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### Article

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1 Improving biodiesel yield of animal waste fats by combination of a pre-treatment  
2 technique and microwave technology

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7 **ABSTRACT:** Recently, due to its low cost there has been increased attention on  
8 Animal Waste Fats (AWFs) as a feedstock for biodiesel production. Advanced  
9 microwave technology has also been reported by many researchers to enhance the  
10 transesterification in biodiesel production. However, esterification of free fatty acids in  
11 the feedstock reported here has not attracted so much attention. AWFs come with its  
12 challenges namely, high free fatty acid (FFA) content and high water content. This  
13 study utilizes AWFs (tallow) containing very large amount of FFA; (25wt.%, 18 wt.%,  
14 and 9.4 wt.% FFA/AWFs) as feedstock for fatty acid methyl ester (FAME) production.  
15 A simple thermal pre-treatment technique followed microwave assisted esterification  
16 with methanol (MeOH) was conducted in a batch process to reduce the FFA content  
17 to as low as 1wt.% FFA, which is then suitable for the alkaline transesterification  
18 process. The pre-treatment of AWFs at 88°C to first reduce water and decrease  
19 viscosity, followed by an operating microwave power of 70W producing a power  
20 density 1.147mW/m<sup>3</sup>, achieved a 15% increase in reduction of FFA over 30W  
21 microwave power and conventional thermal method. Under optimum conditions, using  
22 2.0 wt.wt% sulphuric acid catalyst/AWFs and 1:6 molar ratio AWF/MeOH, the FFA  
23 conversion of 93wt. % was achieved. The results indicated that the pre-treatment and  
24 microwave application provided a faster route to high FFA reduction of AWFs during  
25 esterification process. The proposed technology is promising for the potential scale up  
26 industrial application.

27 *Keywords: Microwave, Free fatty acid, fatty acid methyl ester, animal waste fats,*  
28 *feedstock*

## 29 1. INTRODUCTION

30 The availability and sustainability of adequate supplies of less expensive feedstocks  
31 will, to a large extent, fast track the delivery of competitive biodiesel for commercial  
32 purposes. Waste fat, oil and grease (FOG) from industrial origin and sewers, and  
33 category 1 tallow are valuable alternatives feedstocks, replacing vegetable oils, though  
34 requiring some pretreatment for excellent biodiesel yield. These FOGs and tallow are  
35 generally difficult to handle because they are solid at room temperature, highly  
36 degraded and particularly have a high free fatty acid and water content which requires  
37 pretreatment for commercially acceptable conversion efficiency. Many studies have  
38 reported various feedstocks for biodiesel production, especially from low value plant  
39 oils, but there have been far fewer studies on animal fat. Amongst these Canakci and  
40 Van Gerpen [1] developed a technique to reduce the FFA level of high acid feed stock  
41 to less than 1.0 wt.% FFA with an acid catalysed pre-treatment using 20 wt.% palmitic  
42 and 40 wt.% palmitic acids creating acid values of 41.33 and 91.73 mg.KOH/g  
43 respectively. Canoira et al. [2], Ramadhas et al. [3], Encinar et al. [4] also reported  
44 acid esterification using mixtures of animal fat and plant oil.

45  
46 The production of biodiesel involves the transesterification of a triglyceride, (TG) stock  
47 (vegetable or animal oil or fat) with excess methanol (MeOH) in the presence of an  
48 alkali catalyst such as sodium hydroxide (NaOH) to yield mixed FAME. Reaction rates  
49 and the yield of FAME has been extensively studied and the effect of variables such  
50 as MeOH: TG ratio, concentration of catalyst, temperature, etc. have been  
51 exhaustively examined and reviewed [5]. It is generally accepted that the presence of  
52 FFA in the feedstock adversely affects the reaction and particularly that soap formation  
53 renders efficient settling difficult if not impossible. The acid value must be reduced  
54 below 2 mg.KOH/g of oil for effective processing of the transesterification reaction [1,  
55 6]. The presence of free fatty acid leads to soap formation in the presence of an alkali  
56 catalyst during transesterification reaction. Hence the importance of acid esterification  
57 process. To avoid this problem high FFA feedstock, usually waste oils and fats, are  
58 pre-treated with MeOH in the presence of an acid catalyst such as H<sub>2</sub>SO<sub>4</sub> (sulphuric  
59 acid) thereby esterifying the FFA to FAME. Again, the reaction has been studied,  
60 though by no means as exhaustively as the biodiesel transesterification, though the  
61 effect of variables resembles that of that reaction as for example reported by

62 Gnanaprakasam. et al. [5], Chai et al. [7] , Mohammed and Bhargavi [8].

63

64 The decision to either progress with (a) one step- alkaline transesterification or two  
65 step –acid pre-esterification to reduce the FFA followed by a base-catalysed  
66 transesterification depends significantly on the initial quantity of FFA in the oil/fat  
67 substrate for biodiesel production. Extensive work has been carried out on the yield of  
68 biodiesel with respect to FFA content and it was found that transesterification would  
69 not proceed if FFA content in the oil were > 2 wt. % [3, 9].

70

71 The effect of microwaves in accelerating the rate of chemical reactions is well known.  
72 There have been a wide range of studies, though almost all small scale, on the effect  
73 of microwave heating on the transesterification reaction, generally indicating a positive  
74 correlation between microwave heating on rate and yield [10, 11]. Similarly, of the  
75 application of microwaves to enhance the rate or yield of the esterification is now  
76 attracting more attention [12-16]. Most studies have been at laboratory scale using a  
77 modified domestic microwave as energy source. It is difficult to compare these  
78 laboratory studies, as often there is insufficient detail to estimate parameters such as  
79 power density. However, more recently studies on the scale-up of the  
80 transesterification have started to appear to report that in a continuous flow reactor a  
81 high FAME content of 99.4 wt. % can be obtained in a short residence time of 1.75 min  
82 [17]. This process required an energy consumption of about a half of the conventional  
83 process and all properties of obtained biodiesel were in the range of EN/ASTM  
84 standard limit [18]. It seems reasonable to expect some advantages for the  
85 esterification reaction using similar conditions [13, 19]. This study aims to improve  
86 conversion efficiency and increase reaction rates of mixture of high FFA substrates in  
87 acid esterification process for biodiesel production from animal fat (tallow) using  
88 bespoke microwave methods.

## 89 **2. METHOD**

### 90 **2.1 Material**

91 Methanol, Optima LC/MS Grade of purity 99.9%, sulphuric acid A.R. Grade of purity  
92 97.5%, ethanol absolute of purity 99%, p-cymene of purity 99+% and potassium

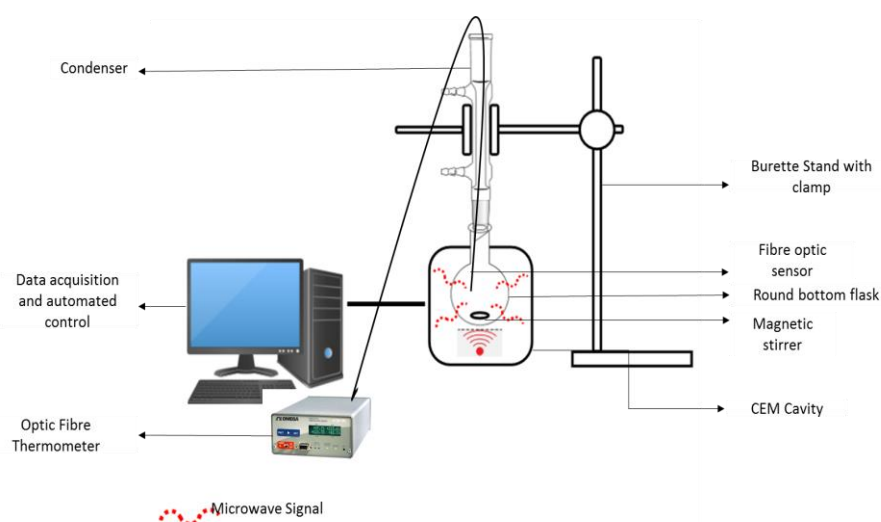
93 hydroxide All reagents used were purchased from Fisher Chemical and Sigma Aldrich.  
94 Tallow samples containing 9.4 wt. %, 18 wt.%, 25 wt.% FFA/AWFs and pre-treated  
95 waste oils containing 17.9 wt.% FFA/AWFs were provided by Argent Energy UK Ltd.  
96 Water in oil test kit was purchased from Hach Company to determine the percentage  
97 water in the oil sample.

98

## 99 2.2 Experimental Procedures

100 The tallow was pre-heated in 250ml bottle on a water-bath at 50° C using a Fisher  
101 Scientific advanced hotplate stirrer. In typical experiments 50.0g of pre-heated tallow  
102 was placed in a round bottom flask and first methanol/AWF (10, 20 wt. %) and then  
103 H<sub>2</sub>SO<sub>4</sub>/AWFs (0.8, 1.0 and 2.0 wt. %) were added to the tallow, shaking vigorously but  
104 gently to avoid spill.

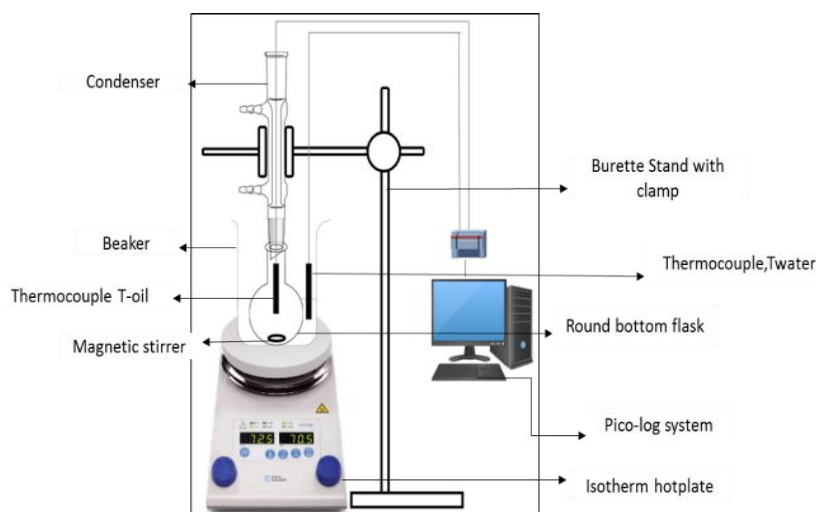
105 The CEM Discover SP Microwave system with Explorer 12 Hybrid Auto sampler with  
106 reflux set up (open vessel) was prepared for the esterification reaction and all  
107 parameters were set as desired for the microwave methods, as shown in Figure 1.  
108 The conventional method employed a water bath with reflux set up (open vessel) for  
109 the esterification reaction, Figure 2.



110

111

**Figure 1: Schematics diagram for CEM method**



112  
113 **Figure 2: Schematics diagram for Conventional method**

114  
115 **2.2.1. Non-pre-treatment (NPT)**

116 *(a) CEM method*

117 The flask was transferred to the CEM Discover SP microwave system with the  
118 following settings; temperature;73°C stirring power; high (300rpm) microwave power  
119 varied ; (30W, 70W). The Initial temperature of the sample was 38°C and microwave  
120 power assisted in ramping temperature from 38 °C to 73°C in 4-6 minutes. Once the  
121 desired operating temperature was attained, the microwave power reduces to as low  
122 as 0W.

123 *(b) Conventional method*

124 The following settings were applied; temperature 73°C, stirring power varied (300rpm).  
125 The initial temperature of the sample was 38°C and temperature gradually increases  
126 to 73°C after 30-40 minutes. The heating was adjusted to maintain reflux, once the  
127 desired operating temperature was attained.

128 **2.2.2 Pre-treatment Option (PTO)**

129 *(a) CEM method*

130 The sample was first preheated at 88°C using microwave power with stirring power  
131 high (300rpm) to achieve a less viscous substrate and reduced water content.

132 Microwave power was varied (30W, 70W) and temperature ramped to 90°C in 4-6  
 133 minutes. Temperature was reduced to 73°C prior to addition of methanol and sulphuric  
 134 acid solution.

135 *(b) Conventional method*

136 The sample was transferred to the conventional water bath system with the following  
 137 parameters settings; temperature; 88°C and stirring power 300rpm. Initial temperature  
 138 of the sample was 38°C and temperature gradually increased to 88°C in 40 minutes.  
 139 The Isotherm advanced hotplate features a thermostat control system, which was used  
 140 for resetting temperature to 73°C prior to the addition of methanol and sulphuric acid.

141

142 A summary of design of experiment for the study is presented in Table 1 and 2.

143

144

**Table 1: Matrix for design of experiment NPT method**

Method	T (°C)	Molar ratio AWF : MEOH	Microwave Power (W)	Stirrer rpm	Reaction time	Acid catalyst (wt.wt%)
CEM	73	1:3, 1:6	30,70	300	120, 60	0.8, 1.0, 2.0
Conventional	73	1:3	0	300-1000	150	0.8, 1.0

145

146

**Table 2: matrix for design of experiment PTO method**

Method	Pre-treatment T (°C)	Operating T (°C)	Molar ratio AWF : MEOH	Microwave power (W)	Stirrer rpm	Reaction time	Acid catalyst (wt.wt%)
CEM	88	73	1:6	70	300	120, 60	2.0
Conventional	88	73	1:6	0	300-1000	150	2.0

147

148 The magnetic stirrer employed for both methods described was 6 x 15mm size oval  
 149 shape. The reaction lasted for 120 minutes, aliquot were taken every 30 minutes (0,  
 150 30, 60, 90 and 120) to determine the reduced FFA.

151 **2.3. Analytical methods**

152 **2.3.1. Washing sample**

153 An aliquot was collected via the condenser using a narrow diameter tube attached to

154 a syringe and the sample was released in 500ml bottle containing hot water. The  
155 mixture was shaken vigorously to remove H<sub>2</sub>SO<sub>4</sub>. The sample was then left to separate  
156 in to oil/fat and water layers. The oil/fat (5ml) was pipetted in to 15ml centrifuge tube  
157 then a further aqueous suspension was made by adding water (10ml) to the pipetted  
158 sample before centrifuging using the benchtop Centrifuge Sigma 3-16PK for 5 minutes.  
159 The result is a well-separated into distinct oil and water fractions.

### 160 **2.3.2. Acid value**

161 The acid value of the reaction was determined by acid -base titration technique ASTM  
162 D 664 (ASTM, 2003). Measured sample was pipetted into a 100ml beaker and then  
163 prepared for titration by dissolving the sample in 3:1 ethanol and p-cymene solution  
164 and titrated against a standard solution of 1M potassium hydroxide solution using a  
165 Metrohm. 848/877 Titrino This study has limited the FFA analysis to acid value which  
166 is an acceptable method for FFA analysis in the biodiesel industry.

167

### 168 **2.3.3. Water content**

169 Water content was determined using the Hach water in oil test kit. Model (W0-1) and  
170 the procedure provided.

## 171 **3. RESULTS and DISCUSSION**

### 172 **3.1. Raw material Content**

173 The raw material parameters are presented in Table 3.

174

175

**Table 3: Parameters of samples A, B and C**

Sample and other parameters	A	B	C
Acid value mgKOH/g	18.3	37.2	51.5
Initial Water content, %	0.60	0.62%	0.60%
FFA content, %	9.4%	18%	25%

### 176 **3.2 Pre-treatment option to reduce FFA**

#### 177 **3.2.1 Pre-treatment of AWF**



178 In order to obtain a high ester yield by pre-esterification with sulphuric acid as catalyst,  
 179 initial water content was reduced to 0.55% by preheating samples at 88°C using  
 180 conventional heating method and microwave method respectively as shown in Table  
 181 4. Water content was measured after 120 minutes using the Hach Lange Water in Oil  
 182 test kit. Both conventional and CEM methods recorded similar results as depicted in  
 183 Table 4.

184  
 185

186 ***Table 4: measurement of water content in oil for after pretreatment option***  
 187 ***using conventional and microwave heating***

Sample ID	Initial H2O Content @0hr	Conventional method Final H2O content @2hrs	CEM method Final H2O content @2hrs
9.4% FFA	0.60%	0.55%	0.55%
18% FFA	0.62%	0.55%	0.55%
25% FFA	0.60%	0.55%	0.55%

188

189 Conversion of fatty acid to biodiesel could be affected if the water content is high [4,  
 190 6]. Chung et al. suggested that water and FFA be kept at 0.06wt. % and 0.5wt.%  
 191 respectively [20]. In acid catalysed method, FAME conversion could be affected by as  
 192 little as 0.1% water content of the fats [21, 22]. In these experiments the water content  
 193 of the AWF was found to have values in the range 0.60-0.62 wt. %. These values  
 194 were further reduced to 0.55 wt.% by pre heating. Due to the peculiarity of AWFs the  
 195 emulsified water is difficult to break free from the emulsion as observed in this study.  
 196 One of the reasons other workers found treatment of this type of waste difficult is that  
 197 reduction of FFA seem to respond to thermal history during heat treatment rather than  
 198 reduction of FFA simply being a function of temperature and time.

199 **3.2.2 Acid esterification condition**

200 It has been reported by many researchers that acid esterification reaction is  
 201 influenced by variables such as: alcohol to fat ratio, amount of catalyst, effect of  
 202 temperature, and stirring power [3, 11, 23-25]. The present study also investigated the  
 203 influenced of these variables; alcohol to fat molar ratio, amount of catalyst, effect of  
 204 temperature and stirring power. The results from the investigation are presented in  
 205 graphical and tabular representation.

206

207 **3.2.2.1. Effect of methanol to oil ratio**208 **Table 5 microwave assisted FAME production at constant temperature 73 °C in**  
209 **comparison with conventional method(0)**

Entry	Method	Molar ratio (AWFs:MeOH)	Reaction time(seconds)	Catalyst wt.wt%	Microwave power(W)	Conversion (%)MW method	Conversion (%) Conventional method
1.	II	1:6	600	2.0	70	34	5
2.	II	1:6	1200	2.0	70	50	10
3.	II	1:6	1800	2.0	70	77	41
4.	II	1:6	3600	2.0	70	88	71
5.	I	1:6	1800	2.0	70	28	12
6.	I	1:6	3600	2.0	70	85	64
7.	I	1:6	7200	2.0	70	93	95
8.	I	1:6	1800	1.0	30	46	34
9.	I	1:6	3600	1.0	30	55	55
10	I	1:6	1800	0.8	30	48	22
11	I	1:3	3600	0.8	30	55	45
12	I	1:3	1800	1.0	70	61	34
13	I	1:3	3600	1.0	70	66	62

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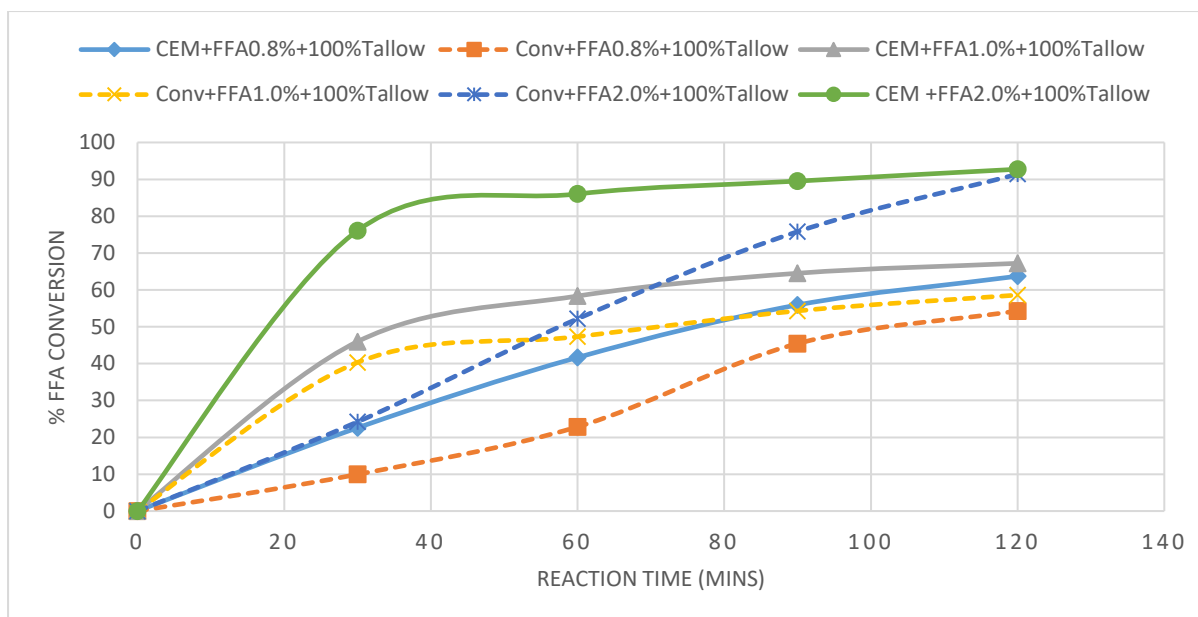
211 A few studies have reported acid catalysed esterification using animal fat feedstock [4,  
212 26-28]. Many studies reported that acid catalyst requires excess alcohol for good fatty  
213 acid methyl ester (FAME) yield [3, 6, 29]. Bhatti et al. [27], Canakci and Van Gerpen  
214 [1] advocated the use of large excess quantities of alcohol. The conversion efficiency  
215 of the acid esterification of different feedstock in relation to molar ratio obtained in the  
216 present study is presented in Table 5. The FAME yield increased with increasing molar  
217 ratio from 66% FFA conversion at 1:3 molar ratio to 88% FFA conversion at 1:6 molar  
218 ration in 3600sec reaction time for the microwave method. A similar trend was  
219 observed with the conventional method with FAME yield increased from 62% to 71%  
220 in 3600sec reaction time. One of the objectives of the study was to optimize material  
221 usage with particular emphasis on methanol reduction. Some studies reported the use  
222 of  $\geq 25\%$  v/v of methanol/AWF in the acid esterification process [28-30]. Ghadge and  
223 Raheman [30] reported 50 wt.% reduction in acid value at low methanol quantities and  
224 over 80% acid value reduction at high- methanol quantities. A few papers reported the

225 use of 10% vol of methanol and suggested that the methanol water fraction was  
226 collected at the top layer while the oil layer settles at the bottom [6, 30]. The present  
227 study, found that with lower percentage volume or weight of methanol used in acid  
228 esterification, the water and acid catalyst fraction migrates to the bottom layer with little  
229 methanol fraction at the top layer. However, the inconsistency in reporting might be  
230 due to the different feedstock and the wt.% acid catalyst used in the acid esterification  
231 reaction.

232 The use of lower percentage of methanol is preferred in the industry for many reasons.  
233 The flammability property of methanol, reduced cost of production and lastly, ease of  
234 phase separation are some clear reasons to reduce methanol usage in the biodiesel  
235 production.

### 236 **3.2.2.2. Effect of acid catalyst amount**

237 Three different concentrations of H<sub>2</sub>SO<sub>4</sub> acid catalyst; 0.8.wt%. 1.0 wt%. and 2.0 wt.  
238 % H<sub>2</sub>SO<sub>4</sub>/AWF were tested to assess the percentage conversion of FFA for substrates  
239 with large amount of FFA contents. Figure 3 shows the percentage conversion FFA  
240 for substrate sample with initial FFA content of 37.2 mg.KOH/g. The percentage  
241 conversion FFA increased with an increase in acid catalyst for both microwave and  
242 conventional methods. A 2 wt. % acid catalyst recorded 93 wt. % and 95 wt. %  
243 conversion FFA for microwave and conventional methods respectively. However,  
244 there seems to be a trend with acid catalyst achieving better reduction in the first 60  
245 minutes with microwave method compared to the conventional method as depicted in  
246 Figure 3 and Table 5.



247

248 **Figure3: Effect of percent amount of sulphuric acid on FFA reduction**

249

250 Improving the conversion efficiency and reaction time of biodiesel production is a clear  
 251 objective of this study and the concentration of acid catalyst is one of the important  
 252 variables for this conversion. Khan et al. demonstrated that 0.4% sulphuric acid  
 253 produces maximum conversion efficiency with high FFA waste cooking oils [31]. In  
 254 addition, few researchers reported 0.5 wt. % H<sub>2</sub>SO<sub>4</sub> as the optimum condition for fats  
 255 with high FFA content [3, 4, 13]. Some researchers reported a range of sulphuric acid  
 256 amount of ≥1.0 wt. % as optimal condition for maximal acquisition of FAME yield [25,  
 257 30]. Canakci and Van Gerpen worked with a range of acid catalyst values (0, 5, 15 and  
 258 25 wt. %) and reported that even at 25 wt.% H<sub>2</sub>SO<sub>4</sub>/oil, the acid value did not reduce  
 259 to 2mgKOH/g after 1 hour reaction time [1]. Gole and Gogate reported catalyst  
 260 concentration over a range 2 to 4 wt. % of H<sub>2</sub>SO<sub>4</sub>/oil using microwave, ultrasound and  
 261 the sequential of both methods recorded 2wt.% as the optimal concentration for  
 262 conversion efficiency [32]. There seems to be a variation in the amount of acid catalyst  
 263 required for optimal conversion, which might necessitate further investigation.

264

265 In this study a range of concentrations of sulphuric acid were investigated with the  
 266 various FFA feedstocks. Concentrations of FFA decrease rapidly initially but as the  
 267 reaction progresses the rate falls following a pseudo first order reaction kinetics. This  
 268 behaviour is consistent with previous studies [33-36]. The slow decrease of FFA later

269 in the reaction may also be due to accumulation of water. In addition, the sulphuric  
270 acid tends to migrate into the water phase from methanol phase when the stirring is  
271 poor and becomes unavailable for the FAME production.

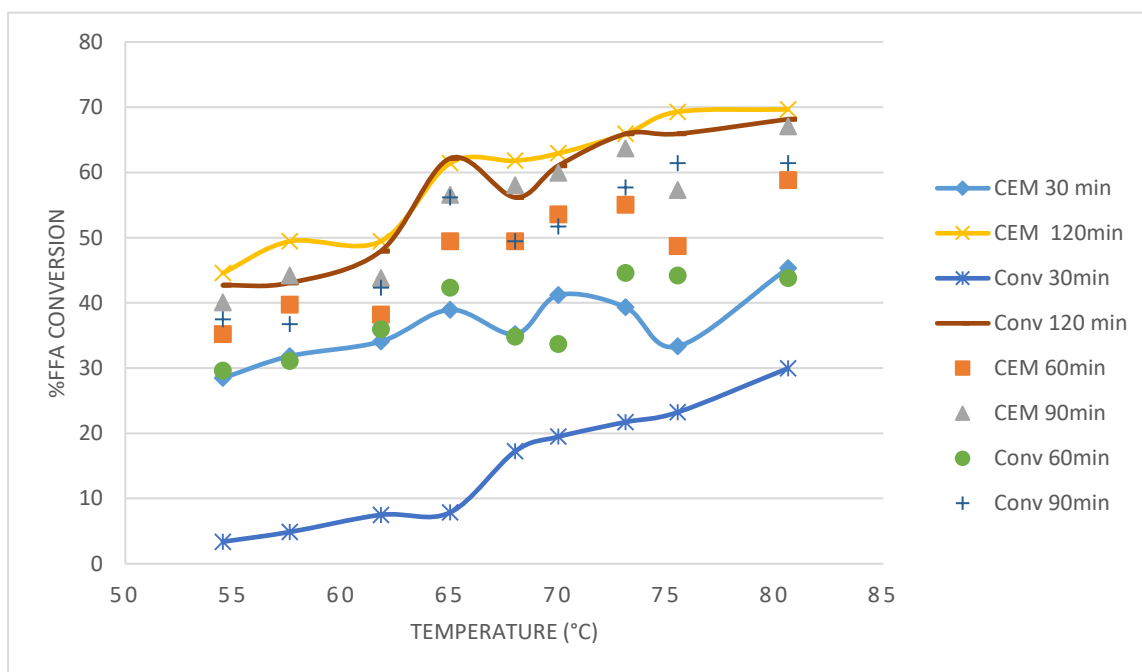
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### 273 **3.2.2.3 The effect of temperature**

274

275 The conversion efficiency is low and reaction rate is very slow at room temperature  
276 even after 2 hours stirring for some feedstocks. With an increase temperature, the  
277 conversion takes place at a faster rate. The optimum temperature for the acid  
278 esterification reaction on a large scale is 73°C, which applies in the industry. Many  
279 researchers suggest that esterification reactions can be performed at lower  
280 temperatures when using microwave heating, compared to the standard heating  
281 process, which was the basis for investigating lower temperatures [4, 6, 26, 28, 29].  
282 Jeong et al. suggested that the optimum reaction temperature depended on catalyst  
283 amount and was between 60-70°C [25]. As expected the reaction temperature also  
284 exerted significant influence on synthesis rate and high reaction temperatures tended  
285 to induce methanol evaporation. Temperatures below the boiling point of methanol  
286 reduced reflux and the methanol/AWF interface. This can be explained due to the fact  
287 that increase temperature favours the acceleration of the forward direction reaction as  
288 the reaction is endothermic under a kinetically controlled regime, which has been also  
289 demonstrated in earlier research [16]. From Le Châtelier's principle, the equilibrium  
290 shifts to the right for endothermic reactions as the temperature increases [37]. The  
291 present study investigated the effect of a range of temperatures using conventional  
292 heating and microwave technology on FFA reduction for feedstock with large amount  
293 of FFA shown in Figure 4. Increased reaction temperature from 55°C to 80°C showed  
294 positive effect on the conversion of FFA. Interestingly, at 30 minutes reaction time, the  
295 microwave method (CEM 30 min) converted 44% FFA to FAME in comparison with  
296 the conventional method (Conventional 30min) which produced 30% FFA conversion  
297 as depicted in Figure 4. Conversely, at 120 minutes reaction time, both microwave and  
298 conventional method converted 70% and 68% FFA to FAME. The results might  
299 suggest that microwave method is effective and showed increased percentage  
300 conversion in the first 30-60 minutes of the esterification reaction in comparison with  
301 conventional method under similar conditions.

302 However, the quantity of FFA were considerably still too high to proceed on to  
 303 transesterification with method I (NPT). Therefore, improving the conversion of high  
 304 FFA tallow using the pretreatment method and conditions specified in the matrix shown  
 305 in Table 2 achieved a least 15% increase over no-pre-treatment method and  
 306 conventional methods as depicted in Figure 4. Preheating the tallow at 88 °C prior to  
 307 injection of methanol and sulphuric acid solution might have further reduced the water  
 308 content in the fat and likewise reduce the viscosity of the fat/oil promoting good stir  
 309 and increasing the methanol/sulphuric/fat contact. The improvement in viscosity is  
 310 dependent on the chain length and the degree of saturation of the fatty acids, and  
 311 temperature [38-40].  
 312 These properties enhance the forward reaction and further reduces the FFA in the  
 313 substrate.

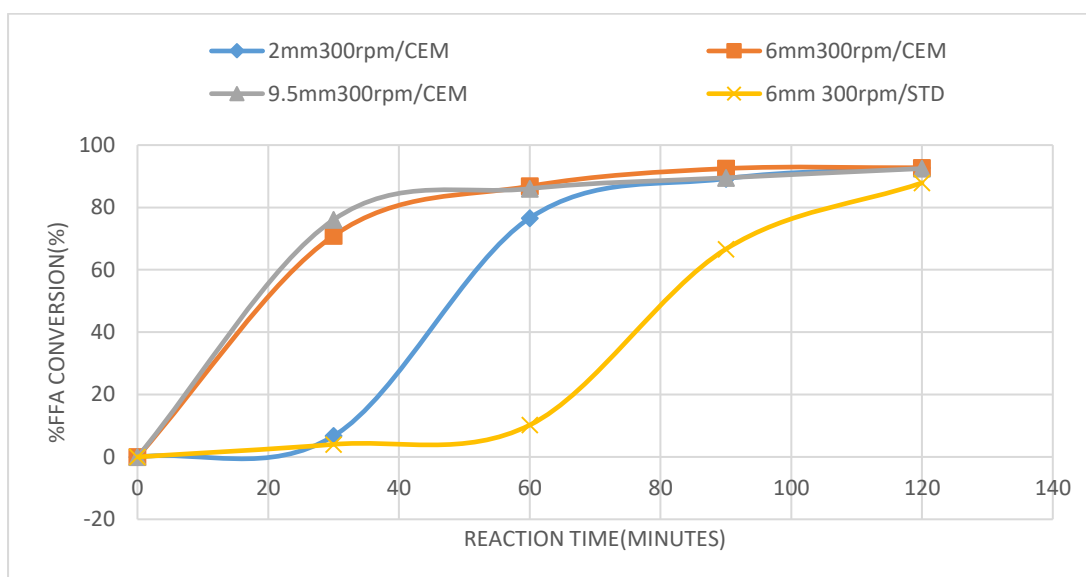


314  
 315  
 316 **Figure 4: The effect of temperature on FFA reduction at (30, 60, 90 & 120**  
 317 **minutes) reaction time for microwave and conventional reactions**

318  
 319 **3.2.2.4 Effect of stirrer sizes and stirring on FFA conversion**

320  
 321 The present study used a range of stirring magnets e.g. the pea-shaped magnetic stir,  
 322 small 2mm, 6mm and 9.5mm magnetic fleas were used. Figure 5 show the difference  
 323 in the flea sizes and effect and its effect on FFA reduction. The 6mm magnetic stir at

324 300rpm stirring presented better results when compared to the 2mm and 9.5mm at  
325 300rpm for CEM and 6mm at 300rpm for conventional method as illustrated in Figure  
326 5.



327  
328

329 **Figure 5: The effect of stirring frequency and stirrer size on %FFA conversion**

330 Results from experiments shown in Figure 5 suggest that the size and shape of  
331 magnetic stirrer bar influences the stirring power and the reactant-catalyst contact.  
332 Although, when using the CEM method, it is important to choose appropriate magnetic  
333 stir to prevent deflection of the electromagnetic waves from the system. Hence, the  
334 9.5mm was ineffective for the microwave method but produced good reactant-catalyst  
335 contact in the conventional method. Stirring during the acid esterification reaction also,  
336 plays a role in uniform mixing of reaction mixture (improve surface contact area). A few  
337 studies reported the stirring rates range between 150-800 rpm [2, 32].

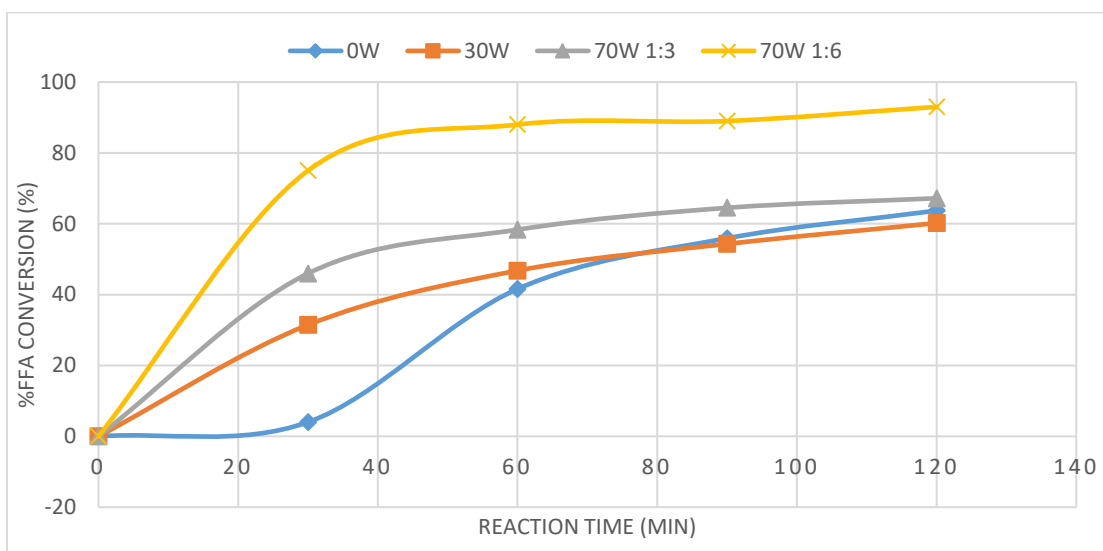
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### 340 3.2.2.5 The effect of microwave on FFA conversion

341

342 Microwave technology has been reported to reduce reaction time in transesterification  
343 to a few minutes [41, 42]. In contrast, Suppalakpanya et al. suggested a reaction time  
344 of 60 minutes for esterification at microwave power 70W but with no reference to  
345 temperature at which reaction occurred [43]. The present study is in agreement with  
346 previous report on microwave increasing the rate of reaction as observed in Figure 6.

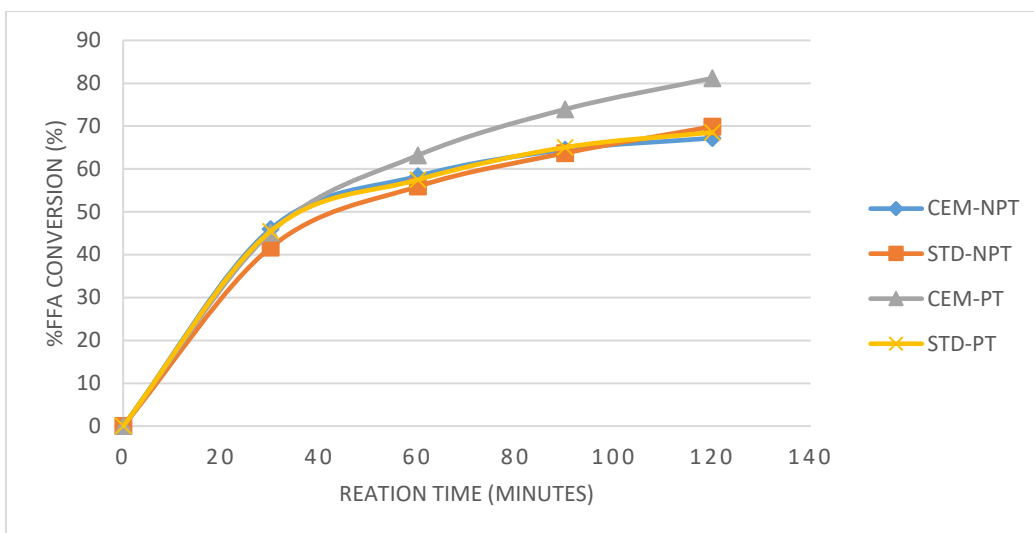
347 Increase in microwave power increase the FFA percentage conversion as presented  
348 in Figure 6. Esterification at microwave power 70 W and 1: 6 AWF: MeoH molar ratio  
349 achieved 93% FFA conversion while conventional method was observed to be slightly  
350 better than the microwave power at 30W. The pretreatment method with microwave  
351 application presented 15% increase in conversion yield over conventional method and  
352 non-pre-treatment option at the same temperatures as depicted in Figure 7.



353  
354 **Figure 6: shows %FFA conversion at 0, 30, &70W in 120 minutes, reaction**  
355 **kept at constant reaction condition, 1:3 AWFs/ methanol molar ratio, 1.0% w/w**  
356 **sulphuric acid and 73°C in comparison with 1:6 AWFs/methanol, 2.0% w/w**  
357 **sulphuric acid**

358  
359 A comparison of the present study with previous studies is presented in Figure 7. The  
360 present study has attempted to reduce AWF with large amount of FFA (>10 wt.%FFA)  
361 via batch process, with pretreatment option using conventional heating and microwave  
362 application. In addition, a reduced concentration of methanol and sulphuric acid with  
363 moderate microwave power exposure is compared with previous studies [23, 33].  
364 Esterification reaction with moderate microwave power, 70W, and a pretreatment  
365 option gave 88% FFA conversion yield in 3600 sec reaction time.





366

367 **Figure 7 A comparison between pre-treatment and non pre-treatment option**  
 368 **and its effect on %FFA conversion with microwave method and conventional**  
 369 **method (1:3 AWFs/methanol molar ratio, 1.0 sulphuric acid at 73°C)**

370

371 **Table 6 : A matrix of experimental conditions and % FFA conversion in**  
 372 **comparison with other studies**

AUTHORS	METHOD	AMOUNT OF ACID CATALYSED	MOLAR RATIO	MICROWAVE POWER	REACTION TIME	INITIAL FFA in oil/fat	% FFA CONVERSION
Kamath et al 2011	2.45GHz Domestic mw Open vessel	3.73%w/w	1:10	180, 300W	190s	8.8%	89-91%
Suwannapa and Tippayawong [33]	2.45GHz Domestic mw Open vessel	1.5%w/w	1:3	340W	1800s	6.18-6.80%	95%
		1.0%w/w	1:6		1200s		94.5%
		2.0%w/w	1:6		2400s		95.6%
		1.5%w/w	1:9		1800s		98.3%
		1.0%w/w	1:12		1200s		97.6%
Present study	2.45GHz CEM Open vessel (73°C)	0.8%w/w	1:3	30W	3600	18%-25%	47%
		1.0%w/w	1:3	30W	3600		55%
		1.0%w/w	1:3	70W	3600		64%
		2.0%w/w	1:6	70W	1800		75%
		2.0%w/w	1:6	70W	3600		88%

373

#### 374 4. CONCLUSION

375 The shift towards animal waste fats as feedstock for biodiesel production on a large

376 scale would be welcome but could be challenging. AWF such as tallow are typically  
377 very low grade with high FFA content (>20 wt. %) making them difficult to use for the  
378 conventional biodiesel process without the preliminary reduction of the FFA.  
379 Esterification, better described as pre-esterification is normally carried out with an acid  
380 catalyst and allows such low-grade raw material to be effectively and economically  
381 converted to biodiesel. However, the esterification reaction adds an additional step to  
382 the overall process and demands either higher reactor volumes or reduced throughput  
383 unless reaction times can be reduced. Therefore, anything that increases yield or  
384 decreases processing time would be extremely welcome. One potential avenue  
385 explored here is the use of microwave heating to accelerate the reaction. This is well  
386 known in laboratory scale studies of the biodiesel trans-esterification, though not  
387 employed significantly commercially. A similar use of microwave heating for  
388 esterification, especially of high FFA fats has not been widely reported and is certainly  
389 not used on an industrial scale. This laboratory-scale study on AWF with FFA content  
390 >20 wt. % has shown that the application of microwave either replacing the  
391 conventional heating or complementing it, could essentially improve the process by  
392 reducing the reaction time for FFA reduction and also increasing FAME yield, thus  
393 making this type of low cost feedstock available for the biodiesel industry. Further  
394 studies are underway to transfer this process to an industrial scale.

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## 401 **CONFLICT OF INTEREST**

402 The authors declare that there is no conflict of interest regarding the publication of this  
403 paper.

## 404 REFERENCES

405

- 406 1. Canakci, M. and J. Van Gerpen, *BIODIESEL PRODUCTION FROM OILS AND FATS WITH*  
407 *HIGH FREE FATTY ACIDS*. Transactions of the ASAE, 2001. **44**(6): p. 1429.
- 408 2. Canoira, L., et al., *Biodiesel from Low-Grade Animal Fat: Production Process Assessment and*  
409 *Biodiesel Properties Characterization*. Industrial & Engineering Chemistry Research, 2008.  
410 **47**(21): p. 7997-8004.
- 411 3. Ramadhas, A.S., S. Jayaraj, and C. Muraleedharan, *Biodiesel production from high FFA rubber*  
412 *seed oil*. Fuel, 2005. **84**(4): p. 335-340.
- 413 4. Encinar, J.M., et al., *Study of biodiesel production from animal fats with high free fatty acid*  
414 *content*. Bioresource Technology, 2011. **102**(23): p. 10907-10914.
- 415 5. Gnanaprakasam., A., et al., *Recent strategy of biodiesel production from waste cooking oil and*  
416 *process influencing parameters: a review*. J Energy, 2013: p. . 1-10.
- 417 6. Berchmans, H.J. and S. Hirata, *Biodiesel production from crude Jatropha curcas L. seed oil*  
418 *with a high content of free fatty acids*. Bioresource Technology, 2008. **99**(6): p. 1716-1721.
- 419 7. Chai, M., et al., *Esterification pretreatment of free fatty acid in biodiesel production, from*  
420 *laboratory to industry*. Fuel Processing Technology, 2014. **125**: p. 106-113.
- 421 8. Mohammed, A.R. and R. Bhargavi, ., *Biodiesel production from waste cooking oil, .* Journal of  
422 *Chemical and Pharmaceutical Research*,, 2015., **7**, .( 12, ): p. 670-681.
- 423 9. Canakci, M., *The potential of restaurant waste lipids as biodiesel feedstocks*. Bioresource  
424 *Technology*, 2007. **98**(1): p. 183-190.
- 425 10. Azcan, N. and A. Danisman, *Microwave assisted transesterification of rapeseed oil*. Fuel, 2008.  
426 **87**(10): p. 1781-1788.
- 427 11. Nomanbhay, S. and M. Ong, *A Review of Microwave-Assisted Reactions for Biodiesel*  
428 *Production*. Bioengineering, 2017. **4**(2): p. 57.
- 429 12. Mazo, P., G. Restrepo, and L. Rios, *Alternative methods for fatty acid alkyl-esters production:*  
430 *Microwaves, radio-frequency and ultrasound*, . Biodiesel—feedstocks and processing  
431 *technologies*, , ed. I.S.M.M.G. (Eds.). 2011, UK: InTech. . 271-290.
- 432 13. Patil, P.D., V.G. Gude, and S. Deng, *Biodiesel Production from Jatropha Curcas, Waste*  
433 *Cooking, and Camelina Sativa Oils*. Industrial & Engineering Chemistry Research, 2009.  
434 **48**(24): p. 10850-10856.
- 435 14. Gole, V.L., K.R. Naveen, and P.R. Gogate, *Hydrodynamic cavitation as an efficient approach*  
436 *for intensification of synthesis of methyl esters from sustainable feedstock*. Chemical  
437 *Engineering and Processing: Process Intensification*, 2013. **71**: p. 70-76.
- 438 15. Abubakar, Z., A.A. Salema, and F.N. Ani, *A new technique to pyrolyse biomass in a microwave*  
439 *system: Effect of stirrer speed*. Bioresource Technology, 2013. **128**: p. 578-585.
- 440 16. Lieu, T., S. Yusup, and M. Moniruzzaman, *Kinetic study on microwave-assisted esterification*  
441 *of free fatty acids derived from Ceiba pentandra Seed Oil*. Bioresource Technology, 2016. **211**:  
442 p. 248-256.
- 443 17. Choedkiatsakul, I., et al., *Biodiesel production in a novel continuous flow microwave reactor*.  
444 *Renewable Energy*, 2015a. **83**: p. 25-29.
- 445 18. Choedkiatsakul, I., et al., *Integrated flow reactor that combines high-shear mixing and*  
446 *microwave irradiation for biodiesel production*. Biomass and Bioenergy, 2015b. **77**: p. 186-191.
- 447 19. Baek, H., et al., *In-Water and Neat Batch and Continuous-Flow Direct Esterification and*  
448 *Transesterification by a Porous Polymeric Acid Catalyst*. Scientific Reports, 2016. **6**: p. 25925.
- 449 20. Chung, K.-H., J. Kim, and K.-Y. Lee, *Biodiesel production by transesterification of duck tallow*  
450 *with methanol on alkali catalysts*. Biomass and Bioenergy, 2009. **33**(1): p. 155-158.
- 451 21. Kusdiana, D. and S. Saka, *Effects of water on biodiesel fuel production by supercritical*  
452 *methanol treatment*. Bioresource Technology, 2004. **91**(3): p. 289-295.
- 453 22. Park, J.-Y., et al., *Effects of water on the esterification of free fatty acids by acid catalysts*.  
454 *Renewable Energy*, 2010. **35**(3): p. 614-618.
- 455 23. Venkatesh Kamath, H., I. Regupathi, and M.B. Saidutta, *Optimization of two step karanja*  
456 *biodiesel synthesis under microwave irradiation*. Fuel Processing Technology, 2011. **92**(1): p.  
457 100-105.
- 458 24. Banković-Ilić, I.B., et al., *Waste animal fats as feedstocks for biodiesel production*. Renewable

- 459 and Sustainable Energy Reviews, 2014. **32**: p. 238-254.
- 460 25. Jeong, G.-T., H.-S. Yang, and D.-H. Park, *Optimization of transesterification of animal fat ester*  
461 *using response surface methodology*. Bioresource Technology, 2009. **100**(1): p. 25-30.
- 462 26. Tashtoush, G.M., M.I. Al-Widyan, and M.M. Al-Jarrah, *Experimental study on evaluation and*  
463 *optimization of conversion of waste animal fat into biodiesel*. Energy Conversion and  
464 Management, 2004. **45**(17): p. 2697-2711.
- 465 27. Bhatti, H.N., et al., *Biodiesel production from waste tallow*. Fuel, 2008. **87**(13): p. 2961-2966.
- 466 28. Montefrio, M.J., T. Xinwen, and J.P. Obbard, *Recovery and pre-treatment of fats, oil and grease*  
467 *from grease interceptors for biodiesel production*. Applied Energy, 2010. **87**(10): p. 3155-3161.
- 468 29. Karmakar, A., S. Karmakar, and S. Mukherjee, *Properties of various plants and animals*  
469 *feedstocks for biodiesel production*. Bioresource Technology, 2010. **101**(19): p. 7201-7210.
- 470 30. Ghadge, S.V. and H. Raheman, *Biodiesel production from mahua (Madhuca indica) oil having*  
471 *high free fatty acids*. Biomass and Bioenergy, 2005. **28**(6): p. 601-605.
- 472 31. Khan, M.A., S. Yusup, and M.M. Ahmad, *Acid esterification of a high free fatty acid crude palm*  
473 *oil and crude rubber seed oil blend: Optimization and parametric analysis*. Biomass and  
474 Bioenergy, 2010. **34**(12): p. 1751-1756.
- 475 32. Gole, V.L. and P.R. Gogate, *Intensification of synthesis of biodiesel from non-edible oil using*  
476 *sequential combination of microwave and ultrasound*. Fuel Processing Technology, 2013. **106**:  
477 p. 62-69.
- 478 33. Suwannapa, P. and N. Tippayawong, *Optimization of Two-Step Biodiesel Production from Beef*  
479 *Tallow with Microwave Heating*. Chemical Engineering Communications, 2017. **204**(5): p. 618-  
480 624.
- 481 34. Gude, V.G., et al., *Microwave energy potential for biodiesel production*. Sustainable Chemical  
482 Processes, 2013. **1**(1): p. 5.
- 483 35. Berrios, M., et al., *A kinetic study of the esterification of free fatty acids (FFA) in sunflower oil*.  
484 Fuel, 2007. **86**(15): p. 2383-2388.
- 485 36. Patil, P., et al., *Transesterification kinetics of Camelina sativa oil on metal oxide catalysts under*  
486 *conventional and microwave heating conditions*. Chemical Engineering Journal, 2011. **168**(3):  
487 p. 1296-1300.
- 488 37. Fogler, H.S., *Element of Chemical Reaction*. Fourth ed. 2006, Upper Saddle River, NJ07458  
489 Westford Manssachusetts.
- 490 38. Knothe, G. and K.R. Steidley, *Kinematic viscosity of biodiesel components (fatty acid alkyl*  
491 *esters) and related compounds at low temperatures*. Fuel, 2007. **86**(16): p. 2560-2567.
- 492 39. Refaat, A., *Correlation between the chemical structure of biodiesel and its physical properties*.  
493 International Journal of Environmental Science & Technology, 2009. **6**(4): p. 677-694.
- 494 40. Knothe, G. and L.F. Razon, *Biodiesel fuels*. Progress in Energy and Combustion Science, 2017.  
495 **58**: p. 36-59.
- 496 41. Gulsen, O., et al., *Microwave Assisted Transesterification of Maize (Zea Mays L.) Oil as a*  
497 *Biodiesel Fuel*. Energy Exploration & Exploitation, 2010. **28**(1): p. 47-57.
- 498 42. Ayas, N. and O. Yilmaz, *Catalytic esterification and transesterification reaction of high acidic*  
499 *value waste oil by microwave heating*. Environmental Progress & Sustainable Energy, 2015.  
500 **34**(2): p. 575-581.
- 501 43. Suppalakpanya, K., S.B. Ratanawilai, and C. Tongurai, *Production of ethyl ester from crude*  
502 *palm oil by two-step reaction with a microwave system*. Fuel, 2010. **89**(8): p. 2140-2144.
- 503