactor scenario could provide more biodiesel and glycerol compared to others, the overall economic performance indicated that it is not an economically feasible alternative. At optimum market values of goods and services, scenario III provides a very high unit cost of biodiesel production, negative NPV at 7% interest and higher payback time, implying that biodiesel produced should be sold at high price to get some profit. This makes the alternative economically unattractive.

Comparatively, scenario II is the least expensive alternative and the second scenario in providing more biodiesel amount. Even though it has the same type and number of equipment with scenario IV, the arrangement of the equipment in scenario II could provide more amount of biodiesel, making the alternative better in its economic performances through increasing the

revenue. This might be due to the process arrangement where glycerol is decanted out before the biodiesel is purified using distillation column and thus the amount of biodiesel lost during glycerol separation is minimized. In addition, this process arrangement favors scenario II to have relatively less utility requirement because the reboiler in the distillation column works at relatively lower temperature compared to the one in scenario IV, which has the same type of equipment as well as the same process arrangement until the separation of the calcium sulfate byproduct. This decreases the over production cost. In terms of the economic terms, scenario II indicates higher NPV, less payback time and minimum unit production cost. Scenarios I and IV are the third and fourth alternatives respectively, in terms of their economic performances. Both show positive NPV, signifying that they are still feasible in the given market values of products.

In terms of the total capital investment cost, scenario III is the highest again because of the double reactor situation, which increases the equipment purchasing cost and the associated utility, installation and instrumentation costs. Among the other scenarios, scenario I is the second most expensive mainly due to larger volume of distillation column required to recover the excess ethanol before glycerol and calcium sulfate separation. Similarly, such larger column volume results in higher equipment, utility, instrumentation, and installation costs among others.

Because of the higher amount of biodiesel and glycerol produced, the superior revenue is recorded in scenario III, whereas scenario II shows the second larger revenue. Having the lower investment cost and second larger revenue, scenario II is the better alternative in terms of achieving lower unit production cost, higher ROI, and lower payback time.

3.3. Sensitivity analysis

The economic feasibility of a biodiesel production process can be dependable when there is a thorough analysis done on how fluctuation of values of market variables affect the profitability of the business. This is because such study would identify the market variables, which affect the profitability of the business more, so that we could take remedial measures, when necessary, to keep the business profitable. In addition, when such analysis is done among a number of alternative processes, it would help to identify the most reliable production alternative that could tolerate market fluctuations of inputs and outputs. Accordingly, in this study, the effects of change of market values of oil feedstock and biodiesel on profitability of the business have been analyzed and the results have also been compared and presented as follows. The economic indicators used to show the sensitivity of the business to changes in prices of the market variables are NPV at 7% interest and payback time.

3.3.1. Effect of change of oil feedstock purchasing cost

The oil feedstock took the higher share of the annual operating cost in all of the studied alternatives. This implies that a change in market price of the feedstock has a high probability in affecting the profitability of the business. To investigate how NPV and payback time change with change in feedstock cost among the studied scenarios, a price range of 0.45 up to 0.65US\$/kg of acidic oil feedstock was set. The effect of change of oil feedstock purchasing cost on NPV is shown in Figure 5 and its effect on payback time is shown in Figure 6.

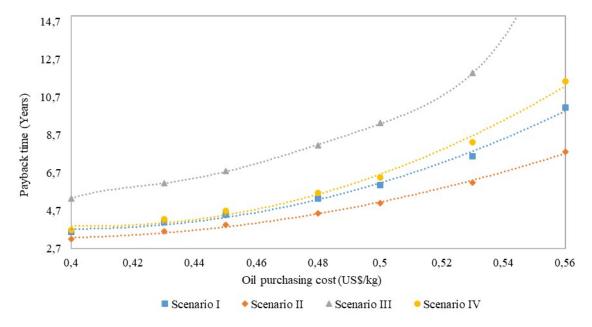


Figure 7: Effect of change of oil purchasing cost on Payback time among the alternative scenarios

Scenario III is the least dependable alternative for sustainable biodiesel production business. In this scenario, an increase in oil cost by 0.1US\$/kg could result in additional 4 years of payback time. At higher oil purchasing cost, above 0.53US\$/kg, the payback time would be beyond the lifetime of the project, making the alternative very sensitive to change to oil purchasing cost. Comparatively, scenario II indicates more tolerance to change in oil purchasing cost, in which the same price change (0.1US\$/kg) could increase the payback time by about 1.9 years.

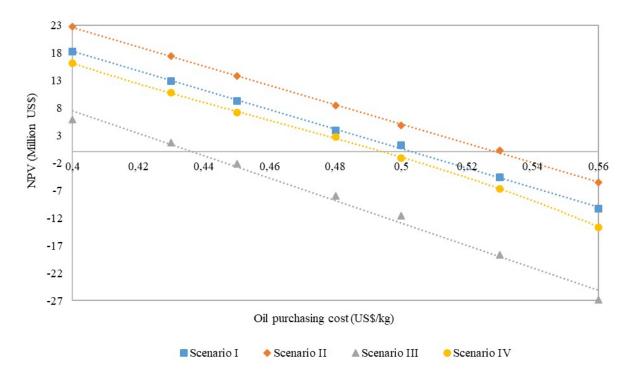


Figure 8: Effect of change of oil purchasing cost on NPV among the alternative scenarios

The effect of change of oil feedstock purchasing cost on the profitability of biodiesel production business could be shown in a better way using NPV. Because NPV denotes the value of the investment calculated by adding the present value of expected future cash flows to the initial cost of the investment. Accordingly, the negative NPV attained in scenario III, as shown in Figure 6, clearly suggests that the alternative is not economically feasible at even medium cost of oil feedstock (above 0.435US\$/kg). Consequently, feedstock has to be purchased with very minimum cost (less than 0.43US\$/kg) in order to be profitable using scenario III. The other less dependable option is scenario IV. It is unprofitable at moderately higher cost of oil feedstock (above 0.49US\$/kg). Comparatively, scenario II could provide positive NPV at higher cost of oil feedstock (up to 0.535US\$/kg), making it more economically dependable alternative for sustainable biodiesel production business.

3.3.2. Effect of change of biodiesel selling price

The other market variable considered to have an effect on the profitability of the alternative scenarios is the biodiesel selling price. Since biodiesel is the main product, its market value could have significant effect on the profitability of the production business. Similarly, NPV and payback time are the two economic indicators used to show how each scenario respond to change in selling price of biodiesel. The biodiesel selling price range of 0.96 up to 1.24US\$/kg is taken for the analysis. The effect of change of biodiesel selling price on NPV is shown in Figure 7 and its effect on payback time is shown in Figure 8.

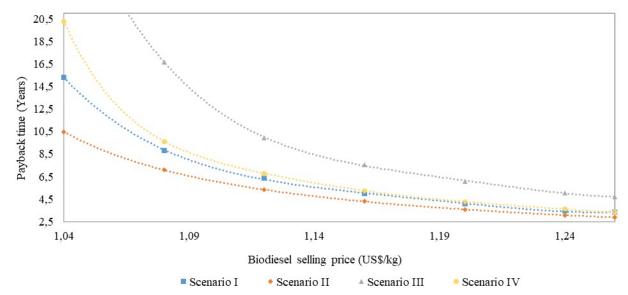


Figure 9: Effect of change of Biodiesel selling price on Payback time among the alternative scenarios

Here again it is indicated that scenario III is the most sensitive for change in biodiesel selling price. Biodiesel price lower than 1.08 US\$/kg would make the project payback time to go beyond its lifetime, making it less practical. The next sensitive alternative is scenario IV, which also required a biodiesel selling price of more than 1.14US\$/kg for its feasibility. Comparatively, scenario II is found to be the most tolerant to a considerable change in the market values of biodiesel selling price, allowing to consider minimum biodiesel price (up to 1.1 US\$/kg) within the feasibility domain.

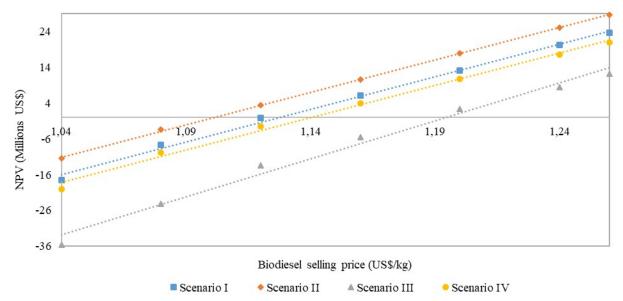


Figure 10: Effect of change of Biodiesel selling price on NPV among the alternative scenarios

As shown in Figure 8, the trend of change of NPV with change in biodiesel prices is the same for all scenarios. However, among them scenario III is found to be more sensitive and get no profit to the business even at higher prices of the biodiesel product. The next less dependable alternative is scenario IV, which indicates negative NPV starting from medium values of the biodiesel selling price (lower than 1.14US\$/kg). Scenario II is the better alternative in this respect, providing positive NPV at 7% interest even at lower values of biodiesel selling price (about 1.1US\$/kg).

4. Conclusion

Four process scenarios for biodiesel production from acidic oil using sulfuric acid as a catalyst were designed, analyzed and evaluated for their techno-economic performances. Accordingly, all scenarios are capable of producing fuel grade biodiesel and could also provide high quality calcium sulfate and glycerol byproducts for additional income. Scenario III, with double reactor, shows better technical performance with very low economic feasibility. In addition, scenario III is found to be the most sensitive alternative to change in market values of inputs and outputs.

Comparatively, scenario II is the cheapest alternative with less total investment cost, less unit cost of production, higher NPV and minimum payback time. It also indicates good technical performance and provides competitive amount of glycerol byproduct. In terms of sensitivity to change in market values of inputs and outputs, scenarios II is found to be more tolerant than the other scenarios.

Scenarios I and IV are relatively technically less efficient and scenario IV is the second most expensive alternative for having higher cost of biodiesel production, and less NPV among others. It is also the second most sensitive alternative to change in market values of inputs and outputs.

_.

Disclaimer

The authors do not have responsibility for a decision made based on the results of these process alternatives. 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

- The authors would like to thank Norwegian University of Life Sciences, NORAD and
- 512 NORHED for their financial support.

Conflict of Interest

All authors declare no conflicts of interest in this paper.

515

516

513

510

References

- 517 [1] US Energy Information and Administration. International energy outlook 2017. Available at
- https://www.eia.gov/outlooks/ieo/pdf/0484(2017).pdf. September 2017.
- 519 [2] Ellabban O, Abu-Rub H, Blaabjerg F. Renewable energy resources: Current status, future
- 520 prospects and their enabling technology. Renewable and Sustainable Energy Reviews.
- 521 2014;39:748-64.
- 522 [3] Stigka EK, Paravantis JA, Mihalakakou GK. Social acceptance of renewable energy sources:
- 523 A review of contingent valuation applications. Renewable and Sustainable Energy Reviews.
- 524 2014;32:100-6.
- 525 [4] Bhattarai K, Stalick WM, McKay S, Geme G, Bhattarai N. Biofuel: an alternative to fossil
- fuel for alleviating world energy and economic crises. J Environ Sci Health A Tox Hazard Subst
- 527 Environ Eng. 2011;46:1424-42.
- 528 [5] Carraretto C, Macor A, Mirandola A, Stoppato A, Tonon S. Biodiesel as alternative fuel:
- experimental analysis and energetic evaluations. Energy. 2004;29:2195-211.
- 530 [6] Fazal M, Haseeb A, Masjuki H. Biodiesel feasibility study: an evaluation of material
- compatibility; performance; emission and engine durability. Renewable and Sustainable Energy
- Fig. 32 Reviews. 2011;15:1314-24.
- [7] Keera ST, El Sabagh SM, Taman AR. Transesterification of vegetable oil to biodiesel fuel
- using alkaline catalyst. Fuel. 2011;90:42-7.
- 535 [8] Dias JM, Alvim-Ferraz MCM, Almeida MF. Comparison of the performance of different
- 536 homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of
- 537 biodiesel quality. Fuel. 2008;87:3572-8.
- 538 [9] Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. The effects of catalysts in
- biodiesel production: A review. J of Industal and Enging Chemis. 2013;19:14-26.
- 540 [10] Abbaszaadeh A, Ghobadian B, Omidkhah MR, Najafi G. Current biodiesel production
- technologies: A comparative review. Energ Convers Manage. 2012;63:138-48.

- 542 [11] Avhad MR, Marchetti JM. A review on recent advancement in catalytic materials for
- biodiesel production. Renew Sust Energ Rev 2015;50:696-718.
- 544 [12] Aransiola EF, Ojumu TV, Oyekola OO, Madzimbamuto TF, Ikhu-Omoregbe DIO. A
- review of current technology for biodiesel production: State of the art. Biomass and Bioenergy.
- 546 2014;61:276-97.
- 547 [13] Živković SB, Veljković MV, Banković-Ilić IB, Krstić IM, Konstantinović SS, Ilić SB, et al.
- Technological, technical, economic, environmental, social, human health risk, toxicological and
- 549 policy considerations of biodiesel production and use. Renewable and Sustainable Energy
- 550 Reviews. 2017;79:222-47.
- 551 [14] Mandolesi de Araújo CD, de Andrade CC, de Souza e Silva E, Dupas FA. Biodiesel
- production from used cooking oil: A review. Renewable and Sustainable Energy Reviews.
- 553 2013;27:445-52.
- 554 [15] Karmee SK, Patria RD, Lin CSK. Techno-economic evaluation of biodiesel production
- from waste cooking oil—a case study of Hong Kong. Intl j of molecul scienc. 2015;16:4362-71.
- 556 [16] Meira M, Quintella CM, Ribeiro EMO, Silva HRG, Guimarães AK. Overview of the
- challenges in the production of biodiesel. Biomass Conversion and Biorefinery. 2014;5:321-9.
- 558 [17] Talebian-Kiakalaieh A, Amin NAS, Mazaheri H. A review on novel processes of biodiesel
- production from waste cooking oil. Applied Energy. 2013;104:683-710.
- 560 [18] Atadashi IM, Aroua MK, Abdul Aziz AR, Sulaiman NMN. Production of biodiesel using
- 561 high free fatty acid feedstocks. Renewable and Sustainable Energy Reviews. 2012;16:3275-85.
- [19] Hama S, Kondo A. Enzymatic biodiesel production: an overview of potential feedstocks and
- process development. Bioresour Technol. 2013;135:386-95.
- 564 [20] Glisic SB, Pajnik JM, Orlović AM. Process and techno-economic analysis of green diesel
- production from waste vegetable oil and the comparison with ester type biodiesel production.
- 566 Appl Energy. 2016;170:176-85.
- 567 [21] Marulanda VF, Anitescu G, Tavlarides LL. Investigations on supercritical transesterification
- of chicken fat for biodiesel production from low-cost lipid feedstocks. The J of Supercriti Fluids.
- 569 2010;54:53-60.
- 570 [22] 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.
- 572 [23] Lam MK, Lee KT, Mohamed AR. Homogeneous, heterogeneous and enzymatic catalysis
- for transesterification of high free fatty acid oil (waste cooking oil) to biodiesel: A review.
- 574 Biotechnology Advances. 2010;28:500-18.

- 575 [24] Miao X, Li R, Yao H. Effective acid-catalyzed transesterification for biodiesel production.
- 576 Energ Conver and Manage. 2009;50:2680-4.
- 577 [25] Kulkarni MG, Gopinath R, Meher LC, Dalai AK. Solid acid catalyzed biodiesel production
- by simultaneous esterification and transesterification. Green Chemistry. 2006;8:1056-62.
- 579 [26] Zhang Y, Dube M, McLean D, Kates M. Biodiesel production from waste cooking oil: 1.
- Process design and technological assessment. Bioresou techno. 2003;89:1-16.
- 581 [27] Marchetti J, Miguel V, Errazu A. Possible methods for biodiesel production. Ren and Sust
- 582 Energ Rev. 2007;11:1300-11.
- 583 [28] M. Canakci JVG. Biodiesel production via acid catalysis. ASAE 1999;42:1203-10.
- 584 [29] Michael J. Goff NSB, Shailesh Lopes, William R. Sutterlin, and Galen J. Suppes. Acid
- Catalyzed alcoholysis of soybean oil. J Am Oil Chem Soc 2004;81:415-20.
- 586 [30] 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.
- 588 [31] Marchetti JM, Errazu AF. Esterification of free fatty acids using sulfuric acid as catalyst in
- the presence of triglycerides. Biomass and Bioenergy. 2008;32:892-5.
- 590 [32] M. Canakci JVG. Biodiesel production from oils and fats with high free fatty acids.
- 591 Transactions of the ASAE 2003;44(6):1429-36.
- 592 [33] Zheng S, Kates M, Dube MA, McLean DD. Acid-catalyzed production of biodiesel from
- waste frying oil. Biomass Bioenerg. 2006;30:267-72.
- 594 [34] Zhang Y, Dube M, McLean D, Kates M. Biodiesel production from waste cooking oil: 2.
- Economic assessment and sensitivity analysis. Bioresourc technol. 2003;90:229-40.
- 596 [35] Marchetti JM, Pedernera MN, Schbib NS. Production of biodiesel from acid oil using
- 597 sulfuric acid as catalyst: kinetics study. International Journal of Low-Carbon Technologies.
- 598 2010;6:38-43.
- 599 [36] Tiwari AK, Kumar A, Raheman H. Biodiesel production from Jatropha oil (Jatropha curcas)
- with high free fatty acids: an optimized process. Biomass Bioener. 2007;31.
- 601 [37] kumar M, Sharma MP. Selection of potential oils for biodiesel production. Renewable and
- Sustainable Energy Reviews. 2016;56:1129-38.
- [38] Zhang Y. Biodiesel production from waste cooking oil: 1. Process design and technological
- assessment. Bioresource Technology. 2003;89:1-16.
- 605 [39] Intelligen Inc. SuperPro Designer®, 1996. Available at
- 606 http://www.intelligen.com/superpro_overview.html
- 607 [40] Aspentech. Aspen Plus®, 2018. Available at
- 608 https://www.aspentech.com/products/engineering/aspen-plus

- 609 [41] Kumar A, Sharma S. Potential non-edible oil resources as biodiesel feedstock: An Indian
- perspective. Renewable and Sustainable Energy Reviews. 2011;15:1791-800.
- 611 [42] Gui MM, Lee KT, Bhatia S. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as
- 612 biodiesel feedstock. Energy. 2008;33:1646-53.
- 613 [43] Bioenergies in East Africa between challenges and opportunities. in: D.Z. Marco Setti,
- 614 (Ed.). Energy-Agro-Food Nexus in East Africa. ACP-EU Cooperation Programme in Higher
- 615 Education (EDULINK)2016
- 616 [44] KEMCORE. Leaching Chemicals, 2018. Available at https://www.kemcore.com/sulphuric-
- 617 <u>acid-98.html#</u>. April 2018
- 618 [45] Wage Indicator Foundation. Salary Scale in Ethiopian Public Sector, 2018. Available at
- 619 https://mywage.org/ethiopia/home/salary/public-sector-wages. March 2018
- 620 [46] NUMBEO. Cost of Living in Ethiopia, 2018. Available at https://www.numbeo.com/cost-
- of-living/country result.jsp?country=Ethiopia. March 2018
- 622 [47] Cost to Travel. Electricity price in Ethiopia, 2015. Available at
- 623 https://www.costtotravel.com/cost/electricity-in-ethiopia. March 2018
- 624 [48] Peters MS, Timmerhaus KD, West RE, Timmerhaus K, West R. Plant design and
- economics for chemical engineers. McGraw-Hill New York1991.
- 626 [49] Chemical Engineering. Essentials for the Chemical Process Industry Professionals, Plant
- 627 Cost Index. Access Intelligence, 2018. Available at http://www.chemengonline.com/site/plant-
- 628 cost-index/. February 2018

636

637

- [50] Sinnott RK. Chemical Engineering Design in: C. Richardson, (Ed.). Chemical Engineering.
- Fourth ed. Elsevier Butterworth-Heinemann, 2005.
- 631 [51] Marchetti JM, Miguel VU, Errazu AF. Techno-economic study of different alternatives for
- biodiesel production. Fuel Proces Technol. 2008;89:740-8.
- [52] Yu Q. Design of environmentally friendly calcium sulfate based building materials towards
- an improved indoor air quality. Technische Universiteit Eindhoven, Eindhoven, 2012.