

RECOVERY OF DIESEL-LIKE FUEL FROM WASTE PALM OIL BY PYROLYSIS USING A MICROWAVE HEATED BED OF ACTIVATED CARBON.

Su Shiung Lam ^{a,e*}, Wan Adibah Wan Mahari ^a, Chin Kui Cheng ^b, Rozita Omar ^c, Cheng Tung Chong ^d, Howard A. Chase ^e

^a Eastern Corridor Renewable Energy Group (ECRE), School of Ocean Engineering, University Malaysia Terengganu, 21030 Kuala Terengganu, Malaysia

^b Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Pahang, Malaysia

^c Department of Chemical and Environmental Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia

^d Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia

^e Department of Chemical Engineering and Biotechnology, University of Cambridge, New Museums Site, Pembroke Street, Cambridge CB2 3RA, United Kingdom

(E-mail: lam@umt.edu.my, adibah.mahari@gmail.com, chinkui@ump.edu.my, rozitaom@upm.edu.my, ctchong@mail.fkm.utm.my, hac1000@cam.ac.uk)

Corresponding author

Su Shiung Lam, Eastern Corridor Renewable Energy Group (ECRE), School of Ocean Engineering, University Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia (E-mail: lam@umt.edu.my; Tel: +60 (9) 668 3844; Fax: +60 (9) 668 3991)

Abstract

Microwave pyrolysis using a well-mixed bed of activated carbon as both the microwave absorber and reaction bed was investigated for its potential to recover useful products from waste palm cooking oil – a cooking oil widely used in Asia. The carbon bed provided rapid heating (~18 °C/min) and a localized reaction hot zone that thermally promoted extensive pyrolysis cracking of the waste oil at 450 °C, leading to increased production of a biofuel product in a process taking less than 25 min. It also created a reducing reaction environment that prevented the formation of undesirable oxidized compounds in the biofuel. The pyrolysis produced a biofuel product that is low in oxygen, free of sulphur, carboxylic acid and triglycerides, and which also contains light C₁₀-C₁₅ hydrocarbons and a high calorific value nearly comparable to diesel fuel, thus showing great potential to be used as fuel. This pyrolysis approach offers an attractive alternative to transesterification that avoids the use of solvents and catalysts, and the need to remove free fatty acids and glycerol from the hydrocarbon product. The pyrolysis apparatus operated with an electrical power input of 1.12 kW was capable of producing a biofuel with an energy content equivalent to about 3 kW, showing a positive energy ratio of 2.7 and ≥73% recovery of the energy input to the system. The results show that the pyrolysis approach has

43 huge potential as a technically and energetically viable means for the recovery of biofuels
44 from the waste oil.

45 Keywords: pyrolysis; microwave pyrolysis; waste cooking oil; palm oil; activated carbon

46 **1. Introduction**

47 Cooking oil can be derived from various biological resources such as seeds from
48 plants (e.g. sunflower oil, sesame oil), nuts (e.g. soybean oil, peanut oil), and fruits (e.g.
49 palm oil, olive oil). Once the cooking oil is used, it becomes an undesirable waste that
50 needs to be properly disposed of. The production of waste cooking oil has been increasing
51 each year throughout the world. For example, United States generated approximately 10
52 million tons of waste cooking oil each year [1], whereas China generated approximately 5
53 million tons/year of waste cooking oil [2]. Due to the large amount of waste cooking oil
54 generated annually, the disposal of waste cooking oil has become a challenge and concern
55 to the modern society.

56 Recently, pyrolysis techniques have been reported to show increased efficiency in
57 transforming biomass and waste materials into potential fuel products [3-8]. Pyrolysis is a
58 thermal degradation process that can be used to treat waste materials in an oxygen-free
59 atmosphere to produce liquid oil, gases and char. It has been reported that the liquid oil and
60 gases can be utilized as a chemical feedstock or they can be upgraded to obtain light
61 hydrocarbons for use as a fuel, and the char produced can also be used as a substitute for
62 activated carbon [9]. There has been further development in the conversion of triglyceride-
63 based vegetable oil into biofuel by pyrolysis techniques [10]. Waste cooking oil, containing
64 significant amounts of triglycerides, represents a potential feedstock to be converted into a
65 biofuel. The waste oil is readily available in large quantity, do not contend with other food
66 crops, and presents a cost effective resource for biofuel production by pyrolysis techniques.

67 Microwave pyrolysis has recently shown advantages over conventional pyrolysis
68 techniques that use traditional thermal heat sources in transforming waste materials into
69 potential fuel products [7, 11-15]. The microwave technique involves the use of
70 carbonaceous materials as a microwave absorber, which is heated by microwave radiation
71 to reach the target temperature in order for extensive pyrolysis to occur. The use of
72 microwave heating shows excellent heat transfer compared to conventional heating since
73 microwave energy can penetrate the material being heated and in turn generates heat
74 throughout the volume of the material, and thus providing a rapid and energy-efficient
75 heating process which also facilitates increased production rates. This type of pyrolysis
76 process may result in a different heating mechanism which can promote certain chemical
77 reactions leading to an improved yield of desirable products.

78 Most pyrolysis studies on biomass conversion have focused on processes heated by
79 a conventional heating source (e.g. furnace, oven). There have been limited reports on the

80 application of pyrolysis to the treatment and recycling of waste cooking oil, except for a
81 study performed by Omar and Robinson [12] on conventional and microwave-assisted
82 pyrolysis of rapeseed oil in which the authors had focused on the effects of temperature and
83 microwave power. These microwave pyrolysis experiments were performed in the absence
84 of specifically added microwave absorber, and it was shown that low amounts microwave
85 energy were absorbed by the waste oil and this resulted in low yields of pyrolysis products.
86 This indicates that waste cooking oil requires heating by contact with materials of high
87 microwave absorbency to achieve higher temperatures in order for extensive pyrolysis to
88 occur.

89 Carbonaceous materials such as particulate carbon have been used as microwave
90 absorber to heat materials that are poor microwave-absorbers to achieve high temperatures
91 by microwave radiation [9]. They are known to have high microwave absorbency, heat
92 tolerance, and low in cost, and thus they are widely used for such heating applications [16].
93 The use of carbonaceous materials as a reaction bed has been shown to be an effective
94 method of recovering and recycling chemicals present in troublesome wastes such as waste
95 engine oil [9, 14, 17] and plastic waste [18].

96 In this study, an alternative pyrolysis approach was proposed for the recovery of
97 diesel fuel from waste palm cooking oil (WPCO) by pyrolysis using a microwave heated
98 bed of activated carbon (AC) - a carbonaceous material with a high surface area. The AC
99 bed can act as both the microwave absorber and the energy transferring agent necessary for
100 heating WPCO, and the AC can also act as a catalyst to pyrolyze the WPCO to yield
101 products that can constitute diesel fuel. Thus, such a pyrolysis approach has the potential to
102 maximize the production of potentially useful pyrolysis products for use as a fuel or
103 chemical feedstock. This paper reports an investigation on the pyrolysis of WPCO over a
104 range of process temperature (200-550 °C). The yield and characteristics of pyrolysis
105 products were examined with an emphasis on the composition of the liquid fraction
106 generated from the pyrolysis process; this fraction is of particular interest due to its high
107 energy content and potential to be upgraded as a substitute for diesel fuel or other bio-based
108 hydrocarbon products [19].

109

110 **2. Materials and methods**

111 *2.1 Preparation of WPCO and AC*

112 WPCO was collected from a fried chicken restaurant in Kuala Terengganu,
113 Malaysia. The WPCO was filtered by Whatman No. 4 filter paper to remove unwanted
114 suspended food particles. The filtered oil was collected and stored in glass bottles wrapped
115 with aluminium foil. The glass bottles were filled up completely to prevent oxidation of the

116 oil during storage. The WPCO was analyzed for its characteristics and these are presented
117 in Table 1.

118 AC with a particle size ranging from 0.5 to 2.0 mm was obtained and used as a bed
119 of microwave absorber to heat and pyrolyze the WPCO. The AC was detected to have a
120 porous structure and a high surface area of 850 m²/g. It was pre-heated to 800 °C for 2
121 hours to remove any water and sulphur-containing compounds.

122

123 *2.3 Microwave pyrolysis experiments on WPCO*

124 Microwave pyrolysis of WPCO was conducted in a stirred batch reactor heated by a
125 modified 800 W microwave oven operating at a frequency of 2.45 GHz (Fig. 1).
126 Approximately 100 g of WPCO was placed in a pyrolysis reactor (150 x 100 x 100 mm).
127 150 g of AC was added to the reactor for use as a bed of the microwave absorber to absorb
128 and convert microwave energy to heat for pyrolyzing the WPCO; the ratio of WPCO to AC
129 is 1:1.5. The AC was stirred to ensure a uniform temperature distribution throughout the
130 reactor. The microwave oven was then switched on to heat the bed of AC and WPCO from
131 room temperature to the target process temperature ranging from 200 °C to 550 °C at which
132 the WPCO was pyrolyzed at the appropriate process temperatures. The process temperature
133 was selected for study as it is the most important parameter that dictates the thermal
134 cracking of the WPCO. A stainless steel type K thermocouple connected to an Autonics
135 dual indicator temperature controller was used to measure the temperature of the reaction
136 zone within the reactor. When the microwave oven had been heated to the target
137 temperature, the temperature controller also functioned to maintain the oven at the target
138 temperature. The reactor was purged with nitrogen gas at a flow rate of 0.2 L/min to
139 maintain an inert atmosphere in the reactor. The reactor was covered with ceramic fiber
140 blanket to minimize the heat loss occurred during the heating and pyrolysis process.

141 Pyrolysis products in gaseous form (termed ‘pyrolysis volatiles’) were generated
142 during the pyrolysis process and these gases then left the reactor and passed through a
143 condensation system consisting of Vigreux and Liebig condensers in addition to an ice
144 bath. The gases were either collected as non-condensable pyrolysis gases or condensed
145 within the collecting vessels and collected as a liquid biofuel product, whereas any solid
146 char residues were collected after the reactor was cooled to the room temperature.

147 The weight increase in the 1st and 2nd collecting vessels were measured to obtain the
148 yield of biofuel. It was previously found that a small amount of biofuel was obtained in the
149 2nd collecting vessel (<1 wt%), thus the collected biofuel was mixed with the biofuel
150 obtained in 1st collecting vessel for further analysis. The yield of char residue was obtained
151 by calculating the weight of reactor and its content before and after pyrolysis process, and
152 the gas yield was determined by resulting mass difference. The biofuel was then transferred

153 into glass bottles and stored for further analysis. All the pyrolysis experiments were
154 repeated for three times to ensure good reproducibility of the data.

155

156 *2.4 Analytical methods*

157 Elemental analysis was performed to determine the content of carbon, hydrogen,
158 nitrogen, sulphur and oxygen of liquid hydrocarbon samples using Vario MACRO
159 Elemental Analyzer (Elementar Analyseysteme GmbH). Fatty acid composition of
160 WPCO was analyzed using Agilent GC-FID. The chemical compositions of the produced
161 biofuel were determined by Shimadzu GC-MS QP2010 Ultra. The column used was a BP-
162 5 capillary column (length 30mm, diameter 0.25mm, film thickness 0.25 μ m) from SGE
163 Analytical Science. The CV of the biofuel were also determined according to ASTM D240
164 using a 1341 Plain Jacket bomb calorimeter instrument (Parr Instrument).

165

166 **3. Results and discussion**

167 *3.1 Characteristics of WPCO*

168 Table 1 shows the characteristics of the WPCO. The high calorific value of the
169 waste oil (39 MJ/kg) suggests that the WPCO can be a suitable feedstock for conversion
170 into a fuel source by exploiting the potential of pyrolysis to recover the energy value of the
171 waste oil. It was found that the WPCO is dominated by palmitic acid and oleic acid, which
172 are considered as carboxylic acids with long hydrocarbon chains. These carboxylic acids
173 are normally attached to a glycerol molecule to form triglycerides that contribute to the
174 majority of the composition of WPCO, thus the overall size of these triglycerides is either
175 C₅₁ equivalent (i.e. 3xC₁₆+3) or C₅₇ equivalent (i.e. 3xC₁₈+3), indicating the presence of
176 very large hydrocarbon molecules that are unsuited for use as a biofuel. However, the
177 WPCO can be a suitable pyrolysis feedstock since the very large hydrocarbon molecules
178 (i.e. C₅₁ or C₅₇ hydrocarbons) could be pyrolyzed and converted into light hydrocarbons for
179 potential use as a fuel.

180

181 *3.2 Microwave pyrolysis of WPCO in the presence of a bed of AC both the microwave 182 absorber and reaction bed*

183 Microwave pyrolysis of WPCO was performed over a range of process
184 temperatures using a microwave-heated bed of AC in order to assess the technical
185 feasibility of using this pyrolysis approach as a route to convert bio-based waste oils into
186 products suitable for use as a potential fuel or chemical feedstock.

187 The microwave-heated bed of AC showed considerable advantages in providing a
188 rapid heating process (~16-18 °C/min) to heat and pyrolyze the WPCO at a desirable high
189 temperature (up to 550 °C) in which the process time taken for the heating and pyrolysis
190 cracking of the WPCO at 450 °C was fully completed in less than 25 min (Fig. 2). In
191 contrast, it has been reported that a longer process time ranging from 60 to 120 min was
192 needed for the conventional fixed-bed pyrolysis of rapeseed oil [12] and palm oil [10] that
193 used furnace as the heat source, albeit in completely different apparatus. The rapid heating
194 represents a favorable feature in providing an energy-efficient pyrolysis process to reduce
195 the power consumption when compared with pyrolysis processes heated by a conventional
196 heating source (e.g. furnace, oven). Conventional pyrolysis processes usually employ an
197 external heating source that needs to heat all the substances in the heating chamber
198 including the evolved pyrolysis-volatiles, the surrounding N₂ gas, and the chamber itself,
199 thus energy is not fully targeted to the material being heated and this results in significant
200 energy losses and in turn leads to a long process time. On the contrary, the use of a well-
201 mixed bed of AC in microwave pyrolysis process provides a localized reaction ‘hot zone’
202 in contact with the added WPCO. The intimate contact of the WPCO with the AC particles
203 in the stirred bed ensures minimal distances for the heat to be transferred to the WPCO
204 rapidly in order for pyrolysis cracking to occur more quickly and extensively. Furthermore,
205 energy is efficiently targeted only to microwave receptive AC bed and not to gases within
206 the heating chamber or to the walls of the chamber itself.

207

208 *3.3 Product yields*

209 Fig. 3 shows the product yields obtained from the pyrolysis of WPCO at different
210 process temperatures. Data are not recorded for temperatures of 300 °C and below, as
211 although some pyrolysis conversion occurred and small amounts of pyrolysis-volatiles were
212 produced, no biofuel had been collected after 1 h of reaction time; so these experiments
213 were terminated.

214 The study showed that the WPCO were thermally cracked to pyrolysis products
215 dominated by biofuel and lower amounts of pyrolysis gases and char residue, except for the
216 pyrolysis performed at 350 °C in which incomplete pyrolysis cracking occurred and most
217 of the WPCO remained unpyrolyzed (77 wt%) and only small amounts of biofuel and
218 pyrolysis gases were generated. It was found that the WPCO needs to be heated to a
219 temperature higher than 350 °C in order for a more extensive pyrolysis cracking to occur.
220 The process temperature was found to have a significant influence on the yields of
221 pyrolysis product. The yield of biofuel was found to increase from 3 wt% to 70 wt% with
222 the increase of temperature from 350 °C to 450 °C. At 500 °C and 550 °C, the yield of
223 biofuel dropped to 69 wt% and 66 wt%, respectively. The reduction in the yield of biofuel
224 at 500 °C and above is likely due the secondary cracking and carbonization of the WPCO

225 (or the evolved pyrolysis-volatiles) to produce higher amounts of incondensable pyrolysis
226 gases and carbonaceous char residues, which can be observed from increased yield of both
227 the pyrolysis gases and char residue. At a high process temperature of 550 °C and above,
228 the occurrence of secondary cracking reactions have further increased the yield of pyrolysis
229 gases. It was likely that carbonization had also occurred during the pyrolysis at higher
230 temperature (≥ 500 °C)[11] and this had increased the yield of the carbonaceous char
231 residues from 1 wt% to 3 wt%.

232 A comparison of the yield of pyrolysis products obtained in this study can be made
233 with the study conducted recently by Omar & Robinson[12] on conventional and
234 microwave-assisted pyrolysis of rapeseed oil. Their study was conducted with and without
235 HZSM-5 as a catalyst and no microwave absorber was used in the pyrolysis process. The
236 authors claimed in their study that the highest conversion of oil was obtained at 14 wt% for
237 the pyrolysis performed at 500 °C, and they explained that the low conversion of oil sample
238 was due to the low energy (~30%) absorbed by the oil sample during the pyrolysis process
239 and this had caused undesirable pyrolysis cracking of the oil that resulted in the low
240 conversion. In contrast in our experiments, a much higher yield of 70 wt% was obtained for
241 the biofuel product at an even lower process temperature at 450 °C, indicating that the use
242 of a microwave-heated bed of AC showed advantages in providing a good heat transfer to
243 the WPCO. Extensive pyrolysis cracking of the WPCO occurred during the pyrolysis
244 process and resulted in a higher yield of liquid hydrocarbon products compared to that
245 obtained by Omar & Robinson[12] from microwave pyrolysis performed with no
246 microwave absorber.

247

248 *3.3.3 Chemical composition of the biofuel product*

249 This section presents the chemical composition of the biofuel obtained from the pyrolysis
250 performed at a process temperature ranging from 400-550 °C. Data are not presented for
251 the biofuel obtained at 350 °C and below due to the low yields obtained.

252 *3.3.3.1 Elemental composition and calorific value (CV)*

253 Table 2 shows the elemental analysis and CV of the biofuel obtained at different
254 process temperatures. Carbon (~76-81 wt%) and hydrogen (~13-14 wt%) represented the
255 main elements present in the biofuel, whereas oxygen (4-10 wt%) and nitrogen (~1 wt%)
256 were detected in low concentrations, and sulphur was not detected in the biofuel.

257 The biofuels showed a H/C ratio of about 2, indicating the presence of aliphatic
258 hydrocarbons (C_xH_y) such as alkanes, naphthenes, alkenes, dialkenes in the oil products.
259 The detection of low oxygen content (4-10 wt%) in the biofuels indicates the presence of
260 low amounts of oxidized species in the biofuel (Table 2). This could be attributed to the use

261 of a bed of activated carbon that also provided a reducing chemical environment at the
262 process temperatures. The bed of activated carbon acted as a reductant to remove oxygen
263 functionalities from the feed oil and to decrease the formation of undesirable oxidized
264 species during the pyrolysis, thus leading to the low oxygen content in the biofuel; the mass
265 loss of activated carbon was regarded as negligible as it was found to be less than 1 wt.%
266 after the pyrolysis operation. In addition, the oxygenated compound that initially present in
267 WPCO might form gaseous compound such as carbon dioxide or light hydrocarbons as a
268 result of deoxygenation reactions (e.g. dehydration, decarbonylation, decarboxylation)
269 during pyrolysis cracking of WPCO[20, 21], and these compounds would remain in the
270 gaseous phase and escape from the reactor, thus leading to the reduction in the oxygen
271 content of the biofuel. Interestingly, sulphur was not detected in the biofuels (Table 2). This
272 indicates the potential of the liquid products to be used as a fuel since their zero sulphur
273 content will result in no SO_x emissions compared to the use of traditional liquid fuels
274 derived from fossil fuels. Nitrogen was detected in low concentrations in the biofuel,
275 recording a concentration of about 1 wt%. It was likely that the nitrogen was obtained from
276 the distillation or evaporation of some of the nitrogen-containing components in the WPCO
277 that occurred during the pyrolysis process; the nitrogen-containing components was likely
278 to derive from the heterocyclic aroma compounds originally present as flavor enhancer in
279 the food and which had been transferred and trapped within the oil during the frying of the
280 food. These processes transferred the nitrogen-containing compounds from the WPCO in
281 the reactor to the condensation system and then into the recovered biofuel. Although the
282 biofuel contains relatively low concentration of nitrogen, given its likely future uses as a
283 fuel in engine operation and if the concentration assessed to pose too great a risk, the
284 nitrogen content can be removed via catalytic upgrading through the use of zeolite catalyst
285 (e.g. ZSM-5, USY). The biofuel obtained showed a CV ranging from 41 to 46 MJ/kg
286 (Table 2), which is higher than the original WPCO before pyrolysis (39.2 MJ/kg; Table 1).

287

288 3.3.3.2 Hydrocarbon composition

289 Fig. 4 shows the main compounds determined by GC-MS analysis for WPCO and
290 the resulting biofuel obtained at different process temperatures. The further breakdown of
291 the main compounds into individual chemical compounds is presented in Table S1 in
292 Appendix A. The main compounds can be classified into seven components according to
293 their structure, namely: alkanes, alkenes, cycloalkanes, carboxylic acids, ketones, aldehydes
294 and other unknown compounds (unidentified GC peaks).

295 This study showed that WPCO was thermally cracked to a liquid hydrocarbon
296 product dominated by aliphatic hydrocarbons (alkanes, alkenes). The aliphatic
297 hydrocarbons were mostly alkanes (~50%), and alkanes from decane (C₁₀H₂₂) to tridecane
298 (C₁₃H₂₈) showed the highest concentration. Alkenes (~34%) with carbon chain lengths

299 ranging from C₉-C₁₈ were also present with 5-octadecene (C₁₈H₃₆) and 8-heptadecene
300 (C₁₇H₃₄) being the most abundant. The biofuel obtained at 500 °C contains the highest
301 concentration of aliphatic hydrocarbons, accounting for 89% of its composition. The
302 aliphatic hydrocarbons accounts for 79 % of the liquid obtained at 450 °C, whereas only
303 76% was recorded at 400 °C. The production of liquid products comprising mainly of
304 aliphatic hydrocarbons represents a potentially high-value chemical feedstock or fuel
305 source. In particular, the C₁₀-C₁₅ alkanes (43-49 %; Table S1) is within the hydrocarbon
306 range of diesel fuel (C₁₀-C₁₅)[22] and thus could be upgraded to produce transport-grade
307 diesel, whereas the alkenes are highly desired chemicals that can be used in plastic
308 manufacture[9].

309 Process temperature was found to have an influence on the chemical composition of
310 the biofuel generated. Increasing the temperature from 450 °C to 550 °C led to an increase
311 in the content of alkanes in the biofuel, and the alkanes content improved towards the
312 presence of smaller hydrocarbon chains (C₁₀-C₁₂) (Table S1). The increase in the process
313 temperature also resulted in greater production of alkenes in the biofuel (up to 37%) with
314 the size of the alkenes being improved towards the presence of smaller hydrocarbon chains
315 (\leq C₁₃; Table S1). In addition, the biofuel obtained at 550 °C showed a higher concentration
316 of light hydrocarbons (C₅-C₁₃) (72 %) compared to the biofuel obtained at 500 °C (60 %),
317 450 (45 %) and 400 °C (4%) (Table S1). These results indicate the increased occurrence of
318 the cracking of heavier hydrocarbons in the WPCO at higher process temperatures to
319 produce lighter hydrocarbons. The higher thermal energy at higher process temperatures
320 enhances secondary cracking of the pyrolysis volatiles evolved from the WPCO being
321 pyrolyzed, thus enhancing the cleavage of larger hydrocarbon chains present in the
322 pyrolyzed volatiles into smaller hydrocarbon chains and this leads to a higher
323 corresponding yield of light hydrocarbons in the biofuel. Overall, increasing process
324 temperature leads to higher production of light hydrocarbons in the biofuel.

325 Interestingly, there was no carboxylic acid detected in the biofuel during the
326 pyrolysis at the process temperature of 450 °C, 500 °C, and 550 °C, suggesting that
327 carboxylic acids, particularly the fatty acids attached to triglycerides in the WPCO (Table
328 1), had been converted to other compounds during the pyrolysis at these process
329 temperatures. The carboxylic acids were likely to be split during the pyrolysis and from
330 which the carboxyl group was converted to an alkane and the remaining bits of the
331 hydrocarbon chain were converted to alkenes; these types of deoxygenation reactions (e.g.
332 decarbonylation, decarboxylation) have been reported to commonly occur during thermal
333 treatment processes like pyrolysis [20, 21]. The production of a biofuel with no carboxylic
334 acids and triglycerides represents a desirable feature because their presence could lead to
335 the occurrence of undesired polymerization reactions during the storage and upgrading in
336 which the carboxylic acids may react to form acidic tar or sludge and this could lead to

337 increased viscosity of the oil and furthermore the tar or sludge could cause problems such
338 as filter plugging and system fouling[9].

339 The hydrocarbons produced in the biofuel (C₁₀-C₁₅ hydrocarbons) are of
340 fundamentally much smaller length (less than one third) than those present in original
341 WPCO (the presence of triglycerides that is equivalent to C₅₁ or C₅₇ hydrocarbons). The
342 production of a biofuel with short hydrocarbon chains and that is also free of carboxylic
343 acids by this pyrolysis approach represents a favorable feature in producing a hydrocarbon
344 product that is much more suited to be used as a fuel, particularly as a diesel fuel
345 considering that the hydrocarbons with short chains are within the hydrocarbon range of
346 diesel fuel (C₁₀-C₁₅)[22].

347 Oxygenated compounds such as aldehydes and ketones were found to be present
348 only in minor quantities in the biofuel ($\leq 6\%$) compared to that present in the biofuel (53%)
349 obtained by conventional pyrolysis of palm oil using a furnace [10]. Combined with the
350 results of no carboxylic acids being detected in the biofuel, this provides useful information
351 as to the extent of oxidation that had occurred and resulted in the formation of oxygenated
352 by-products such as aldehydes, ketones, and carboxylic acids in the biofuel during
353 pyrolysis. The presence of only small amounts of aldehydes and ketones with no detection
354 of carboxylic acids indicates little occurrence of such oxidation reactions in this pyrolysis
355 process, since the AC bed had acted as a reductant to convert some of the oxygen present in
356 the feedstock to CO or CO₂ which then leaves the system in the gas phase, thus reducing
357 the amount of oxygen that is transformed into oxygenated by-products in the biofuel. This
358 corroborates the low oxygen contents found in the biofuel by elemental analysis (Table 2),
359 and the beneficial effects of the activated carbon bed (acting as a reducing reaction
360 environment) in decreasing both the extent of oil oxidation and the resulting formation of
361 oxygenated by-products that could generate undesirable acidic tar or sludge in the biofuel.

362

363 *3.3.3.3 Chemical composition of biofuel compared to transport-grade diesel and biodiesel*

364 The biofuel obtained from this pyrolysis approach was assessed for its suitability to
365 be used as a fuel based on its elemental content, carbon components, and CV, and these
366 values were also compared to those of transport-grade diesel and biodiesel obtained from
367 the literature[22-27]. The biofuel obtained at a process temperature of 450 °C in this study,
368 which showed the highest yield of biofuel, and the conventional biodiesel produced from
369 palm oil and waste cooking oil via transesterification were selected for comparison (Table
370 3).

371 Our biofuel shows lower oxygen content (5 wt%) than that of biodiesel (11 wt%).
372 and represents a favorable feature in producing a fuel with improved stability and higher
373 heating value compared to conventional biodiesel that shows a higher oxygen content.

374 However, the biofuel was found to have a higher oxygen content compared to fossil
375 transport-grade diesel, which is oxygen-free. This suggests that additional steps are needed
376 to eliminate oxygen from the biofuel if it is to be used as a diesel fuel. Although the biofuel
377 contains a relatively low level of oxygen given their likely future uses as a fuel (e.g. diesel),
378 were the concentration of oxygen assessed to pose too great a risk, or if complete removal
379 of oxygen was required, one potential route would be to perform deoxygenation or
380 decarboxylation to convert the oxygenated compounds that remained in the biofuel to
381 alkanes or aromatics.

382 The biofuel is formed mainly by light C₄-C₁₈ hydrocarbons (84 %; Table S1), and in
383 particular the C₁₀-C₁₅ hydrocarbons, which are within the hydrocarbon range of diesel fuel
384 (C₁₀-C₁₅), account for 65% of the light hydrocarbons (Table 3). It was also found that the
385 the biofuel is formed by lighter hydrocarbons compared to that present in the biodiesel. The
386 CV is an important fuel property that allows evaluation of the potential of the material to be
387 used as a fuel. The biofuel obtained in this study showed a CV of 46 MJ/kg, which is within
388 the range of the CV reported for the traditional liquid fuels derived from fossil fuel (42-46
389 MJ/kg)[25]. The CV of the biofuel is higher than that reported for the biodiesel derived
390 either from palm oil (37-38 MJ/kg)[25] or waste cooking oil (43 MJ/kg)[26], and is nearly
391 similar to that reported for diesel fuel (45 MJ/kg)[23, 28].

392 It is clear that the pyrolysis approach offers a promising alternative to
393 transesterification and produces a biofuel that may have advantages over conventional
394 biodiesel. This approach also offers advantages over transesterification in avoiding the use
395 of solvents and catalysts such as the methanol and acid or base catalyst required to perform
396 transesterification. In addition, there is no need to remove oxygenated compounds
397 (particularly glycerol and any non-esterified fatty acids) from the products formed during
398 transesterification. The use of catalyst and the presence of free fatty acid and glycerol as
399 by-products in the resulting biodiesel are common problems associated with
400 transesterification that could lead to many drawbacks such as slow reaction rate, corrosion,
401 and difficulty in separating catalyst from the biodiesel [29, 30], and also the formation of
402 undesired soap that can lead to reduction in biodiesel yield, decreased catalyst efficiency,
403 and increased formation of gel and viscosity of biodiesel[31].

404 It can also be inferred from these results that the diesel-like biofuel can be used as
405 an energy source for oil-fired power plant or internal combustion engines with an electricity
406 generation efficiency of about 39 - 44%[32]. Thus, the biofuel used as a diesel fuel through
407 these applications could show a higher electricity generation efficiency compared to that
408 shown by electricity generating plant fueled by biomass such as biodiesel (~35%).

409

410

411 3.3.4 Energy balance

412 Table 4 shows estimates of the energy recovery compared with the energy
413 consumption in the microwave pyrolysis of WPCO. These estimations provide a useful
414 measure of the energy efficiency of the pyrolysis process, which is an important factor that
415 determines the viability of this process, especially in scaling and optimizing the design and
416 operation to the commercial level. In particular, it allows the evaluation on whether the
417 energy recovered by the biofuel could sustain the energy consumed during the pyrolysis
418 process. It should be noted that the estimations are limited by the following assumptions:

- 419 1. The energy consumption is assumed to derive mainly from the usage of electricity
420 to generate the microwave radiation for pyrolysis to occur. The electrical
421 consumption is based on the electrical power input (1.12 kW) during the pyrolysis
422 treatment, which is estimated to be approximately 1.5 times the nominal power
423 output of the magnetron (0.75 kW) for the sum of the periods when they are
424 switched on during the pyrolysis operation, assuming that the energy conversion
425 efficiency of electricity into microwave energy is about 0.67 as reported by others in
426 the literature [33-35]. It should be mentioned that the 1.12 kW of electrical input is
427 an overestimate of the actual electrical consumption, considering the simplicity of
428 the pyrolysis reactor and the fact that the actual amount of absorbed microwave
429 power is not measured in this operation. Adding a device to record the absorbed
430 power would improve the estimate of the energy consumption in the process, and
431 would further increase the apparent energy conversion efficiency.
432
- 433 2. Heat losses from the pyrolysis reactor are substantial and would not be
434 representative of the losses that would occur at pilot or industrial scale. No attempt
435 has been made to fully insulate the pyrolysis reactor and fittings nor to recover
436 energy during the condensation of the pyrolysis products.
437
- 438 3. The CV of the pyrolysis gases and char are ignored in this assessment since only the
439 biofuel is of particular interest in this study.
440

441 The electrical energy ($E_{\text{pyrolysis}}$) supplied to power the pyrolysis process varied
442 between 16800 to 23520 kJ/kg over a process temperature ranging from 450 °C to 550 °C.
443 This is equivalent to 43-60% of the CV of the WPCO pyrolyzed. Less electrical energy was
444 needed to pyrolyze the WPCO at lower process temperature. This can be attributed to the
445 need for less energy to heat the WPCO to a lower operational temperature and to supply the
446 enthalpy to drive the endothermic pyrolysis reaction, resulting in lower electrical energy
447 consumption observed at lower process temperature.

448 The microwave pyrolysis process showed a positive energy ratio ranging from 1.96-
449 2.73 and a net energy output (E_{balance}) of 22480-29200 kJ/kg. This demonstrates that this

450 pyrolysis approach is capable of recovering an oil product with an energy content much
451 greater than the amount of electrical energy used for operating the pyrolysis process. These
452 results suggest that the setup of a pyrolysis equipment using the apparatus described from
453 this pyrolysis approach with an electrical power input of 1.12 kW is capable of processing
454 WPCO at a process temperature of 450 °C to produce a biofuel product with an energy
455 content equivalent to about 3.06 kW (i.e. 1.12 kW * energy ratio of 2.73).

456 Despite the fact that there was energy loss occurred during the pyrolysis operation
457 (18-27% of E_{input}), the pyrolysis process still showed significantly high recovery ($\geq 73\%$) of
458 the energy input to the system. It should however be noted that the high energy recovery
459 observed in this study involve the assumption that the only energy input of the process is
460 the electrical energy used to operate the pyrolysis operation. In practice lower energy
461 recovery would be realized in which additional energy inputs have been considered,
462 including the energy needed for the collection and transport of WPCO to the processing
463 plant, and for the refining or upgrading of the biofuel if it needs to be further processed to
464 produce a transport-grade diesel fuel. However, it is envisaged that inclusion of heat
465 integration and recovery systems to recover energy loss from the prototype reactor, which
466 are normally implemented during pilot or industrial scale operation, could further increase
467 the amount of energy that can be recovered from the pyrolysis system. In addition, the CV
468 of the pyrolysis gases and char have been ignored in this assessment. Inclusion of the
469 energy content from these pyrolysis products would further increase the energy recovery.

470 Furthermore, the recovered energy in the form of these pyrolysis products,
471 particularly the diesel-like biofuel, can potentially be used as a fuel source for on-site
472 generation of electrical energy to power the pyrolysis system. It can be inferred that if the
473 biofuel is used as a diesel fuel in an internal combustion engine, which shows an electricity
474 generation efficiency of about 33-40% [32], the electrical energy generated by this
475 application, which is about 15180-18400 kJ/kg, is capable of providing either all or most of
476 the electrical energy needed for the pyrolysis operation (16800 kJ/kg of $E_{pyrolysis}$). The use
477 of the diesel-like biofuel also showed advantages over the use of biodiesel as the fuel
478 source as indicated by its higher electricity generation efficiency ($\geq 33\%$) compared to that
479 shown by biodiesel ($\sim 30\%$)[32]. Overall, our results show that the pyrolysis approach using
480 a microwave-heated bed of AC is also an energetically viable means of converting the
481 WPCO into a useful biofuel product.

482

483 **4. Conclusion**

484 Pyrolysis using a microwave-heated bed of activated carbon provided rapid heating
485 (~ 18 °C/min) which heated and pyrolyzed the waste oil at 450 °C in a process taking less
486 than 25 min. It also showed advantages in providing a localized reaction hot zone that

487 thermally promoted extensive cracking to produce higher yield of a biofuel product, while
488 simultaneously created a reducing environment that prevented the formation of undesirable
489 oxidized compounds in the biofuel.

490 The pyrolysis produced a biofuel product that is low in oxygen, free of sulphur,
491 carboxylic acid and triglycerides, and which also contains light C₁₀-C₁₅ hydrocarbons and a
492 high calorific value nearly comparable to diesel fuel. The biofuel shows lower oxygen
493 content, lighter hydrocarbon content, and a higher calorific value than that reported for
494 biodiesel derived from transesterification of waste cooking oil.

495 The pyrolysis apparatus operated with an electrical power input of 1.12 kW was
496 capable of producing a biofuel with an energy content equivalent to about 3 kW, showing a
497 positive energy ratio of 2.7 and $\geq 73\%$ recovery of the energy input to the system.

498

499 **Acknowledgements**

500 The authors acknowledge the financial support by the Ministry of Science, Technology, and
501 Innovation and the Ministry of Higher Education Malaysia for the conduct of the research
502 under the E-Science fund (Vot No:52072) and the FRGS grant (Vot No:59296).

503

504 **References**

- 505 [1] Sawangkeaw R, Ngamprasertsith S. A review of lipid-based biomasses as feedstocks for
506 biofuels production. *Renewable and Sustainable Energy Reviews*. 2013;25:97-108.
- 507 [2] Chen G, Liu C, Ma W, Zhang X, Li Y, Yan B, et al. Co-pyrolysis of corn cob and waste
508 cooking oil in a fixed bed. *Bioresource technology*. 2014;166:500-7.
- 509 [3] Lam SS, Chase HA. A Review on Waste to Energy Processes Using Microwave
510 Pyrolysis. *Energies*. 2012;5(12):4209-32.
- 511 [4] Lam SS, Russell AD, Chase HA. Pyrolysis Using Microwave Heating: A Sustainable
512 Process for Recycling Used Car Engine Oil. *Industrial & Engineering Chemistry Research*.
513 2010;49(21):10845-51.
- 514 [5] Ganesapillai M, Manara P, Zabaniotou A. Effect of microwave pretreatment on
515 pyrolysis of crude glycerol-olive kernel alternative fuels. *Energy Conversion and*
516 *Management*. 2016;110:287-95.
- 517 [6] Chen W, Shi S, Zhang J, Chen M, Zhou X. Co-pyrolysis of waste newspaper with high-
518 density polyethylene: Synergistic effect and oil characterization. *Energy Conversion and*
519 *Management*. 2016;112:41-8.
- 520 [7] Huang Y-F, Shih C-H, Chiueh P-T, Lo S-L. Microwave co-pyrolysis of sewage sludge
521 and rice straw. *Energy*. 2015;87:638-44.
- 522 [8] Huang Y-F, Chiueh P-T, Shih C-H, Lo S-L, Sun L, Zhong Y, et al. Microwave
523 pyrolysis of rice straw to produce biochar as an adsorbent for CO₂ capture. *Energy*.
524 2015;84:75-82.

525 [9] Lam SS, Russell AD, Lee CL, Chase HA. Microwave-heated pyrolysis of waste
526 automotive engine oil: Influence of operation parameters on the yield, composition, and
527 fuel properties of pyrolysis oil. *Fuel*. 2012;92(1):327-39.

528 [10] Phung TK, Casazza AA, Perego P, Capranica P, Busca G. Catalytic pyrolysis of
529 vegetable oils to biofuels: Catalyst functionalities and the role of ketonization on the
530 oxygenate paths. *Fuel Processing Technology*. 2015;140:119-24.

531 [11] Lam SS, Russell AD, Lee CL, Lam SK, Chase HA. Production of hydrogen and light
532 hydrocarbons as a potential gaseous fuel from microwave-heated pyrolysis of waste
533 automotive engine oil. *International Journal of Hydrogen Energy*. 2012;37(6):5011-21.

534 [12] Omar R, Robinson JP. Conventional and microwave-assisted pyrolysis of rapeseed oil
535 for bio-fuel production. *Journal of Analytical and Applied Pyrolysis*. 2014;105:131-42.

536 [13] Ferrera-Lorenzo N, Fuente E, Bermudez JM, Suarez-Ruiz I, Ruiz B. Conventional and
537 microwave pyrolysis of a macroalgae waste from the Agar-Agar industry. Prospects for
538 bio-fuel production. *Bioresource technology*. 2014;151:199-206.

539 [14] Lam SS, Liew RK, Cheng CK, Chase HA. Catalytic microwave pyrolysis of waste
540 engine oil using metallic pyrolysis char. *Applied Catalysis B: Environmental*. 2015;176-
541 177:601-17.

542 [15] Mushtaq F, Mat R, Ani FN. Fuel production from microwave assisted pyrolysis of coal
543 with carbon surfaces. *Energy Conversion and Management*. 2016;110:142-53.

544 [16] Menéndez JA, Arenillas A, Fidalgo B, Fernández Y, Zubizarreta L, Calvo EG, et al.
545 Microwave heating processes involving carbon materials. *Fuel Process Technol*.
546 2010;91(1):1-8.

547 [17] Lam SS, Liew RK, Jusoh A, Chong CT, Ani FN, Chase HA. Progress in waste oil to
548 sustainable energy, with emphasis on pyrolysis techniques. *Renewable and Sustainable
549 Energy Reviews*. 2016;53:741-53.

550 [18] Russell AD, Antreou EI, Lam SS, Ludlow-Palafox C, Chase HA. Microwave-assisted
551 pyrolysis of HDPE using an activated carbon bed. *RSC Advances*. 2012;2(17):6756.

552 [19] Bridgwater AV. Review of fast pyrolysis of biomass and product upgrading. *Biomass
553 Bioenergy*. 2012;38:68-94.

554 [20] Boey P-L, Saleh MI, Sapawe N, Ganesan S, Maniam GP, Ali DMH. Pyrolysis of
555 residual palm oil in spent bleaching clay by modified tubular furnace and analysis of the
556 products by GC-MS. *Journal of Analytical and Applied Pyrolysis*. 2011;91(1):199-204.

557 [21] Ong YK, Bhatia S. The current status and perspectives of biofuel production via
558 catalytic cracking of edible and non-edible oils. *Energy*. 2010;35(1):111-9.

559 [22] Capunitan JA, Capareda SC. Assessing the potential for biofuel production of corn
560 stover pyrolysis using a pressurized batch reactor. *Fuel*. 2012;95:563-72.

561 [23] Ong HC, Silitonga AS, Masjuki HH, Mahlia TMI, Chong WT, Boosroh MH.
562 Production and comparative fuel properties of biodiesel from non-edible oils: *Jatropha
563 curcas*, *Sterculia foetida* and *Ceiba pentandra*. *Energy Conversion and Management*.
564 2013;73:245-55.

565 [24] Atabani AE, Silitonga AS, Ong HC, Mahlia TMI, Masjuki HH, Badruddin IA, et al.
566 Non-edible vegetable oils: A critical evaluation of oil extraction, fatty acid compositions,
567 biodiesel production, characteristics, engine performance and emissions production.
568 *Renewable and Sustainable Energy Reviews*. 2013;18:211-45.

569 [25] Sanjid A, Masjuki HH, Kalam MA, Rahman SMA, Abedin MJ, Palash SM. Impact of
570 palm, mustard, waste cooking oil and *Calophyllum inophyllum* biofuels on performance
571 and emission of CI engine. *Renewable and Sustainable Energy Reviews*. 2013;27:664-82.

572 [26] Yaakob Z, Mohammad M, Alherbawi M, Alam Z, Sopian K. Overview of the
573 production of biodiesel from Waste cooking oil. *Renewable and Sustainable Energy*
574 *Reviews*. 2013;18:184-93.

575 [27] Ong HC, Mahlia TMI, Masjuki HH, Norhasyima RS. Comparison of palm oil,
576 *Jatropha curcas* and *Calophyllum inophyllum* for biodiesel: A review. *Renewable and*
577 *Sustainable Energy Reviews*. 2011;15(8):3501-15.

578 [28] Kumaran P, Mazlini N, Hussein I, Nazrain M, Khairul M. Technical feasibility studies
579 for Langkawi WCO (waste cooking oil) derived-biodiesel. *Energy*. 2011;36(3):1386-93.

580 [29] Qian K, Shen X, Wang Y, Gao Q, Ding H. In-situ transesterification of *Jatropha* oil
581 over an efficient solid alkali using low leaching component supported on industrial silica
582 gel. *Energy*. 2015;93:2251-7.

583 [30] Román-Figueroa C, Olivares-Carrillo P, Paneque M, Palacios-Nereo FJ, Quesada-
584 Medina J. High-yield production of biodiesel by non-catalytic supercritical methanol
585 transesterification of crude castor oil (*Ricinus communis*). *Energy*. 2016;107:165-71.

586 [31] Talebian-Kiakalaieh A, Amin NAS, Mazaheri H. A review on novel processes of
587 biodiesel production from waste cooking oil. *Applied Energy*. 2013;104:683-710.

588 [32] Lawson B. Energy Efficiency. *The Electropaedia*. <www.mpoweruk.com> [accessed
589 11.08.15].

590 [33] Barnard TM, Leadbeater NE, Boucher MB, Stencil LM, Wilhite BA. Continuous-
591 Flow Preparation of Biodiesel Using Microwave Heating. *Energy & Fuels*.
592 2007;21(3):1777-81.

593 [34] Nüchter M, Müller U, Ondruschka B, Tied A, Lautenschläger W. Microwave-Assisted
594 Chemical Reactions. *Chemical Engineering & Technology*. 2003;26(12):1207-16.

595 [35] Nuchter M, Ondruschka B, Bonrath W, Gum A. Microwave assisted synthesis - a
596 critical technology overview. *Green Chemistry*. 2004;6(3):128-41.

597

598

599

600

601

602

603

604

605

606

607

608

609

610

611

612

613

614

615 **List of Tables**

616 **Table 1** Characteristics of WPCO

617 **Table 2** Elemental composition and CV of biofuel obtained at different process
618 temperatures

619 **Table 3** Chemical composition of the biofuel compared to transport-grade diesel and
620 biodiesel

621 **Table 4** Energy recovery and consumption in microwave pyrolysis of WPCO

622

623 **Table 1**

624 Characteristics of WPCO

Elemental composition (wt%)	
C	71.2
H	13.3
N	0.8
S	0
O^a	14.7
Calorific value (CV) (MJ/kg)	
	39.2
Fatty acid composition (wt%)	
Palmitic acid (C₁₆H₃₂O₂)	25
Stearic acid (C₁₈H₃₆O₂)	8
Oleic acid (C₁₈H₃₄O₂)	29
Linoleic acid (C₁₈H₃₂O₂)	12

625 ^a Oxygen calculated by mass difference

626

627 **Table 2**

628 Elemental composition and CV of biofuel obtained at different process temperatures

Biofuel properties	Temperatures			
	400°C	450°C	500°C	550°C
Elemental analysis (wt%)				
C	75.7	80.1	79.4	80.5
H	13.3	13.5	13.6	14.4
N	1.4	1.1	1.1	1.1
S	0.0	0.0	0.0	0.0
O (calculated by mass difference)	9.6	5.3	5.9	4.0
H/C (mol/mol)	2.0	2.1	2.1	2.1
CV (MJ/kg)	41	46	46	46

629

630

631

632

633 **Table 3**

634 Chemical composition of the biofuel compared to transport-grade diesel and biodiesel

Biofuel properties	Biofuel^a from microwave pyrolysis (this study)	Biodiesel^b from transesterification	Diesel^c (Transport-grade)
Elemental analysis (wt%)			
C	80.1	77	87
H	13.5	12	13
N	1.1	-	-
S	0.0	-	-
O^d	5.3	11	0.0
Carbon components	C ₄ -C ₁₈ (5% by C ₆) (65% by C ₁₀ -C ₁₅) (30% by C ₁₇ -C ₁₈)	C ₁₄ -C ₂₄ ^e (1% by C ₁₄) (43% by C ₁₆) (55% by C ₁₈) (1% by C ₂₀₋₂₄)	C ₁₀ -C ₁₅ ^f
Calorific value (MJ/kg)	46	37-43 ^e	45

635 ^a Process conditions: Pyrolysis was performed at a process temperature of 450°C.636 ^b ASTM D6751 specifications of biodiesel [23, 24]637 ^c ASTM D975 specifications of diesel [23, 24]638 ^d Calculated by mass difference639 ^e Carbon range of biodiesel (C₁₄-C₂₄) [27]640 ^f Hydrocarbon range of diesel fuel (C₁₀-C₁₅)[22]641 ^g CV of biodiesel derived from palm oil and waste cooking oil from previous studies [25,
642 26]

643 (-) not available

644

645

646

647

648

649

650

651

652

653

654

655

656

657

658

659

660 **Table 4**

661 Energy recovery and consumption in microwave pyrolysis of WPCO

Process temperature	E_{wo}^a (kJ/kg)	E_{BO}^b (kJ/kg)	$E_{pyrolysis}^c$ (kJ/kg)	$E_{pyrolysis}/E_{wo}^d$ (%)	E_{ratio}^e	$E_{balance}^f$ (kJ/kg)
450 °C	39200	46000	16800	43	2.73	29200
500 °C	39200	46000	20160	51	2.28	25840
550 °C	39200	46000	23520	60	1.96	22480

662

E_{input}^g (kJ/kg)	E_{loss}^h (kJ/kg)	$E_{recovery}^i$ (kJ/kg)
56000	10000	46000
59360	13360	46000
62720	16720	46000

663

664 ^a Energy content or CV of WPCO.665 ^b Energy content of biofuel, i.e. CV of biofuel*amount of biofuel obtained/amount of WPCO666 ^c Electrical energy consumed during the pyrolysis treatment, i.e. 1.12 kW of electrical power input*duration of pyrolysis treatment/amount of WPCO667 ^d Amount of energy (from E_{wo}) consumed by $E_{pyrolysis}$ 668 ^e Energy ratio, defined as the energy content of the biofuel divided by the electrical energy input needed to operate the system, i.e. $E_{BO}/E_{pyrolysis}$ 669 ^f Energy balance, defined as the energy content of the biofuel minus the electrical energy input needed to operate the system, i.e. $E_{BO}-E_{pyrolysis}$ 670 ^g Energy input of the system, defined as the sum of the total CV of the WPCO (E_{wo}) and the electrical energy input needed to operate the system ($E_{pyrolysis}$), i.e. $E_{wo}+E_{pyrolysis}$.671 ^h Energy losses from the system, includes the heat losses from the prototype reactor, the energy loss from the conversion of microwave energy into thermal energy, and the CV of the pyrolysis-gases and the char, i.e. $(E_{wo}+E_{pyrolysis})-E_{BO}$.672 ⁱ Energy recovered from the system, i.e. $(E_{wo}+E_{pyrolysis}) - E_{loss}$.

673

680

681

682

683

684

685

686

687

688

689 **List of Figures**

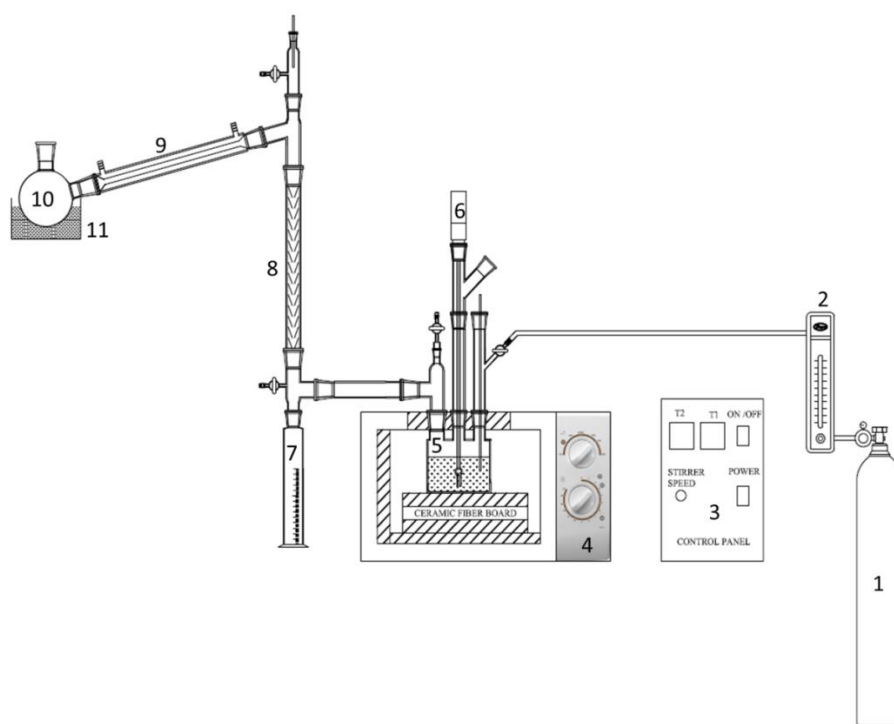
690 **Fig. 1** Schematic drawing of the microwave pyrolysis system. (1) Nitrogen gas, (2)
691 Flowmeter, (3) Temperature controller, (4) Modified microwave oven, (5) Pyrolysis
692 reactor, (6) Stirrer, (7) 1st collecting vessel, (8) Vigreux column, (9) Liebig condenser, (10)
693 2nd collecting vessel, (11) Ice bath.

694 **Fig. 2** Temperature profiles shown by microwave pyrolysis of WPCO at different process
695 temperature.

696 **Fig. 3** Product yield (wt%) from microwave pyrolysis of WPCO performed at different
697 process temperatures.

698 **Fig. 4** Main compounds (peak area%) detected in WPCO and the biofuel obtained at
699 different process temperatures.

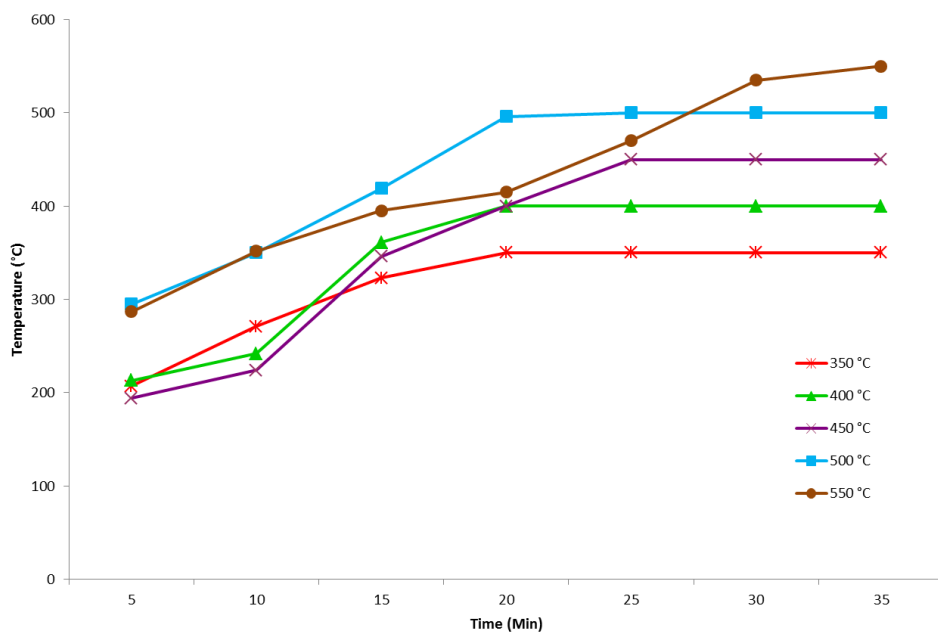
700



701

702 **Fig. 1** Schematic drawing of the microwave pyrolysis system. (1) Nitrogen gas, (2)
703 Flowmeter, (3) Temperature controller, (4) Modified microwave oven, (5) Pyrolysis
704 reactor, (6) Stirrer, (7) 1st collecting vessel, (8) Vigreux column, (9) Liebig condenser, (10)
705 2nd collecting vessel, (11) Ice bath.

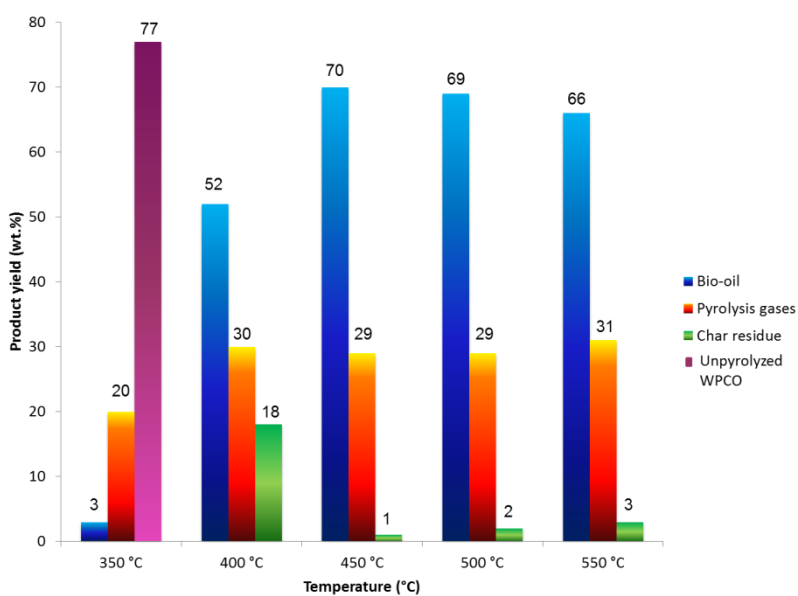
706



707

708 **Fig. 2** Temperature profiles shown by microwave pyrolysis of WPCO at different process
709 temperature.

710

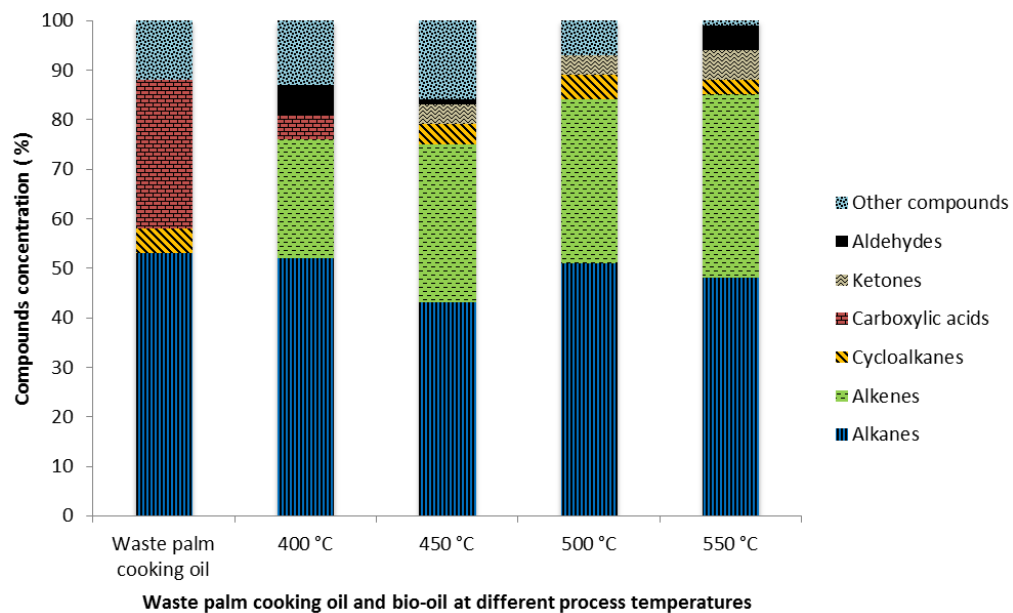


711

712 **Fig. 3** Product yield (wt%) from microwave pyrolysis of WPCO performed at different
713 process temperatures

714

715



716

717 **Fig. 4** Main compounds (peak area%) detected in WPCO and the biofuel obtained at
 718 different process temperatures

719

720

721

722