

1                   **Catalytic microwave pyrolysis of waste engine oil using**  
2                                   **metallic pyrolysis char**

3                   Su Shiung Lam <sup>a,c,\*</sup>, Rock Keey Liew <sup>a</sup>, Chin Kui Cheng <sup>b</sup>, Howard A. Chase <sup>c</sup>

4                   <sup>a</sup> Eastern Corridor Renewable Energy Group (ECRE), School of Ocean Engineering,  
5                   University Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia

6                   <sup>b</sup> Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang,  
7                   Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

8                   <sup>c</sup> Department of Chemical Engineering and Biotechnology, University of Cambridge,  
9                   New Museums Site, Pembroke Street, Cambridge CB2 3RA, United Kingdom

10                  lam@umt.edu.my, lrklrk1991@gmail.com, chinkui@ump.edu.my, hac1000@cam.ac.uk

11                  \* Corresponding author. Tel: +609 6683844; fax: +609 6683991; E-mail address:  
12                  lam@umt.edu.my, sushiong@gmail.com (S.S. Lam); Postal address: Eastern Corridor  
13                  Renewable Energy Group (ECRE), School of Ocean Engineering, University Malaysia  
14                  Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.

15                  **Abstract**

16                  Microwave pyrolysis was performed on waste engine oil pre-mixed with different amounts  
17                  of metallic-char catalyst produced previously from a similar microwave pyrolysis process.  
18                  The metallic-char catalyst was first prepared by pretreatment with calcination followed by  
19                  analyses to determine its various properties. The heating characteristics of the mixture of  
20                  waste oil and metallic-char during the pyrolysis were investigated, and the catalytic influence  
21                  of the metallic-char on the yield and characteristics of the pyrolysis products are discussed

22 with emphasis on the composition of oil and gaseous products. The metallic-char, detected to  
23 have a porous structure and high surface area ( $124 \text{ m}^2/\text{g}$ ), showed high thermal stability in a  
24  $\text{N}_2$  atmosphere and it was also found to have phases of metals and metal oxides attached or  
25 adsorbed onto the char, representing a potentially suitable catalyst to be used in pyrolysis  
26 cracking process. The metallic-char initially acted as an adsorptive-support to adsorb metals,  
27 metal oxides and waste oil. Then, the char became a microwave absorbent that absorbed  
28 microwave energy and heated up to a high temperature in a short time and it was found to  
29 generate arcing and sparks during microwave pyrolysis of the waste oil, resulting in the  
30 formation of hot spots (high temperature sites with temperature up to  $650 \text{ }^\circ\text{C}$ ) within the  
31 reactor under the influence of microwave heating. The presence of this high temperature  
32 metallic-char, the amounts of which are likely to increase when increasing amounts of  
33 metallic-char were added to the waste oil (5, 10, and 20 wt% of the amount of waste oil  
34 added to the reactor), had provided a reducing chemical environment in which the metallic-  
35 char acted as an intermediate reductant to reduce the adsorbed metals or metal oxides into  
36 metallic states, which then functioned as a catalyst to provide more reaction sites that  
37 enhanced the cracking and heterogeneous reactions that occurred during the pyrolysis to  
38 convert the waste oil to produce higher yields of light hydrocarbons,  $\text{H}_2$  and CO gases in the  
39 pyrolysis products, recording a yield of up to 74 wt% of light  $\text{C}_5\text{-C}_{10}$  hydrocarbons and 42  
40 vol% of  $\text{H}_2$  and CO gases. The catalytic microwave pyrolysis produced 65-85 wt% yield of  
41 pyrolysis-oil containing  $\text{C}_5\text{-C}_{20}$  hydrocarbons that can potentially be upgraded to produce  
42 transport-grade fuels. In addition, the recovered pyrolysis-gases (up to 33 wt%) were  
43 dominated by aliphatic hydrocarbons (up to 78 vol% of  $\text{C}_1\text{-C}_6$  hydrocarbons) and significant  
44 amounts of valuable syngas (up to 42 vol% of  $\text{H}_2$  and CO in total) with low heating values  
45 (LHV) ranging from 4.7 to  $5.5 \text{ MJ}/\text{m}^3$ , indicating that the pyrolysis-gases could also be used  
46 as a gaseous fuel or upgraded to produce more hydrogen as a second-generation fuel. The

47 results indicate that the metallic-char shows advantages for use as a catalyst in microwave  
48 pyrolysis treatment of problematic waste oils.

49

50 **Keywords: pyrolysis; char; catalyst; waste; oil**

51

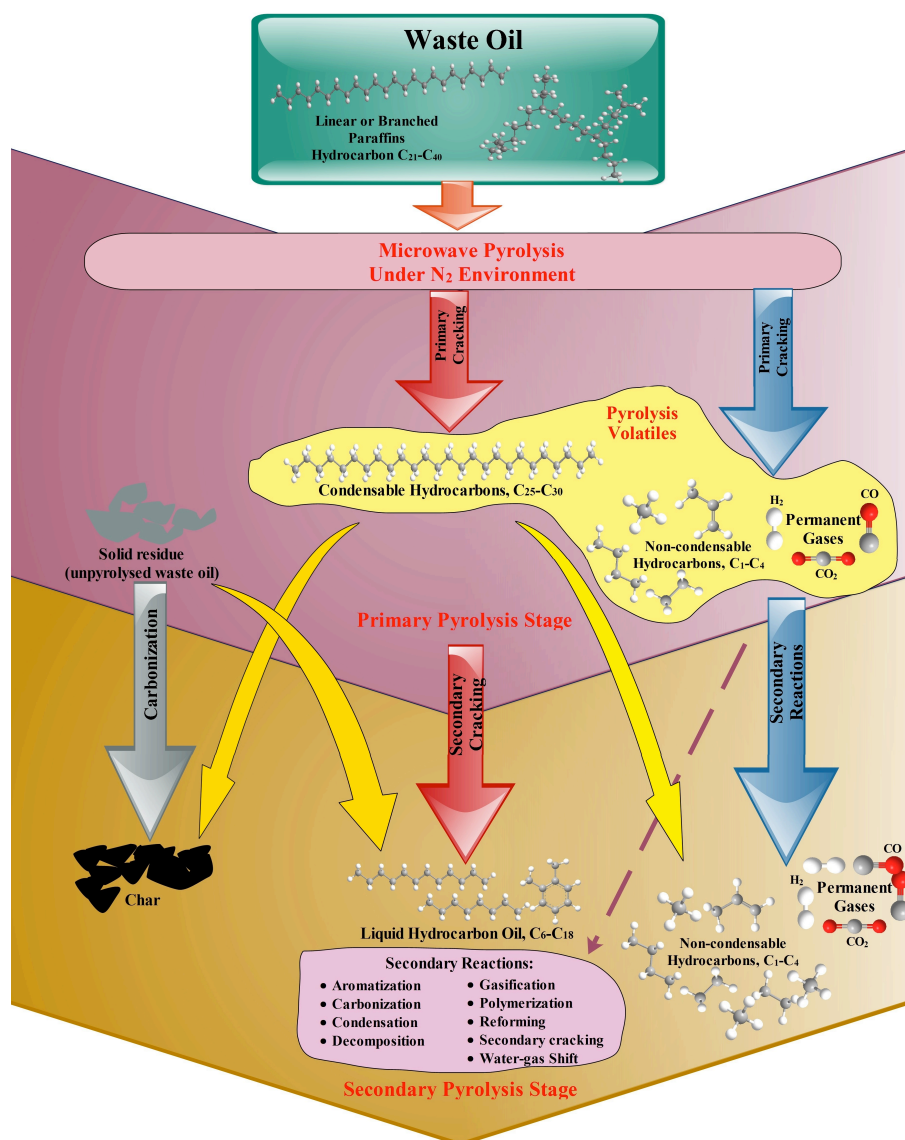
## 52 **1. Introduction**

53 Waste engine oil is an environmentally hazardous waste that is difficult to dispose of due to  
54 the presence of undesirable species such as soot and metals. On a global basis, nearly 24  
55 million metric tons (Mt) of the waste oil are generated each year [1]. In particular, nearly 7.6  
56 Mt are produced in the United States in addition to the approximately 2.2 Mt produced in the  
57 European Union [2]. Existing treatment processes such as incineration, combustion, and  
58 catalytic hydro-treatment are becoming increasingly impracticable due to concerns of  
59 environmental pollution and the difficulties of disposing of the sludge generated by these  
60 processes [3, 4].

61 Microwave pyrolysis has recently shown promise as an environmentally friendly disposal  
62 method for waste oil [5, 6]. In this process, waste oil is mixed with a bed of highly  
63 microwave-absorbent material such as particulate-carbon in an inert atmosphere. As a result  
64 of microwave heating, the oil is thermally cracked into shorter hydrocarbon chains, producing  
65 hydrocarbon oils, gases, and char. The oil product can be catalytically upgraded to produce  
66 transport-grade fuels [7], and the gaseous product can be used as a source of chemical  
67 feedstock [5] or be reformed to produce hydrogen for use as a second-generation fuel [8].

68 The main processes occurring during microwave pyrolysis of waste oil have been described  
69 in previous works [8, 9] and can be summarized in Fig. 1. During the pyrolysis process, the  
70 waste oil ( $\approx C_{40}$  hydrocarbons) is pyrolyzed through a **primary pyrolysis stage** in which the

71 waste oil undergoes **primary cracking** and transforms into pyrolysis volatiles formed by a  
72 mixture of hydrocarbon gases and liquid oils existing in a vapour phase. The pyrolysis  
73 volatiles are generated from the primary cracking of waste oil that proceeds via a free-radical-  
74 induced random scission mechanism as predicted by Rice's theory [10-12], consisting of  
75 permanent gas species (e.g. H<sub>2</sub>, CO, CO<sub>2</sub>), non-condensable gaseous hydrocarbons (C<sub>1</sub>-C<sub>4</sub>  
76 hydrocarbons), and condensable light hydrocarbons ( $\approx$  C<sub>25</sub> hydrocarbons). The pyrolysis  
77 volatiles then undergo a **secondary pyrolysis stage** whereby serial and parallel secondary  
78 reactions could occur and this results in the formation of products consisting of even lighter  
79 condensable hydrocarbons ( $\approx$ C<sub>6</sub>-C<sub>18</sub> hydrocarbons collected as liquid hydrocarbon oil) and  
80 higher amounts of non-condensable gaseous hydrocarbons (C<sub>1</sub>-C<sub>4</sub> hydrocarbons), and  
81 permanent gas species (e.g. H<sub>2</sub>, CO, CO<sub>2</sub>) in addition to the production of a char product.  
82 Homogenous or heterogeneous secondary reactions could occur such as secondary cracking,  
83 aromatization, reforming, deoxygenation, dehydrogenation, condensation, and carbonization  
84 [8] (Fig. 1).



85  
 86 **Fig. 1.** Main processes occurring during microwave pyrolysis of waste oil: Primary pyrolysis  
 87 consisting of primary cracking, and secondary pyrolysis consisting of serial and parallel  
 88 secondary reactions occurring either homogeneously or heterogeneously.  
 89

90 The use of microwave radiation as a heat source is known to offer additional advantages  
 91 over traditional thermal heat sources [13, 14], and the combination of carbon-based material  
 92 and the novel use of microwave heating in pyrolysis processes is of increasing interest as  
 93 reflected by considerable recent research reported in the literature [15-18]. Microwave  
 94 systems show a distinct advantage in providing a rapid, energy-efficient, and targeted heating  
 95 process compared to conventional technologies, thus facilitating increased production rates  
 96 and decreased production costs. Moreover, thermal energy is targeted only to microwave

97 receptive materials and not to gases within the heating chamber or to the chamber itself. It  
98 can promote certain chemical reactions by selectively heating the reactants, leading to a more  
99 uniform temperature profile and improved yield of desirable products [16, 19].

100 The char produced is also a product of particular interest due to its potential use as a solid  
101 fuel or as a catalyst in thermal cracking process. However, in order for the char products to be  
102 put to these uses it must first be shown that they do not contain the toxic species originally  
103 present in waste oil; these species, particularly the undesired metals (e.g. Cd, Cr), are  
104 hazardous to human health and may not be emitted to the environment either in their current  
105 form or when converted to other substances as a result of their further use (e.g. combustion).  
106 Metals derived from engine wear and oil additives are both toxic to humans and severely  
107 regulated in their disposal, preventing materials containing them to be disposed of via  
108 conventional routes (e.g. incineration) due to concerns over their potential dispersal to the  
109 environment.

110 It can also be inferred that if the microwave pyrolysis is to be performed in a continuous  
111 operation over a long period of time, the amount of the char product trapped within the  
112 particulate-carbon bed in the reactor would increase as a result of the prolonged period of  
113 operation. The presence of increasing amounts of this char is likely to have an influence on  
114 the product distribution in this pyrolysis process. This carbonaceous char, likely to contain  
115 involatile metals originally present in waste oil, could act as a microwave-absorbent and heat  
116 up by microwave radiation, and in turn pyrolyse the waste oil added into the reactor. It could  
117 also promote certain heterogeneous reactions by heating the pyrolysis-volatiles evolved from  
118 the pyrolysis of waste oil, leading to a different product composition observed in the  
119 pyrolysis products. It has been reported that the metal-containing char product could  
120 potentially be used as an inorganic catalyst in thermal cracking processes [20]; the presence  
121 of some metals (e.g. Fe, Ni) in the char could have a catalytic effect on some of the

122 heterogeneous reactions (e.g. methane decomposition reaction) that occurred as have been  
123 reported by others in pyrolysis studies of other materials [19, 21, 22]. In addition, the use of  
124 char produced from pyrolysis processes as a catalyst has recently shown advantages in  
125 transforming biomass materials (e.g. sewage sludge, coffee hulls) into valuable gases such as  
126 H<sub>2</sub> and syngas in microwave pyrolysis process [16, 23-25]; the waste materials were mixed  
127 with small amounts of the char and subjected to pyrolysis treatment.

128 In this study, microwave pyrolysis using a reactor bed of particulate-carbon was performed  
129 on waste oil in the additional presence of different amounts of metallic-char produced  
130 previously from the pyrolysis process as the catalyst in order to understand the influence of  
131 the chemical nature and amount of the metallic-char on the yield of pyrolysis products and  
132 with an emphasis on the chemical composition of the oil and gaseous products. The metallic-  
133 char catalyst was pre-treated by calcination and characterized by different analytical methods  
134 before and after being subjected to pyrolysis. In addition, a study was performed to examine  
135 the heating characteristics of the mixture of waste oil and metallic-char in the presence of a  
136 microwave-heated bed of particulate-carbon through monitoring its temperature profile  
137 during the pyrolysis. These evaluations are important to examine if the metallic-char could  
138 act as a microwave-absorbent and heat up by microwave radiation, and if the metallic-char  
139 could be used as a catalyst in the pyrolysis of waste oil. Most existing waste oil pyrolysis  
140 studies focus on conventional electric-resistance-heated and electric-arc-heated pyrolysis [26-  
141 28], and there are very few studies about the pyrolysis products generated from microwave  
142 pyrolysis of waste oil, and in particular no similar studies have been reported on the  
143 application of metallic-char as a catalyst in microwave pyrolysis of waste oil; this study aims  
144 to rectify these deficiencies.

145

146

## 147 2. Experimental Section

### 148 2.1. Materials

149 Shell 10W-40 motor oil was used throughout the experiments. The waste oil was sampled  
150 from the crankcase of diesel engines run on unleaded fuel. Before pyrolysis, the oil samples  
151 were filtered such that the size of any remaining particulates (i.e. metal particles, carbon soot,  
152 and other impurities) was less than 100  $\mu\text{m}$ . The oil samples were then examined for  
153 hydrocarbon composition by Gas Chromatography-Mass Spectrometry (GC-MS), metal  
154 composition by atomic-absorption spectrometry (AAS), phosphorus content by X-ray  
155 Fluorescence (XRF) analyzer, and sulphur content by elemental analysis. The GC-MS  
156 analysis (Table 1) revealed that the waste oil is formed from a mixture of low and high  
157 molecular weight aliphatic and aromatic hydrocarbons, and the majority of the hydrocarbon  
158 compounds were detected in the range of  $\text{C}_7\text{-C}_{41}$ . Phosphorus and sulphur were detected in  
159 very low concentrations (phosphorus: < 0.1 wt%; sulphur: < 0.8 wt%); the sulphur content of  
160 the waste oil has been reported and discussed in previous work [7]. The low concentrations of  
161 sulphur and phosphorus could be explained by the removal of some oil additives containing  
162 sulphur and phosphorus during the pre-filtration treatment of the waste oil, and also possibly  
163 due to the transport of some additives into the vehicle exhaust system during engine operation  
164 [29].

165 **Table 1**  
166 Chemical composition (wt%) of the waste oils.

Chemical composition	Waste oil
Aliphatics	91.3
Alkanes	90.4
Naphthenes	0.5
Alkenes	0.4
Carbon components	$\text{C}_7\text{-C}_{41}$
Aromatics	1.2
Others <sup>a</sup>	7.5

167 <sup>a</sup>Unknown compounds due to unidentified peaks.

168



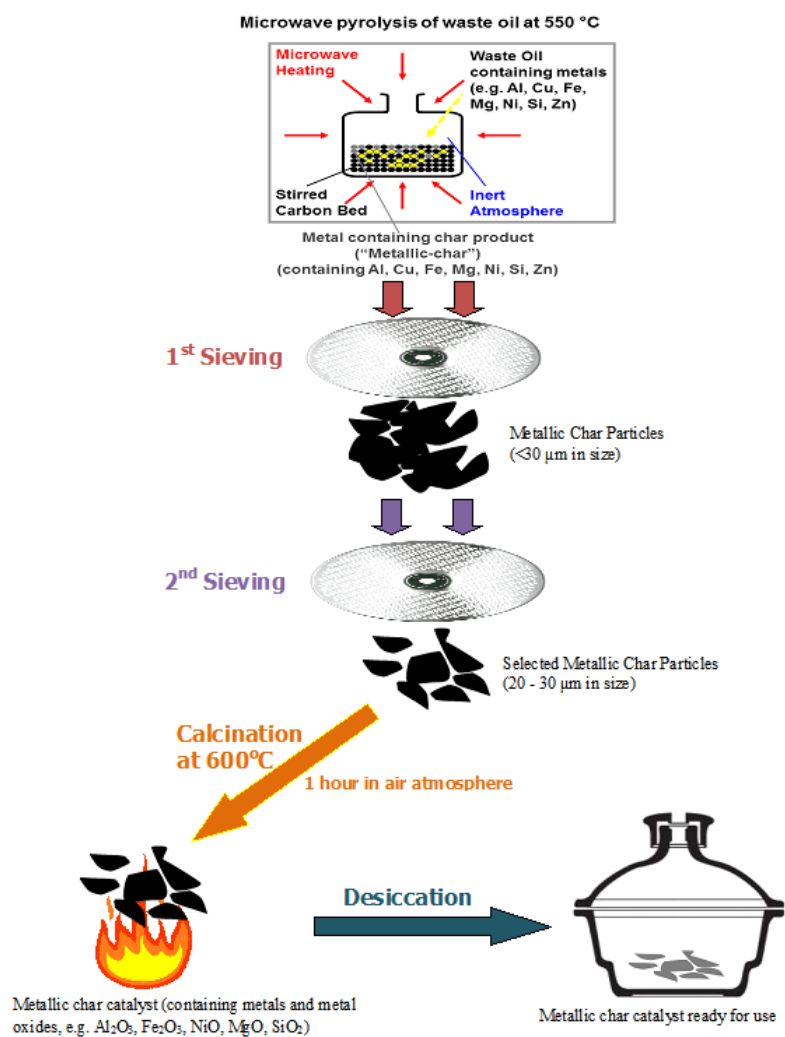
169 Particulate-carbon (TIMREX FC250 Coke, TIMCAL Ltd, Bodio, Switzerland) with a  
 170 particle size ranging from 90 – 250  $\mu\text{m}$  was used as a microwave-absorbent to heat the waste  
 171 oil. The specifications of the carbon are presented in Table 2. The particulate-carbon was pre-  
 172 heated to 800°C for 50 minutes to remove any water and sulphur-containing compounds. The  
 173 sulphur content of the particulate-carbon was vaporized as sulphur-containing gases (e.g.  
 174  $\text{H}_2\text{S}$ ,  $\text{SO}_x$ ), which were then passed through a closed chamber filled with activated carbon that  
 175 acted as a sorbent to clean and retain sulphur from the gas streams. The pre-heated carbon  
 176 was then analyzed for its sulphur content by elemental analysis and that analysis showed that  
 177 the sulphur content had been reduced to  $\leq 0.05$  wt% after the heat treatment at 800 °C.

178 **Table 2**  
 179 Characteristics of particulate carbon.

Parameter	Carbon (TIMREX FC250 Coke as provided by TIMCAL Ltd)
Carbon	99.91 – 99.10 wt%
Ash	0.07 – 0.30 wt%
Moisture	0.02 – 0.60 wt%
Sulphur	1.3 wt%
Sieve size	<250 $\mu\text{m}$ (2% >250 $\mu\text{m}$ , 75% >125 $\mu\text{m}$ , 85% >90 $\mu\text{m}$ )
Density	0.80 – 0.91 $\text{g}/\text{cm}^3$

180  
 181 *2.1.1. Preparation of metallic-char as catalyst and its characterization*

182 Particles of metallic-char were obtained from the previous pyrolysis of waste oil at 550 °C.  
 183 These chars with a particle size of < 30  $\mu\text{m}$  were separated from the particulate-carbon  
 184 particles (90 – 250  $\mu\text{m}$  in size) that formed the bed that was used to conduct the pyrolysis  
 185 using sieves. Then, the char with a particle size ranging from 20 – 30  $\mu\text{m}$  was separated from  
 186 this previously sieved batch of chars (< 30  $\mu\text{m}$  in size) using a narrow-range sieve, and used  
 187 for this study. The metallic-char was calcined at 600 °C in air atmosphere for 1 h and then  
 188 stored in a desiccator until further use as a catalyst. The preparation of the metallic-char for  
 189 use as a catalyst is briefly summarized in Fig. 2. The metallic-char was then examined for use  
 190 as a microwave-absorbent to heat the waste oil and also tested as a catalyst in the microwave  
 191 pyrolysis treatment of waste oil.



192  
193  
194

**Fig. 2.** Preparation of metallic pyrolysis char for use as a catalyst

195 The metallic-char catalyst before being subjected to pyrolysis was analyzed for its C, H, N,  
196 S, and O content by elemental analysis, and its proximate composition by thermogravimetric  
197 analysis (TGA). The remaining metallic-ash from TGA analysis was collected and analyzed  
198 for its chemical composition by XRF, and its proximate composition was also analyzed by  
199 TGA. Automatic sorption analysis (ASA) of the catalyst was performed to characterize its  
200 porous structure and to determine its surface area and pore volume. The catalyst was also  
201 analyzed by AAS to identify its metal composition.

202 X-ray diffraction (XRD) analyses using a X-Ray Diffractometer (Rigaku Corporation,  
203 Japan) were also performed on the catalyst before and after being subjected to pyrolysis to

204 investigate its chemical composition. SEM/EDX was also performed on both the fresh and  
205 used catalyst to investigate the size, morphology, presence of metals, and coke deposition on  
206 the particles present in the catalyst. In addition, TGA was performed on the catalyst in an N<sub>2</sub>  
207 atmosphere to evaluate its thermal stability, whereas temperature programmed oxidation  
208 (TPO) was performed on the used catalyst in an air atmosphere to investigate the reactivity of  
209 the used catalyst with oxygen and also the oxidation of coked carbons deposited on the  
210 surface of the used catalyst; these analyses were performed using a Q500 Thermogravimetric  
211 Analyzer (TA Instruments UK Ltd, Crawley, West Sussex) in which the catalyst sample (~20  
212 mg) was heated from ambient temperature to a final temperature at 950 °C at a heating rate of  
213 15 °C/min with a final holding time of 15 min.

214

## 215 *2.2. Experimental details*

216 The experimental apparatus and method developed for this investigation have been  
217 described in detail in previous work [6, 8]. The only change from this description is the  
218 addition of a Type-K metallic thermocouple to measure the evolution of the temperature of  
219 the gases and pyrolysis-volatiles (evolved from the waste oil being pyrolyzed) present in the  
220 vapor zone before they are driven out of the reactor into the product collection system by the  
221 N<sub>2</sub> purge gas. The thermocouple enters the reaction chamber through a side port on the top of  
222 the reactor and is positioned in the space above the carbon bed. In addition, a thermocouple  
223 was used to monitor the temperature of the carbon load in the system; temperature  
224 measurement in the reactor and its limitations are not the main focus of this paper and thus  
225 are presented in Appendix A.

226 In outline, microwave pyrolysis was performed in a bell-shaped quartz reactor on waste oil  
227 pre-mixed with small amounts of the metallic-char catalyst. The reactor was initially filled  
228 with 1 kg of particulate-carbon as the reaction bed, which was then heated to 550 °C by

229 microwave radiation (1). The particulate-carbon, added initially into the reactor in one batch,  
230 was stirred (3) to ensure a uniform temperature distribution throughout the reactor and to  
231 maximize heat transfer during pyrolysis. N<sub>2</sub> purge-gas at a flow rate of 0.25 L/min was  
232 vented through the system to maintain the apparatus in an inert atmosphere. The microwave  
233 generator was initially turned on to heat the carbon bed to the target pyrolysis temperature of  
234 550 °C; the oven was then left for 5 min to ensure complete thermal equilibrium. The waste  
235 oil was blended with different amounts of metallic-char (5, 10, and 20 wt% of the amount of  
236 waste oil added to the reactor, i.e. 5, 10, and 20 g of metallic-char/ 100 g of waste oil) to  
237 create a waste oil-char mixture, which was then continuously added to the reactor (4) at a  
238 constant feeding rate of 1 kg/h when the temperature of the carbon bed had reached 550 °C.  
239 Products generated during pyrolysis, termed generally as pyrolysis volatiles (consisting of a  
240 mixture of hydrocarbon gases, liquids, and suspended solids existing in a vapor phase), leave  
241 the reactor and pass through a condensation system (6, 7, 8, 9). The heavier volatiles are  
242 condensed into pyrolysis-oil (10, 11), and the lighter volatiles are collected as incondensable  
243 pyrolysis-gases (13, 14), which can be sampled before being vented from the system. The  
244 same procedure was repeated with the particulate-carbon as a control and all these results  
245 were compared to the microwave pyrolysis experiments performed on waste oil in the  
246 presence of only the particulate-carbon bed in the reactor. All the pyrolysis experiments were  
247 performed under ambient atmospheric pressure.

248 The amount of additional residue material not converted to gaseous or liquid products (both  
249 of which leave the reactor) was determined by measurement of the weight change in the  
250 reactor and its contents before and after pyrolysis. The residue materials are likely to be chars  
251 produced from tertiary cracking reactions of the pyrolysis process [5]. The char particles in  
252 the reactor consisted of the char residues (i.e. the new char produced in this round of  
253 pyrolysis, termed generally as “char product”) together with the metallic-char catalyst added

254 in combination with the waste oil into the reactor. These char particles mostly accumulated  
255 on the surface of the carbon bed and they were separated from the particulate-carbon particles  
256 (90 – 250  $\mu\text{m}$  in size) using 90 and 250  $\mu\text{m}$  sieves. Then, the new char product, consisting of  
257 char particles with the majority of particles present being  $\leq 10 \mu\text{m}$ , was separated from the  
258 original pyrolysis-char (20 – 30  $\mu\text{m}$  in size) using a 20  $\mu\text{m}$  sieve. It should be noted that the  
259 new char product contained a relatively small amount of char particles larger than 10  $\mu\text{m}$  but  
260 these larger char particles could not be analyzed due to the limitations involved in separating  
261 them from the 20 - 30  $\mu\text{m}$  metallic-char that had been added in combination with the waste  
262 oil into the reactor.

263 The yield of pyrolysis-oil was determined by measuring the weight increase in the  
264 collecting vessels and filter. The gas yield was determined by mass balance and it was  
265 assumed that whatever mass of added sample that was not accounted for by the pyrolysis-  
266 char and pyrolysis-oil measurements left the system in gaseous form. All the pyrolysis  
267 experiments were repeated for at least 5 times and the data recorded was the average of the  
268 results obtained from three valid repeated runs performed under identical conditions and  
269 excluded data from any experiments that were stopped due to equipment errors (e.g.  
270 malfunctioning of stirrer, thermocouple, pump failure). These repeated experiments showed  
271 good reproducibility and precision with low standard deviations shown in the product yields  
272 ( $\pm 1 - 5 \text{ wt}\%$ ).

273 The waste oils, pyrolysis-oils, and pyrolysis-gases were examined for chemical  
274 composition by different methods of gas chromatography analysis (i.e. GC-MS, GC-FID, and  
275 GC-TCD); the detailed description of these analytical methods, e.g. the sample preparation,  
276 the type of column used for the analysis, and the operating temperature program, have been  
277 described in previous work [7, 8].

278 Studies were performed to measure the temperature versus time profile of the mixture of

279 waste oil and metallic-char in the presence of a microwave-heated bed of particulate-carbon  
280 as an indication of its heating characteristic during pyrolysis by microwave radiation. The  
281 reactor was initially filled with 1 kg of particulate-carbon. The particulate-carbon was then  
282 stirred and heated to 550 °C by microwave radiation, and the temperature profile was  
283 monitored during the heating process. Waste oil pre-blended with metallic-char (i.e. a 80:20  
284 wt% mixture of waste oil and metallic-char) was continuously added to the reactor at a  
285 constant feeding rate of 1 kg/h when the temperature of the carbon had reached 550 °C. The  
286 temperature versus time profile of the mixture of particulate-carbon and waste oil-char  
287 mixture continued to be monitored during the subsequently pyrolysis of the added waste oil-  
288 char mixture.

289

### 290 *2.3. Analytical methods*

291 Oil samples were analyzed using a 6890/5973 GC-MS instrument (Agilent Technologies,  
292 Palo Alto, CA), allowing the quantification of compounds by both species and size; the  
293 detailed description of this analytical method has been reported in previous work [5, 7].  
294 Gases such as H<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, were analyzed using a Varian 3380 gas chromatograph  
295 (Varian Inc, Palo Alto, CA) fitted with two thermal conductivity detectors (GC-TCD),  
296 whereas gaseous hydrocarbons from C<sub>1</sub> to C<sub>4</sub> were analyzed using a 6890 GC (Agilent  
297 Technologies, Palo Alto, CA) coupled with a flame ionization detector (GC-FID); the  
298 detailed description of these analytical methods have been reported in previous work [8].  
299 Compounds were identified using the NIST 2005 mass spectral library using similarity  
300 indices of >70%, or by comparison with published GC-MS data for similar products, and  
301 quantification of compounds was obtained by external standard method and relative retention  
302 times once the component has been identified.

303 Elemental analyses of solid samples were performed using a LECO CHNS-932 elemental

304 analyzer (LECO Corporation, Michigan, USA); the detailed description of this analytical  
305 method is presented in Appendix B. TGA analysis of solid samples was performed using a  
306 Q500 Thermogravimetric Analyzer (TA Instruments UK Ltd, Crawley, West Sussex),  
307 allowing the proximate quantification of moisture, volatile matter, fixed carbon, and ash  
308 content of compounds. Detailed analysis (Appendix C) was performed according to ASTM  
309 Standard E1131-08 [30]. The oil and solid samples were also analyzed using a Varian Spectr  
310 AAS instrument; the detailed description of this analytical method, and the sample  
311 preparation, has been reported in previous work [6]. Experimental analysis of each metal was  
312 performed according to Lazaro et al. [31] and the standard working conditions specified in  
313 the Varian AAS instruction manual for metal determination. The samples were analyzed for  
314 their content of Al, As, Ba, Ca, Cd, Cu, Cr, Fe, Mg, Mo, Ni, Pb, Si, V and Zn.

315 ASA analysis of the solid samples was performed using a Micromeritics ASAP 2010  
316 Automatic Sorption Analyzer (Micromeritics UK Ltd, Dunstable, Bedfordshire) to  
317 characterize their porous structure and to determine their surface area. 90 mg of sample was  
318 degassed at 120 °C for 2 h prior to analysis. Then, the sample was exposed to varying  
319 pressures of N<sub>2</sub> gas at a temperature of 77 K, and the volume of N<sub>2</sub> adsorbed onto the  
320 sample's surface at different pressures was recorded. The data were used to plot the N<sub>2</sub>  
321 adsorption and desorption isotherms that allow the characterization of porous structure and  
322 calculation of surface area of the sample using the Multipoint Brunauer, Emmett, and Teller  
323 (BET) equation [32, 33]. External surface area and micropore volume were calculated based  
324 on the *t*-plot method, and the total pore volume was determined at P/P<sub>0</sub> of 0.99.

325

### 326 **3. Results and Discussion**

327 Microwave pyrolysis of waste oil was performed in order to convert the waste oil into  
328 potentially valuable products suitable for use as a fuel. The pyrolysis was performed in a

329 continuous operation using the apparatus described, which is fitted with magnetrons capable  
 330 of delivering 5 kW of microwave power and capable of sustaining a waste oil feed rate of 5  
 331 kg/h with a positive energy ratio of 11 (energy content of hydrocarbon products/ electrical  
 332 energy supplied for microwave heating) and a net energy output of 170 MJ/h.

333 **Table 3**  
 334 Characteristics of the metallic-char and metallic-ash.

	Metallic-char <sup>a</sup>		Metallic-ash <sup>b</sup>
Elemental composition (wt%)			
C	86.3		n.p. <sup>c</sup>
H	4		n.p.
N	0.2		n.p.
S	0.5		n.p.
O	9		n.p.
Proximate composition (wt%)			
Moisture	- <sup>d</sup>		-
Volatile matter	5		2
Fixed carbon	85		4
Ash	10		94
Particle size	20 – 30 $\mu\text{m}$		n.p.
Surface area	124 $\text{m}^2/\text{g}$		n.p.
External surface area ( $\text{m}^2/\text{g}$ )	28		n.p.
Micropore area ( $\text{m}^2/\text{g}$ )	97		n.p.
Micropore volume ( $\text{cm}^3/\text{g}$ )	0.065		n.p.
Total pore volume ( $\text{cm}^3/\text{g}$ )	0.13		n.p.
Metal composition of metallic-char (ppm)			
Al	6.1	Mg	229
Ca	910	Ni	4.3
Cd	0.3	Pb	1.2
Cu	1.6	Si	23.6
Fe	42.8	Zn	488
Chemical composition of metallic-ash by XRF analysis (wt%)			
SiO <sub>2</sub>	5.2	MgO	15.1
Al <sub>2</sub> O <sub>3</sub>	4.3	ZnO	16.7
Fe <sub>2</sub> O <sub>3</sub>	7.3	CuO	1.1
CaO	21.0	NiO	3.2
K <sub>2</sub> O	0.3	PbO	0.3
Na <sub>2</sub> O	0.5		

335 <sup>a</sup> Obtained from microwave pyrolysis of waste oil at 550°C followed by calcination at 600 °C  
 336 in air atmosphere for 1 h.

337 <sup>b</sup> Ash collected from heating the metallic-char at 950 °C in air atmosphere for 20 min.

338 <sup>c</sup> n.p.- Analysis not performed.

339 <sup>d</sup> Not detectable.

340



341 *3.1. Characteristics of metallic-char catalyst*

342 The metallic-char was analyzed to determine its elemental, proximate, and metal  
343 composition, and also its surface area, external surface area, micropore area, micropore  
344 volume, and total pore volume. In addition, the metallic-ash was collected from heating the  
345 metallic-char at 950 °C in air atmosphere for 20 min and the ash was analyzed for its  
346 chemical composition. Table 3 summarizes the main characteristics of the metallic-char and  
347 metallic-ash.

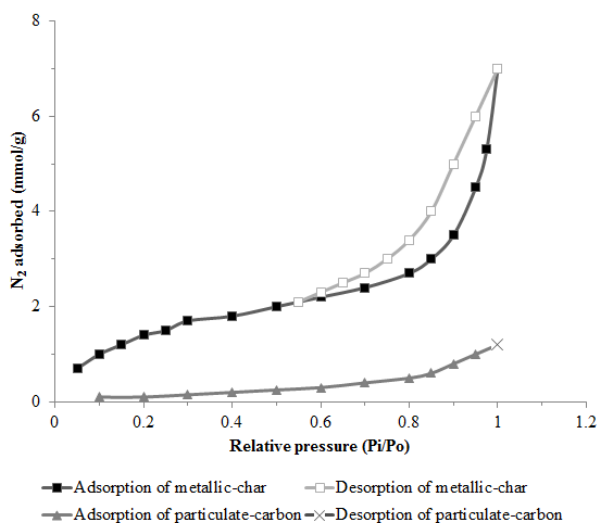
348 The results from elemental analysis show that carbon (~86 wt%) and oxygen (9 wt%)  
349 represented the main elements present in the metallic-char, whereas hydrogen (4 wt%),  
350 nitrogen (0.2 wt%), and sulphur (0.5 wt%) were detected in very low concentrations. The  
351 detection of oxygen in the metallic-char indicates that char oxidation had occurred to some  
352 extent to form possibly metal oxides during the preparation of the metallic-char for use as a  
353 catalyst by calcination the char at 600 °C in air for 1 h (See Section 2.1.1, Fig. 2).

354 Proximate analysis revealed that the metallic-char comprised mainly of fixed carbon (85  
355 wt%) and smaller amounts of ash (10 wt%) and volatile matter (5 wt%), whereas moisture  
356 was not detected in the metallic-char. The high content of carbon (also detected from  
357 elemental analysis) and the relatively low content of volatile matter show that a carbonaceous  
358 char with a high elemental carbon content was obtained from the previous pyrolysis of waste  
359 oil at 550 °C. The ash is likely to derive from the metals originally present in the waste oil  
360 [6], which were then transferred and either adsorbed onto or trapped within the metallic-char  
361 during the previous pyrolysis of waste oil.

362 The metallic-ash was further analyzed and examined for its chemical composition by  
363 proximate and XRF analysis. As expected, ash represented the main elements (94 wt%)  
364 present in the metallic-ash as demonstrated by proximate analysis, whereas volatile matter  
365 and fixed carbon were detected in very low concentrations (2 wt% and 4 wt%, respectively).

366 XRF analysis revealed that the metallic-char contained metal oxides comprising mainly of  
367 CaO, ZnO, MgO, Fe<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and NiO. The detection of these metal oxides suggests  
368 that some of the metals originally attached or adsorbed onto the metallic-char were likely to  
369 have reacted with oxygen to form metal oxides that were retained within the metallic-char  
370 during the preparation of the metallic-char as a catalyst by calcination.

371 The results from AAS showed that the metallic-char also contained metals such as Ca, Zn,  
372 Mg, Fe, Si, Al, and Ni; this supports the proposed occurrence of char oxidation that had led to  
373 the formation of metal oxides during the calcination of the metallic-ash. These metals were  
374 originally derived from the involatile metals attached or adsorbed onto the metallic-char  
375 during the previous pyrolysis of waste oil. The involatile metals were derived from the wear  
376 and corrosion of the iron and alloy engine components or additives present in the engine oil  
377 [6]. The concentrations of Ca, Fe, Mg, Si and Zn in the metallic-char were found to be  
378 relatively high compared to the amounts of other metals present. In contrast, Cu, Cd, and Pb  
379 were detected in low concentrations (< 1.6 ppm). Some of these metals such as Fe, Ni, Si, Al  
380 may have catalytic effects on the reaction pathways that occur in this pyrolysis process as  
381 reported by others in pyrolysis studies of other materials [34-36] and this could lead to a  
382 different product composition compared to that observed in previous works [7, 8].



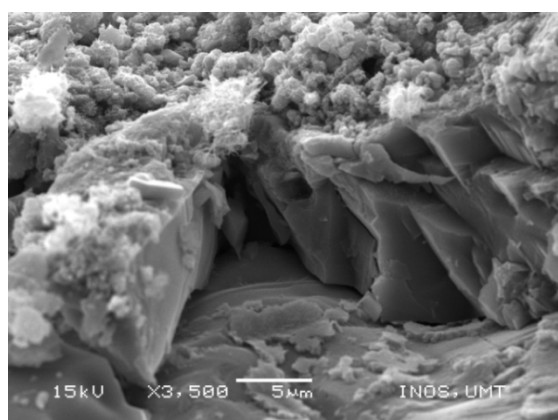
383

384 **Fig. 3.** N<sub>2</sub> adsorption and desorption isotherms of metallic-char and particulate-carbon

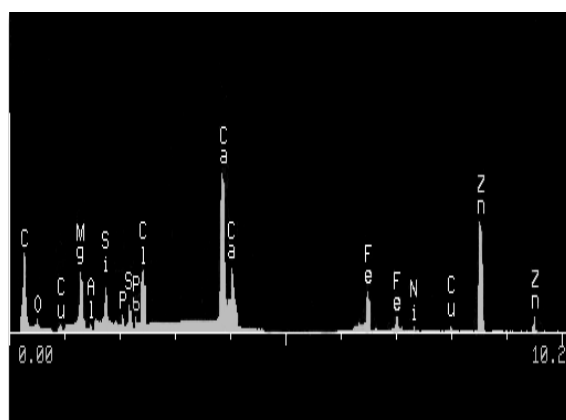
385 Fig. 3 shows the N<sub>2</sub> adsorption and desorption isotherms plotted from the volume of N<sub>2</sub>  
386 adsorbed onto the surface of metallic-char and particulate-carbon at different pressures of N<sub>2</sub>  
387 gas. The adsorption-desorption isotherm obtained for the metallic-char indicates a  
388 combination between the isotherms of Type I and Type IV according to the classification of  
389 adsorption isotherms by International Union of Pure and Applied Chemistry (IUPAC) and  
390 Brunauer, Deming, Deming, and Teller (BDDT system) [37]. The plot at lower relative  
391 pressures ( $P_i/P_o \leq 0.5$ ) shows a Type I adsorption isotherm indicative of a microporous  
392 structure whereas the plot at higher relative pressures ( $P_i/P_o > 0.5$ ) indicates a Type IV  
393 adsorption isotherm in which capillary or pore condensation occurred and this generated a  
394 hysteresis loop indicating the presence of mesoporosity. These observations suggest that the  
395 metallic-char had both microporous and mesoporous structure; porous solid is classified as  
396 microporous with a pore size of up to 2 nm and mesoporous with a pore size of 2 - 50 nm by  
397 IUPAC.

398 The metallic-char showed a type H1 hysteresis loop according to the classification of  
399 hysteresis loops by IUPAC as indicated by adsorption and desorption branches that are nearly  
400 vertical and parallel, indicating the presence of a porous structure containing relatively  
401 uniform cylindrical pores with a narrow distribution of pore size. The presence of type H1  
402 hysteresis loop is also indicative of both delayed condensation and little hold-up of  
403 percolation, showing a characteristic of good adsorption capacity by the metallic-char,  
404 particularly for adsorbing metal ions [38]. The data from the N<sub>2</sub> adsorption and desorption  
405 isotherms were calculated for determination of the surface area and the metallic-char was  
406 found to have a surface area of 124 m<sup>2</sup>/g, the majority of which was comprised of micropores  
407 (97 m<sup>2</sup>/g), and a micropore volume of 0.065 cm<sup>3</sup>/g, indicating that this char had a relatively  
408 high internal porosity (Table 3). These results support the highly porous structure with many  
409 cavities observed in the SEM/EDX scans of the metallic-char (Fig. 4).

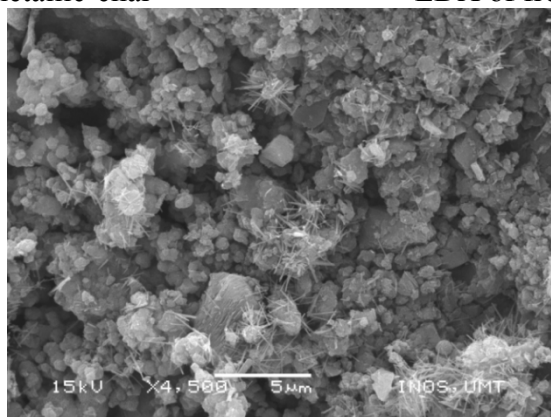
410 In contrast, the particulate-carbon that was used as a microwave-absorbent in this study  
411 showed a plot of a convex curve to the relative pressure axis and with no sign of hysteresis  
412 loop (Fig. 3), indicating a Type III adsorption isotherm. The presence of Type III adsorption  
413 isotherm is commonly associated with characteristics of non-porous structure, low surface  
414 area, pore volume, weak adsorbate-adsorbent interactions, and low adsorption capacity [38].  
415 The different adsorption isotherm observed between the metallic-char and particulate-carbon  
416 indicated that the metallic-char showed a higher adsorption capacity compared to the  
417 particulate-carbon, suggesting that the metallic-char could be a more suitable adsorptive-  
418 support to adsorb metal ions and waste oil (or the evolved pyrolysis-volatiles) in order for  
419 catalytic heterogeneous reactions to occur during the use of the metallic-char as a catalyst in  
420 the microwave pyrolysis conversion of the waste oil.



SEM of fresh metallic-char



EDX of fresh metallic-char



SEM of used metallic-char

421  
422 **Fig. 4.** SEM micrograph and EDX spectrum of particulate matter in the metallic-char before  
423 and after pyrolysis. These highly magnified scans show example areas of the samples;  
424 numerous areas were scanned and examined for consistency.

425 *3.1.1. SEM analysis of metallic-char before and after pyrolysis*

426 Fig. 4 presents the SEM-micrograph and EDX-spectrum of the fresh metallic-char. The  
427 SEM/EDX scans demonstrated that the metallic-char had a porous structure nearly  
428 comparable to activated char with most of the particles having a nearly spherical shape. The  
429 presence of highly porous structure indicates that the metallic-char can be a suitable  
430 candidate for use as a catalyst support or adsorbent as has been reported by Y. Shen et al.  
431 [38]. Cavities and particles having a particle size of about 1 – 5  $\mu\text{m}$  were found distributed  
432 over the metallic-char, indicating the presence of a porous network with a high surface area.  
433 The small particles were likely to be formed by smaller char and metallic particles either  
434 attached or adsorbed onto the metallic-char.

435 The EDX spectrum of the metallic-char (Fig. 4) showed the presence of metalloid (Si),  
436 non-metals (C, O, P, S), halogen (Cl), and metals (Cu, Mg, Al, Ca, Fe, Ni, Zn, Pb). Some of  
437 these metal elements (Cu, Al, Mg, Fe, Ni) have been reported to show catalytic effect on the  
438 heterogeneous reactions that occurred in pyrolysis process [19, 21, 22]; this further indicates  
439 the potential of the metallic-char to be used as a catalyst.

440 The SEM-micrograph of the used metallic-char is also presented in Fig. 4. As shown in  
441 Fig. 4, the used metallic-char was covered with a layer consisting of small particles of  
442 different sizes. The layer of small particles were likely to be coked carbons produced during  
443 the pyrolysis process. In addition, some of the small particles could be the metal particles  
444 formed from the reduction of metal oxides originally present in the metallic-char (Table 3).

445

446 *3.1.2. XRD analysis of metallic-char before and after pyrolysis*

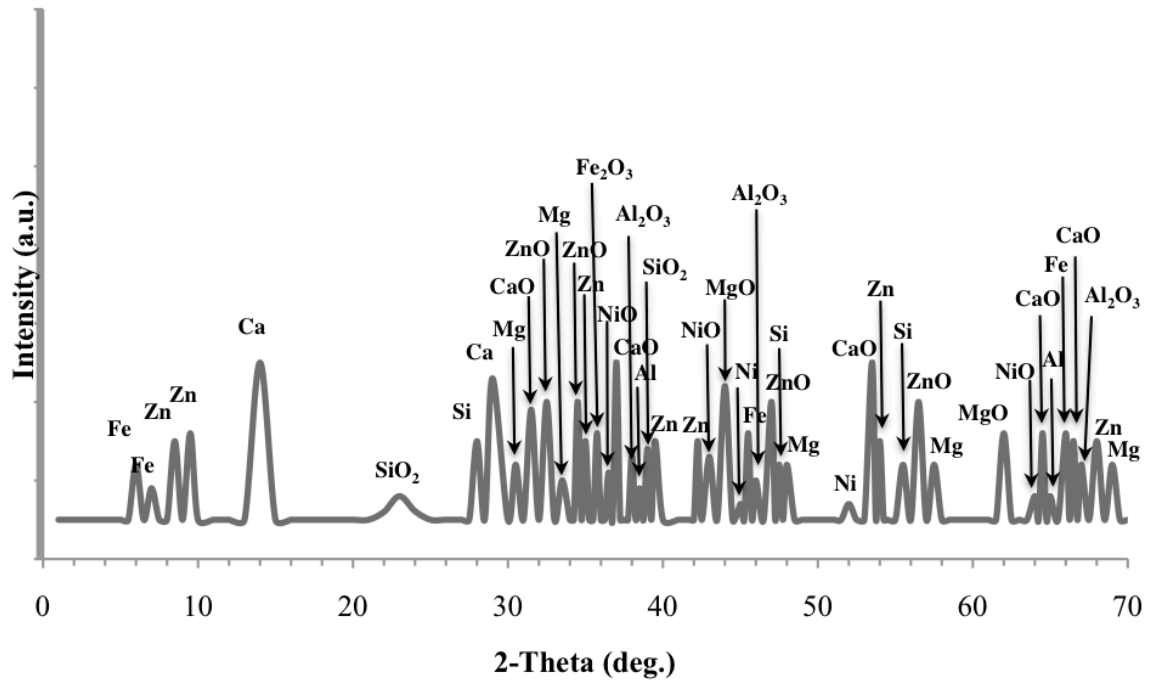
447 The metallic-char was analyzed by XRD to investigate the presence and change of  
448 crystalline phases on the metallic-char structure before and after pyrolysis. Fig. 5 shows the  
449 XRD plots of the fresh and used metallic-char from microwave pyrolysis experiments

450 performed on waste oil. The XRD of the fresh metallic-char showed the presence of metal  
451 phases containing Al, Ca, Fe, Mg, Ni, Si, and Zn, and also phases of metal oxides comprising  
452  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{ZnO}$ , and  $\text{NiO}$ . Although other metals (e.g. Cd, Cu, Pb) and  
453 metal oxides (e.g.  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{CuO}$ ,  $\text{PbO}$ ) were detected in the metallic-char by XRF and  
454 AAS analyses, their peaks were not detectable by XRF analysis, probably due to their low  
455 concentrations in the metallic-char (Table 3).

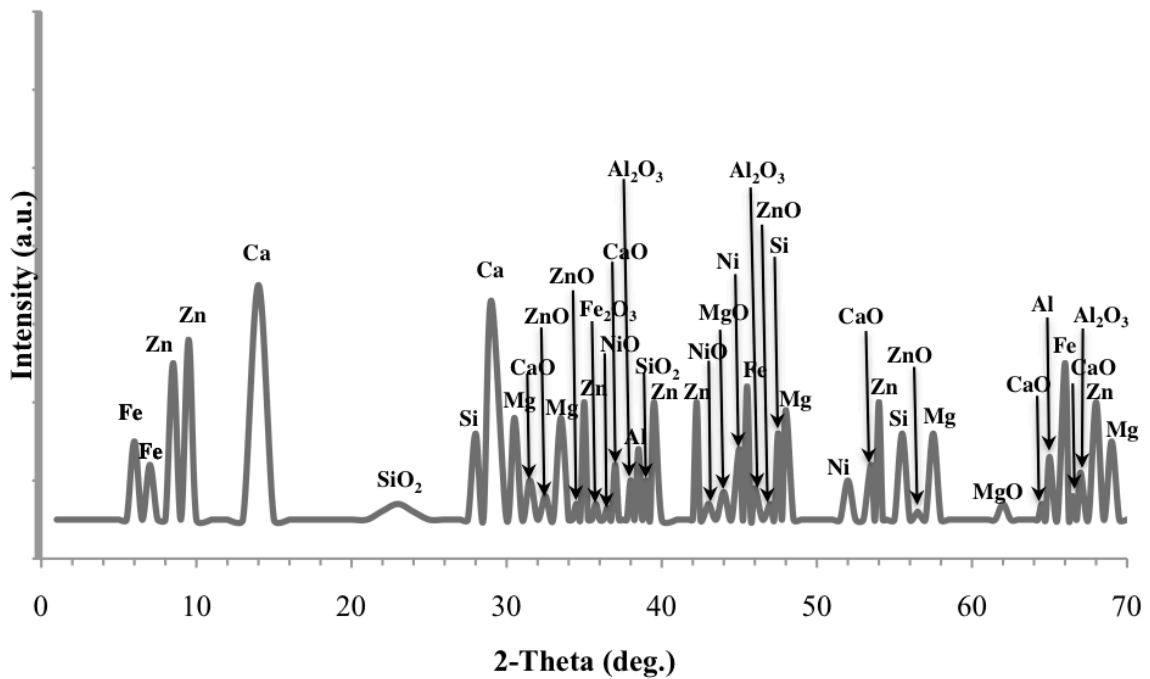
456 For used metallic-char, lower peaks were observed for the metal oxides and relatively  
457 higher peaks identified as Al, Fe, Mg, Zn, and Ni phase were detected compared to those  
458 observed in the fresh metallic-char (Fig. 5). This suggests that some of the metal oxides  
459 (originally attached to the metallic-char) had been reduced to form their metal elements  
460 through the reductive and heterogeneous reactions (e.g. steam reforming) that occurred  
461 between the waste oil (or the evolved pyrolysis-volatiles) and the carbon and metal oxides in  
462 the metallic-char during the pyrolysis at a high temperature of 550 °C. It was likely that the  
463 metallic-char, being a carbonaceous material that can be heated and transformed into a high  
464 temperature site under the influence of microwave heating, had provided a reducing chemical  
465 environment in which the metallic-char acted as an intermediate reductant to reduce the  
466 adsorbed metal oxides into its metallic states (R10, R11; see Section 3.4.2). In addition,  
467 sintering of metal particles such as Ni could occur as a result of the high temperature  
468 provided under the microwave pyrolysis condition [39].

469

### Fresh metallic-char



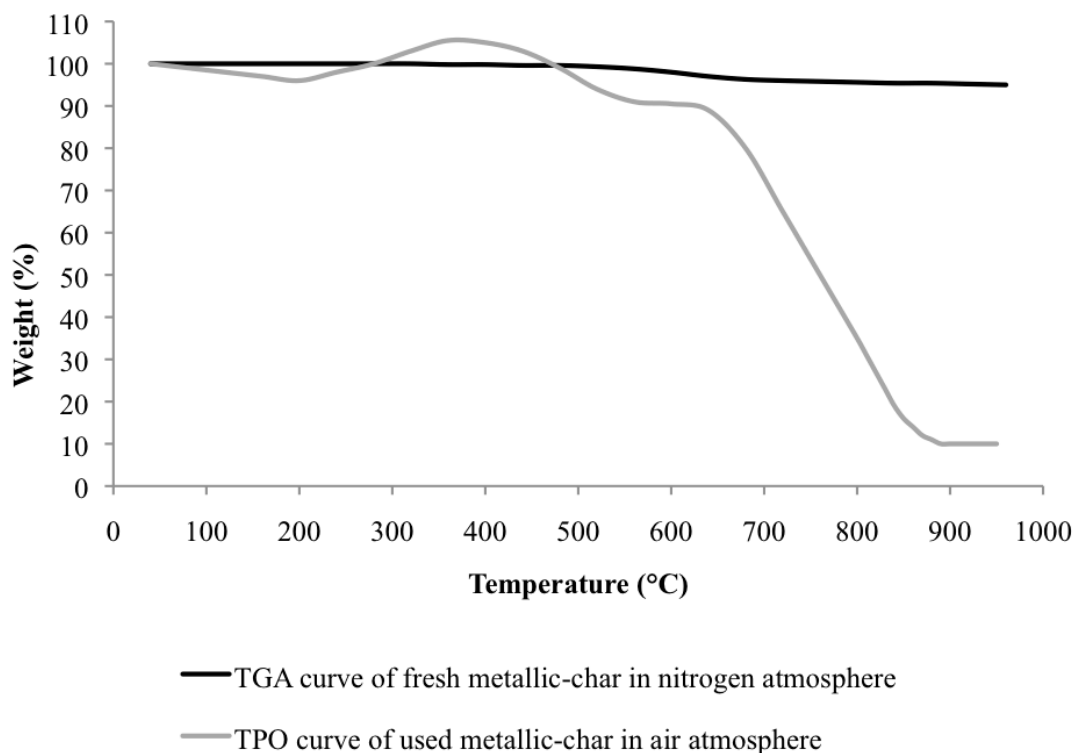
### Used metallic-char



470

**Fig. 5.** XRD analysis of fresh and used metallic-char

471



472

473

**Fig. 6.** TGA and TPO analysis of metallic-char

474

### 3.1.3. TGA and TPO analysis of metallic-char before and after pyrolysis

475

The metallic-char before pyrolysis was analyzed by TGA as an evaluation of its thermal stability under pyrolysis environment in an N<sub>2</sub> atmosphere, and the resulting plot is presented in Fig. 6. It was revealed that the metallic-char showed high thermal stability in a N<sub>2</sub> atmosphere as indicated by only a small reduction in weight (5%) with the increase of temperature up to 900 °C. This indicates that the metallic-char is durable to be used in a pyrolysis conversion process due to its high thermal stability under pyrolysis environment in an N<sub>2</sub> atmosphere.

482

The used metallic-char was analyzed by TPO to investigate its reactivity with oxygen in an air atmosphere and also the oxidation of coked carbons deposited on the surface of the used catalyst. The TPO curve of the used metallic-char under air atmosphere is demonstrated in Fig. 6. The weight of the used metallic-char was found to decrease about 4% initially when it was heated to about 200 °C, which was likely due to the evaporation of water present in the

486



487 char. The weight of the char then increased slightly for about 9% from 200 - 400 °C, which  
488 could possibly be attributed to the oxidation of metallic elements present in the used char (see  
489 Fig. 5 for the metallics phase observed in the used metallic-char from XRD analysis), e.g.  
490 oxidation of metallic Ni as has been reported by Wu and Williams [40]. After 400 °C, the  
491 used metallic-char showed a reduction in weight for about 13% when it was heated to 560 °C,  
492 and the weight remained at about 90% until 600 °C. The reduction in weight between 400 °C  
493 and 600 °C could be explained by the oxidation of the coke carbons deposited on the used  
494 metallic-char. This result is in agreement with the findings of other workers in which the  
495 authors have reported that the oxidation or combustion of carbon deposited on the surface of  
496 a catalyst normally happens at temperatures between 400 and 600 °C [34, 35]. The metallic-  
497 char then showed a dramatic reduction of about 80% of weight when it was heated from 600 -  
498 900 °C in air, and the weight remained at 10% through the remaining heating period. The  
499 dramatic reduction of weight at this temperature range suggests that the fixed carbon  
500 originally present in the metallic-char (Table 3) was likely to have reacted with the oxygen  
501 present in the air to form carbon oxides at temperature above 600 °C. It can also be inferred  
502 from these results that a temperature of 600 °C can be selected for thermal regeneration of the  
503 metallic-char in order to extend its service life since this temperature represents the optimum  
504 balance between sufficiently high temperature needed to remove the coked carbon deposited  
505 on the used metallic-char, while not being so high as to promoting the oxidation of the fixed  
506 carbon in the metallic-char that would result in weight reduction of the char.

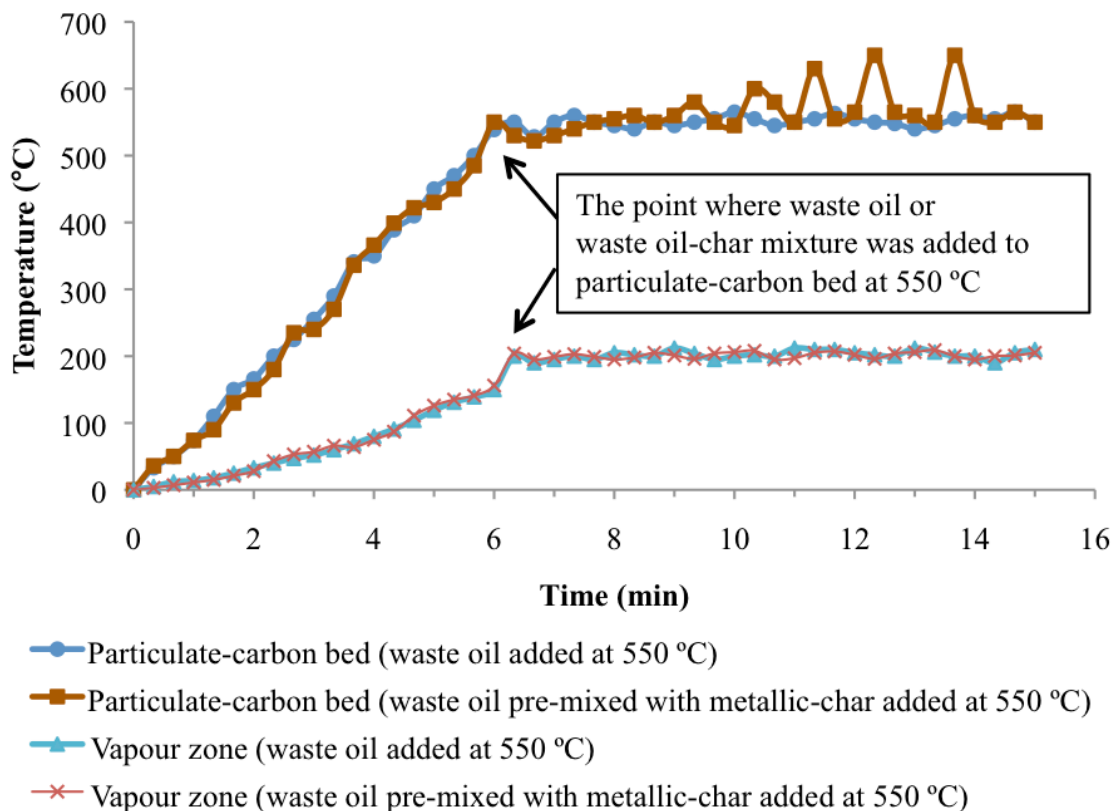
507

508

509

510

511



512 **Fig. 7.** Temperature profiles during microwave pyrolysis of waste oil by contact with a bed of  
 513 particulate-carbon (1 kg) in the additional presence of a small amount of metallic-char pre-  
 514 added to the waste oil (20 wt% of the amount of waste oil added to the reactor). The data  
 515 presented show typical results for the temperature profile obtained in experiments with low  
 516 standard deviations shown in the temperature reading ( $\pm 1 - 6$  °C) for each reference point.  
 517  
 518

519 *3.2. Temperature profile of the mixture of waste oil and metallic-char during the pyrolysis by*  
 520 *microwave radiation*

521 Fig. 7 shows the temperature profile of the mixture of waste oil and metallic-char after  
 522 addition to a bed of particulate-carbon during the pyrolysis by microwave radiation. The  
 523 temperature profiles shown in Fig. 7 are limited to the particular configuration of the  
 524 microwave pyrolysis system used in the experimental apparatus developed for this  
 525 investigation.

526 The waste oil-char mixture (80:20 wt%) was continuously added to the reactor containing a  
 527 bed of particulate-carbon maintained at the target temperature of 550 °C by microwave  
 528 heating. This initiated the pyrolysis process and the waste oil was pyrolyzed and transformed

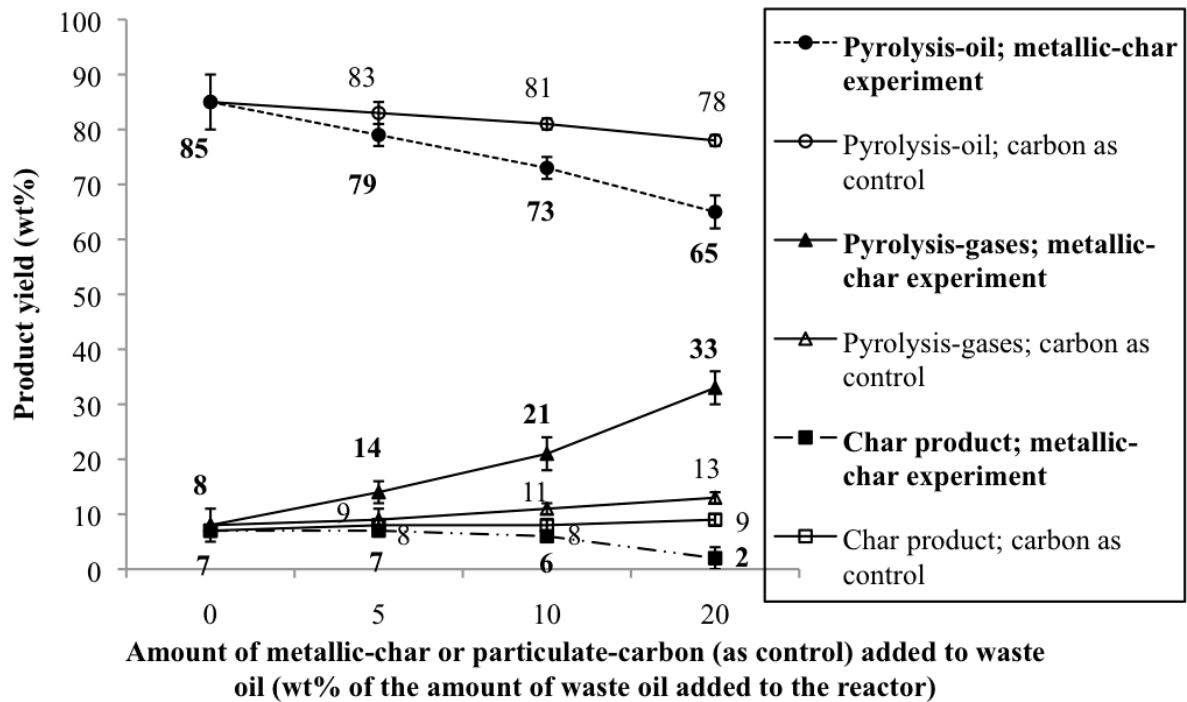
529 into pyrolysis-volatiles, which then left the reactor and passed through the product collection  
530 system. Electrical arcing was found to occur and sparks were observed 3 minutes after the  
531 initial injection of the waste oil-char mixture into the hot carbon bed. Such a phenomenon  
532 was found to occur intermittently within and on the surface of the carbon bed and this  
533 resulted in a series of transient rises of temperature readings to a maximum of 650 °C during  
534 the pyrolysis of the waste oil-char mixture. Nevertheless, the temperature of the carbon bed  
535 was able to be maintained predominantly at the desired target pyrolysis temperature (550 °C)  
536 by the magnetron control system, except with some intermittent rises to 650 °C during  
537 pyrolysis in the presence of metallic-char.

538 The sparks and the intermittent rises of temperature were likely to have been caused by  
539 electrical arcing that occurred as a result of the metals present in the waste oil and those  
540 metallic elements that were retained within the metallic-char (Table 3); the presence of  
541 metals in the waste oil has been reported in previous works [6]. It has also been reported in  
542 other microwave pyrolysis studies [23] that sparks (regarded as “microplasmas”) were  
543 observed during the heating of pyrolysis-char and they also exhibited a very high  
544 temperature. In addition, the particles of metallic-char were observed to be incandescent  
545 (exhibiting a bright-red color) against the background of dark waste oil within a dark  
546 particulate-carbon bed, suggesting that they were transformed into hot spots (high  
547 temperature sites) during the pyrolysis, probably due to their being more rapidly heated by  
548 microwave radiation. These observations suggest that hot spots were formed during the  
549 pyrolysis of the waste oil-char mixture, and they were most likely created as a result of the  
550 addition of metallic-char to the reactor. The addition of metallic-char is thought to have an  
551 effect on the pyrolysis of waste oil as the resulting hot spots could promote heterogeneous  
552 reactions between the metallic-char and the waste oil (or the evolved pyrolysis-volatiles) and  
553 lead to a different product composition. This is consistent with results from microwave

554 pyrolysis studies of other materials, where the formation of H<sub>2</sub> was observed even at a low  
555 pyrolysis temperature of 500 °C [23, 41, 42]. It can also be inferred from these results that  
556 hot spots would form in the reactor if the microwave pyrolysis of waste oil (with no added  
557 metallic-char) is performed in a continuous operation over a long period of time due to the  
558 increased amount of metallic-char that is generated and remained trapped within the  
559 particulate-carbon bed over a prolonged period of operation.

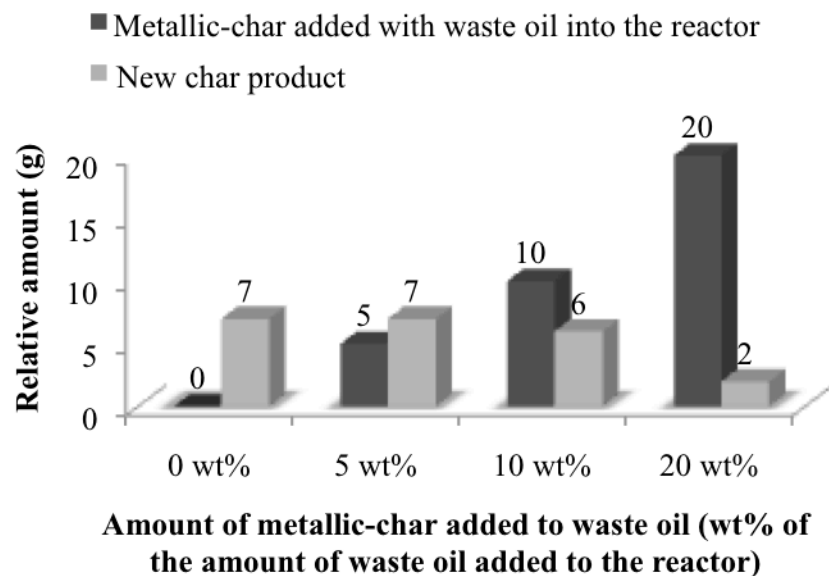
560 The temperature measured in the vapor zone (the space above the carbon bed in the reactor)  
561 showed interesting results (Fig. 7). There was a slow increase of temperature to ~150 °C as  
562 the particulate-carbon bed was heated to the target temperature at 550 °C, and this was  
563 probably due to a convective heating effect resulting from the heating of the carbon bed by  
564 microwave radiation and also the associated radiative heat transfer between the carbon bed  
565 and the thermocouple. When the waste oil or the 80:20 wt% mixture of waste oil and  
566 metallic-char was added to reactor for pyrolysis treatment in a carbon bed at 550 °C, there  
567 was a sudden increase of temperature in the vapor zone from 150 to 200 °C, and the  
568 temperature remained at around this level throughout the remaining pyrolysis period. The  
569 sudden rise of temperature was likely due to the evolution of hot pyrolysis-volatiles from the  
570 waste oil that entered the vapor zone. The lower temperature in the vapor zone (~200 °C)  
571 compared to the temperature in the particulate-carbon bed (≥550 °C) showed that different  
572 temperature distributions are present within the reactor during the microwave pyrolysis and  
573 this may be partly due to the continuous addition of cold N<sub>2</sub> purge gas into the reactor. The  
574 different heat distributions in different sections of the reactor may have effects on the reaction  
575 pathways that occur in this pyrolysis process.

576



577  
578  
579  
580  
581  
582  
583  
584

**Fig. 8.** Product yields (wt%) as a function of the amount of metallic-char or particulate-carbon (as control) added to waste oil. Process conditions: Pyrolysis was performed on waste oil by contact with 1 kg of particulate-carbon bed when the effects of varying the amount of metallic-char added to the waste oil were studied, and all experiments were performed at a constant temperature of 550 °C, waste oil feed rate of 1 kg/h, and N<sub>2</sub> purge rate of 250 ml/min.



585  
586  
587  
588

**Fig. 9.** The relative amounts of metallic-char and char product as a function of the amount of metallic-char added to waste oil.

589 *3.3. Product yield in the presence of metallic-char as catalyst*

590 Fig. 8 and Fig. 9 outline the effect of the amount of metallic-char on the fraction of waste  
591 oil converted to pyrolysis-gases, pyrolysis-oil, and char product. The study showed that the  
592 waste oils were thermally cracked to pyrolysis products dominated by pyrolysis-oil (65-85  
593 wt.%) and smaller amounts of pyrolysis-gases (8-33 wt.%) and char product (2-7 wt.%). The  
594 amount of metallic-char was found to have a significant influence on the yields of pyrolysis  
595 product. The yield of pyrolysis-gases was found to increase with increasing amounts of  
596 metallic-char fed together with the waste oil into the reactor. Hot spots were observed on  
597 addition of the waste oil-char mixture into the particulate-carbon bed during the pyrolysis  
598 process (see Section 3.2). The formation of hot spots was likely to have promoted the  
599 heterogeneous reactions between the metallic-char and the waste oil (or the evolved  
600 pyrolysis-volatiles) to produce greater quantities of gases such as H<sub>2</sub> and CO as reported by  
601 others in microwave pyrolysis studies of other wastes [25, 43]. Thus, the presence of higher  
602 amounts of metallic-char was likely to enhance the heterogeneous reactions that occurred  
603 during the pyrolysis and this resulted in a higher yield of pyrolysis-gases and a lower  
604 corresponding yield of pyrolysis-oil. However, the amount of new char production was found  
605 to decrease with increasing amounts of metallic-char added to the waste oil (Fig. 4). This  
606 could be explained by the gasification of the chars to produce H<sub>2</sub> and CO, this being one of  
607 the heterogeneous reactions that have been reported to be highly promoted in microwave  
608 pyrolysis systems [14, 15, 20, 24]; this is likely to have contributed to the lower yield of the  
609 new char product. The results show that the addition of metallic-char to the waste oil could  
610 promote different product compositions due to additional heterogeneous reactions that  
611 occurred during the pyrolysis in the presence of metallic-char.

612

613 *3.4. Product chemical composition in the presence of metallic-char as catalyst*

614 Table 4 demonstrates the main chemical components identified in the pyrolysis-oil and  
615 pyrolysis-gases obtained from the experiments performed with different amounts of metallic-  
616 char. The pyrolysis-oil comprised mainly of C<sub>5</sub>–C<sub>30</sub> hydrocarbons, which were dominated by  
617 aliphatic hydrocarbons (58–65 wt%) and significant amounts of aromatic hydrocarbons (29–  
618 38 wt%). The composition of the pyrolysis-gases was dominated by aliphatic hydrocarbons  
619 (58-78 vol%) and significant amounts of permanent gases (i.e. H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>S, 23–42  
620 vol%). These results indicate the cracking of waste oil (C<sub>7</sub>–C<sub>41</sub> hydrocarbons; see Table 1) to  
621 small hydrocarbon components (C<sub>1</sub>–C<sub>30</sub> hydrocarbons; see Table 4), and the subsequent  
622 formation of aromatics and permanent gases (H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>S) through cracking,  
623 aromatization, and heterogeneous reactions that were likely to have occurred during  
624 pyrolysis. The production of pyrolysis-oil (comprising C<sub>5</sub> to C<sub>20</sub> aliphatic hydrocarbons) and  
625 valuable gases such as CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>, and CO represents a potentially high-value chemical  
626 feedstock or fuel source. The alkanes in the pyrolysis-oil could be upgraded to produce  
627 transport-grade fuels, whereas the alkenes and aromatics constitute a feedstock that is highly  
628 desired in the petrochemical industry, especially in plastic manufacture. The low heating  
629 values (LHV) of the pyrolysis-gases was estimated based on the concentration of CO, H<sub>2</sub>, and  
630 CH<sub>4</sub> in the pyrolysis-gases [44]. The pyrolysis-gases show a LHV ranging from 4.7 to 5.5  
631 MJ/m<sup>3</sup>, suggesting that the pyrolysis-gases could be used as a gaseous fuel and burned  
632 directly in gas engines or fuel cells, or upgraded to produce hydrogen and synthetic fuel (via  
633 a Fischer-Tropsch process). In particular, the hydrogen obtained can potentially be used as a  
634 second-generation fuel or as a synthesis chemical, and the CO could be steam-reformed to  
635 produce more hydrogen.

636

637

638

639 **Table 4**  
 640 Main chemical components identified in the pyrolysis-oil and pyrolysis-gases produced under  
 641 various conditions <sup>a</sup>.

	Metallic-char added to waste oil							
	0 wt%		5 wt%		10 wt%		20 wt%	
	Control <sup>b</sup>	Treated	Control <sup>b</sup>	Treated	Control <sup>b</sup>	Treated	Control <sup>b</sup>	Treated
Pyrolysis-oil (wt%)								
Aliphatics <sup>c</sup>	<b>65.1</b>	64.6	<b>63.6</b>	63.9	<b>61.5</b>	62.2	<b>57.5</b>	
Aromatics <sup>d</sup>	<b>29.1</b>	29.7	<b>29.2</b>	30.8	<b>32.6</b>	32.6	<b>38.3</b>	
Carbon components								
C <sub>5</sub> -C <sub>10</sub>	<b>56.4</b>	57.6	<b>58.3</b>	59.9	<b>64.3</b>	62.4	<b>73.5</b>	
C <sub>11</sub> -C <sub>15</sub>	<b>16.7</b>	16.3	<b>16.4</b>	15.9	<b>14.8</b>	15.5	<b>13.0</b>	
C <sub>16</sub> -C <sub>20</sub>	<b>15.2</b>	14.7	<b>13.6</b>	13.7	<b>12.1</b>	12.4	<b>8.2</b>	
C <sub>21</sub> -C <sub>30</sub>	<b>5.9</b>	5.7	<b>4.5</b>	5.2	<b>2.9</b>	4.5	<b>1.1</b>	
Pyrolysis-gases (vol%)								
H <sub>2</sub>	<b>11.7</b>	12.6	<b>16.4</b>	13.7	<b>21.3</b>	15.3	<b>28.6</b>	
CO	<b>9.6</b>	9.9	<b>10.2</b>	10.1	<b>11.5</b>	10.3	<b>13.2</b>	
CO <sub>2</sub>	<b>0.6</b>	0.6	<b>0.4</b>	0.5	<b>0.1</b>	0.4	<b>0.1</b>	
H <sub>2</sub> S	<b>0.6</b>	0.6	<b>0.4</b>	0.6	<b>0.1</b>	0.5	<b>0.0</b>	
CH <sub>4</sub>	<b>6.1</b>	6.6	<b>4.9</b>	7.5	<b>3.3</b>	8.6	<b>2.1</b>	
C <sub>2</sub> H <sub>2</sub>	<b>0.2</b>	0.2	<b>0.2</b>	0.2	<b>0.1</b>	0.2	<b>0.1</b>	
C <sub>2</sub> H <sub>4</sub>	<b>21.5</b>	21.9	<b>23.8</b>	23.5	<b>30.9</b>	25.8	<b>34.0</b>	
C <sub>2</sub> H <sub>6</sub>	<b>2.5</b>	2.5	<b>2.1</b>	2.5	<b>1.4</b>	2.2	<b>0.9</b>	
C <sub>3</sub> H <sub>6</sub>	<b>10.2</b>	11.5	<b>14.0</b>	12.6	<b>17.5</b>	13.9	<b>19.3</b>	
C <sub>3</sub> H <sub>8</sub>	<b>0.1</b>	0.2	<b>0.1</b>	0.3	<b>0.1</b>	0.5	<b>0.2</b>	
C <sub>4</sub> H <sub>6</sub>	<b>8.7</b>	7.6	<b>6.8</b>	6.9	<b>3.1</b>	4.9	<b>0.5</b>	
C <sub>4</sub> H <sub>8</sub>	<b>15.5</b>	14.3	<b>11.9</b>	10.9	<b>6.1</b>	8.8	<b>0.6</b>	
C <sub>4</sub> H <sub>10</sub>	<b>0.6</b>	0.6	<b>0.5</b>	0.7	<b>0.3</b>	0.8	<b>0.2</b>	
C <sub>5</sub> and C <sub>6</sub> <sup>e</sup>	<b>12.7</b>	11.5	<b>8.3</b>	9.5	<b>4.2</b>	7.6	<b>0.2</b>	
C <sub>1</sub> -C <sub>6</sub> <sup>f</sup>	<b>78.1</b>	76.9	<b>72.6</b>	74.6	<b>67.0</b>	73.3	<b>58.1</b>	
LHV (MJ/m <sup>3</sup> )	4.7	-	4.8	-	4.9	-	5.5	

642 <sup>a</sup> Process conditions: Pyrolysis was performed on waste oil by contact with 1 kg of  
 643 particulate-carbon bed when the effects of varying the amount of metallic-char added to the  
 644 waste oil were studied, and all experiments were performed at a constant temperature of  
 645 550°C, waste oil feed rate of 1 kg/h, and N<sub>2</sub> purge rate of 250 ml/min.

646 <sup>b</sup> Particulate-carbon was used as a control.

647 <sup>c</sup> Aliphatics –alkanes, naphthenes, alkenes, dialkenes.

648 <sup>d</sup> Aromatics –benzene, toluene, xylene, alkyl-benzenes.

649 <sup>e</sup> C<sub>5</sub> and C<sub>6</sub> compounds detected in the pyrolysis-gases are grouped and presented in a total  
 650 value.

651 <sup>f</sup> The sum of C<sub>1</sub>-C<sub>6</sub> aliphatic hydrocarbons.

652 <sup>g</sup> Low heating value (LHV) of the gas product (kJ/m<sup>3</sup>) is calculated based on the  
 653 concentration of CO, H<sub>2</sub>, and CH<sub>4</sub> in the pyrolysis-gases [44], i.e. [(30\*CO) + (25.7\*H<sub>2</sub>) +  
 654 (85.4\*CH<sub>4</sub>)] x 4.2.

655

656 The amount of metallic-char added to the waste oil was found to have a substantial  
 657 influence on the chemical composition of the pyrolysis-oil and pyrolysis-gases. Increasing the



658 amount of metallic-char led to an increase in aromatic content along with a decrease in  
659 aliphatic content in the pyrolysis-oil, and the hydrocarbon content improved towards the  
660 presence of smaller hydrocarbon chains ( $C_5$ - $C_{10}$ ). The increase in the amount of metallic-char  
661 also resulted in greater production of  $H_2$  and  $CO$  in the pyrolysis-gases (up to 42 vol% of  
662  $H_2+CO$ ). This was accompanied by a decrease in  $CO_2$  and aliphatic contents in the pyrolysis-  
663 gases with the composition of the aliphatics being improved towards the presence of smaller  
664 hydrocarbon chains ( $\leq C_3$ ). The yields of  $H_2$ ,  $CO$ ,  $C_2H_4$ , and  $C_3H_6$  were found to increase with  
665 increasing amounts of metallic-char; these compounds are believed to comprise the bulk of  
666 the increased amount of pyrolysis-gases produced when higher amounts of metallic-char  
667 were added to the waste oil before the pyrolysis. In contrast, a reduction in  $CO_2$  content was  
668 observed although  $CO_2$  was detected only in minor quantities ( $\leq 0.6$  vol%), and this was also  
669 accompanied by a reduction in  $CH_4$  content.

670 In this study, the increase in the amount of metallic-char added to the waste oil was thought  
671 to have led to the formation of hot spots within the reactor (see Section 3.2), and in turn  
672 promoted heterogeneous reactions between the metallic-char and the waste oil (or the evolved  
673 pyrolysis-volatiles) to produce greater yields of  $H_2$  and  $CO$  and lower yields of  $CO_2$  and  $CH_4$ .  
674 In addition, the hot spots created by the metallic-char (homogeneously mixed with the waste  
675 oil) appeared to promote cracking reactions during the pyrolysis and resulted in the observed  
676 formation of higher amounts of lighter hydrocarbons in both the pyrolysis-oil (i.e.  $C_5$ - $C_{10}$   
677 hydrocarbons) and pyrolysis-gases (i.e.  $\leq C_3$  hydrocarbons). This agrees with the findings  
678 reported by other researchers working on microwave pyrolysis studies of other materials [15,  
679 25, 43], which propose that char particles may absorb microwave energy and heat up, then  
680 transform into hot spots, which in turn act in a catalytic manner to promote the cracking and  
681 heterogeneous reactions during the microwave pyrolysis process, e.g. the decomposition  
682 reactions of hydrocarbons to produce  $H_2$ , and the aromatization reactions to generate  $H_2$  and

683 benzene [8].

684 The catalytic effect could also be attributed to the high surface area ( $124 \text{ m}^2/\text{g}$ ) and the  
685 presence of metals and metal oxides in the metallic-char (Table 3), the amounts of which are  
686 likely to increase with increasing amounts of metallic-char added to the waste oil, providing  
687 more reaction sites in order for these reactions to occur. The metallic-char was likely to act as  
688 an intermediate reductant that had reduced the adsorbed metals or metal oxides into metallic  
689 states which in turn enhanced the cracking and heterogeneous reactions that occurred during  
690 the pyrolysis process.

691 Furthermore, the catalytic activity of metallic-char could be explained by a microwave-  
692 specific mechanism. As previously observed by others in microwave pyrolysis studies [17,  
693 18, 23, 45, 46], the interaction of the electromagnetic microwave field with particular types of  
694 carbon (e.g. metallic-char) generates “microplasmas” (i.e. electrical discharges resulting  
695 from the rapidly oscillating electromagnetic microwave field) which create charge  
696 imbalances that are restricted by the physical boundaries of the carbon particles. The  
697 temperature of these microplasmas is considerably higher than that of the bulk carbon bed,  
698 and consequently waste oil exposed to these microplasmas will be cracked to a greater extent.  
699 Such microplasmas were observed during pyrolysis in the additional presence of the metallic-  
700 char (pre-mixed with waste oil), but not at all when pyrolysis was conducted with only the  
701 waste oil (i.e. in the absence of added metallic-char). Thus, it is likely that this additional  
702 mechanism due to the presence of microplasmas contributed to the additional cracking  
703 observed when using the waste oil-char mixture.

704

705 *3.5. Possible chemical reaction mechanisms accounting for the catalytic conversion of waste*  
706 *oil using the metallic-char catalyst coupled with microwave pyrolysis.*

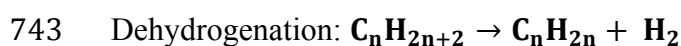
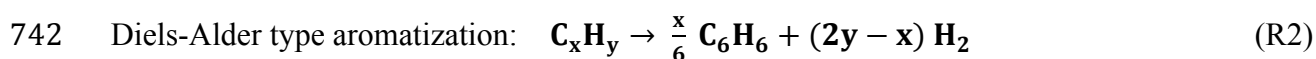
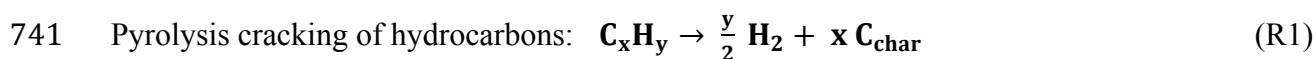
707 The results have shown that microwave pyrolysis in the presence of the metallic-char as the

708 catalyst cracked the waste oil to produce a unique product distribution of compounds  
709 comprising predominantly light hydrocarbons, H<sub>2</sub> and CO gases, and char product in the  
710 pyrolysis products. The production of these compounds could derive mainly from the primary  
711 and secondary pyrolysis cracking reactions occurring via a free-radical-induced mechanism  
712 [10-12], and secondary reactions comprising both homogenous and heterogeneous reactions  
713 such as Diels-Alder type aromatization reactions (i.e. condensation, dehydrogenation),  
714 reforming, dehydrogenation, decomposition, gasification, carbon reduction, and  
715 carbonization.

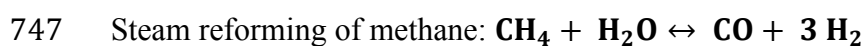
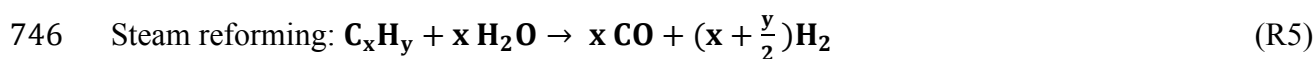
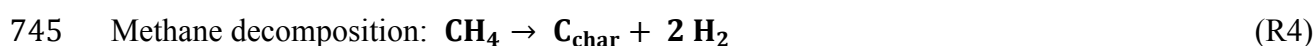
716 The wide distribution of aliphatic chains in the pyrolysis products supports the proposed  
717 free-radical-induced random scission mechanism for the catalytic pyrolytic cracking of waste  
718 oil; the reaction mechanism, comprising random scission reaction, H-atom-abstraction  
719 reactions,  $\beta$ -scission reaction, and termination reactions, has also been proposed for the  
720 pyrolysis of polyolefins based on the wide distribution of aliphatic chains found in the  
721 pyrolysis products [47-50]. Hydrocarbon radicals were likely to be generated from this  
722 mechanism through which the radicals were then stabilized by the capture of hydrogen atoms  
723 from the molecules nearby and this resulted in the conversion of heavy hydrocarbons in the  
724 waste oil into lighter hydrocarbons by H-atom abstraction and  $\beta$ -scission reactions; this  
725 accounts for the light aliphatic hydrocarbons detected in both the pyrolysis-oil and pyrolysis-  
726 gases. The free-radical mechanism could proceed further during the pyrolysis cracking of  
727 waste oil whereby the large aliphatic hydrocarbons (e.g. large alkenes) might undergo  
728 secondary pyrolysis cracking and decompose to form aliphatic hydrocarbons of shorter  
729 chains as proposed by Miller [51]. The short-chained aliphatic hydrocarbons (e.g. alkenes and  
730 dialkenes) produced from the free-radical-induced random scission mechanism could then  
731 proceed to form aromatic hydrocarbons observed in the pyrolysis products by Diels-Alder  
732 type aromatization reactions, which involve condensation of alkenes followed by

733 dehydrogenation to form aromatic hydrocarbons. Depending on the extent of these secondary  
 734 actions and the amount of thermal energy generated by the microwave radiation at the  
 735 pyrolysis temperature, carbonization could occur and lead to the production of carbonaceous  
 736 char as the char product.

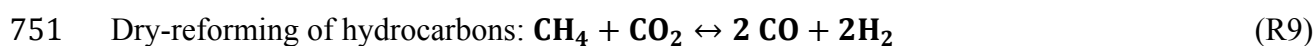
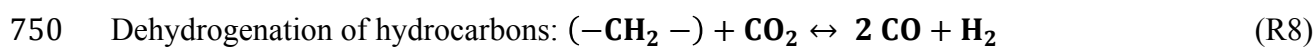
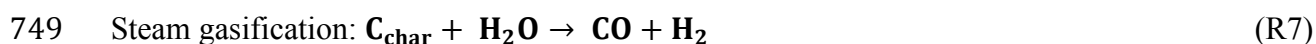
737 The production of permanent gases species (e.g. H<sub>2</sub>, CO, CO<sub>2</sub>) and char product could be  
 738 attributed to the secondary reactions occurring either homogeneously or heterogeneously in  
 739 the presence of the metallic-char as the catalyst during the pyrolysis process. The proposed  
 740 secondary reactions are termed as R1 – R11 as below:



744 (R3)



748 (R6)



752 Reduction of metal ions (Me<sup>2+</sup>) and metallic oxides (Me<sub>m</sub>O<sub>n</sub>) to metal (Me) by carbon:



755 H<sub>2</sub> gas was likely to be generated via the catalytic heterogeneous reactions (R1, R2)  
 756 occurring between the metallic-char and the waste oil or the evolved pyrolysis-volatiles [14,  
 757 15, 24, 41], since significant amount of H<sub>2</sub> (up to 29 vol%) was detected in the pyrolysis-

758 gases (Table 4). In addition, the decreasing yield of aliphatic hydrocarbons with increasing  
759 amount of metallic-char added to the pyrolysis process (Table 4) suggest that it was the  
760 increased occurrence of the R1 and R2 reactions that had converted some of the aliphatic  
761 hydrocarbons into H<sub>2</sub> and aromatics, resulting in higher yields of these compounds detected  
762 in the pyrolysis products; this supports the occurrence of the proposed catalytic  
763 heterogeneous reactions (R1, R2) for H<sub>2</sub> formation. Al-containing catalyst has been reported  
764 to have the ability to enhance aromatization reactions (R2) in producing aromatics [52], thus  
765 the increasing amount of metallic-char containing Al (Table 3) was likely to have promoted  
766 the R2 reactions to generate higher yield of aromatics as observed in the pyrolysis-oil.

767 The high yield of ethylene observed in the pyrolysis-gases (up to 34 vol%, Table 4) was  
768 likely to arise from the dehydrogenation of ethane to ethylene (R3) during the catalytic  
769 microwave pyrolysis of the waste oil. This reaction was found to be promoted under the  
770 influence of microwave heating within microwave pyrolysis systems [14, 16, 24]; this also  
771 contributes to the higher yield of H<sub>2</sub> and lower yield of ethane observed in the pyrolysis-gases  
772 (Table 4). In addition, the presence of metals and metal oxides such as Al and Al<sub>2</sub>O<sub>3</sub> were  
773 reported to have a catalytic effect on this reaction [19]. The increase in the amount of  
774 metallic-char added to the waste oil led to the presence of higher amounts of these metal  
775 elements in the reactor, thus promoting the occurrence of dehydrogenation reactions and  
776 resulting in the increased yields of ethylene observed in the pyrolysis-gases; this also  
777 contributes to the increased yield of H<sub>2</sub> and lower yield of ethane.

778 A reduction in CH<sub>4</sub> content was observed with an increase in the amount of metallic-char  
779 added to the waste oil (Table 4), suggesting that a portion of the CH<sub>4</sub> was transformed into H<sub>2</sub>  
780 by the methane decomposition reactions (R4) that occurred during the pyrolysis; this also  
781 contributes to the production of char product and the increased yield of H<sub>2</sub> during the  
782 pyrolysis. This reaction was found to be promoted under the influence of microwave heating

783 and the formation of hot spots within the microwave pyrolysis system [43]. In addition,  
784 carbon materials and metal-containing catalysts (e.g. Fe-Al<sub>2</sub>O<sub>3</sub>, Ni, Al) were reported to show  
785 catalytic effects on this reaction [21, 22]. The use of metallic-char as a catalyst followed by  
786 the formation of hot spots by the addition of the carbonaceous metallic-char containing Fe,  
787 Ni, Al<sub>2</sub>O<sub>3</sub>, (see Table 3 and Fig. 5) support the proposed occurrence of methane  
788 decomposition reactions for the formation of char product and H<sub>2</sub>.

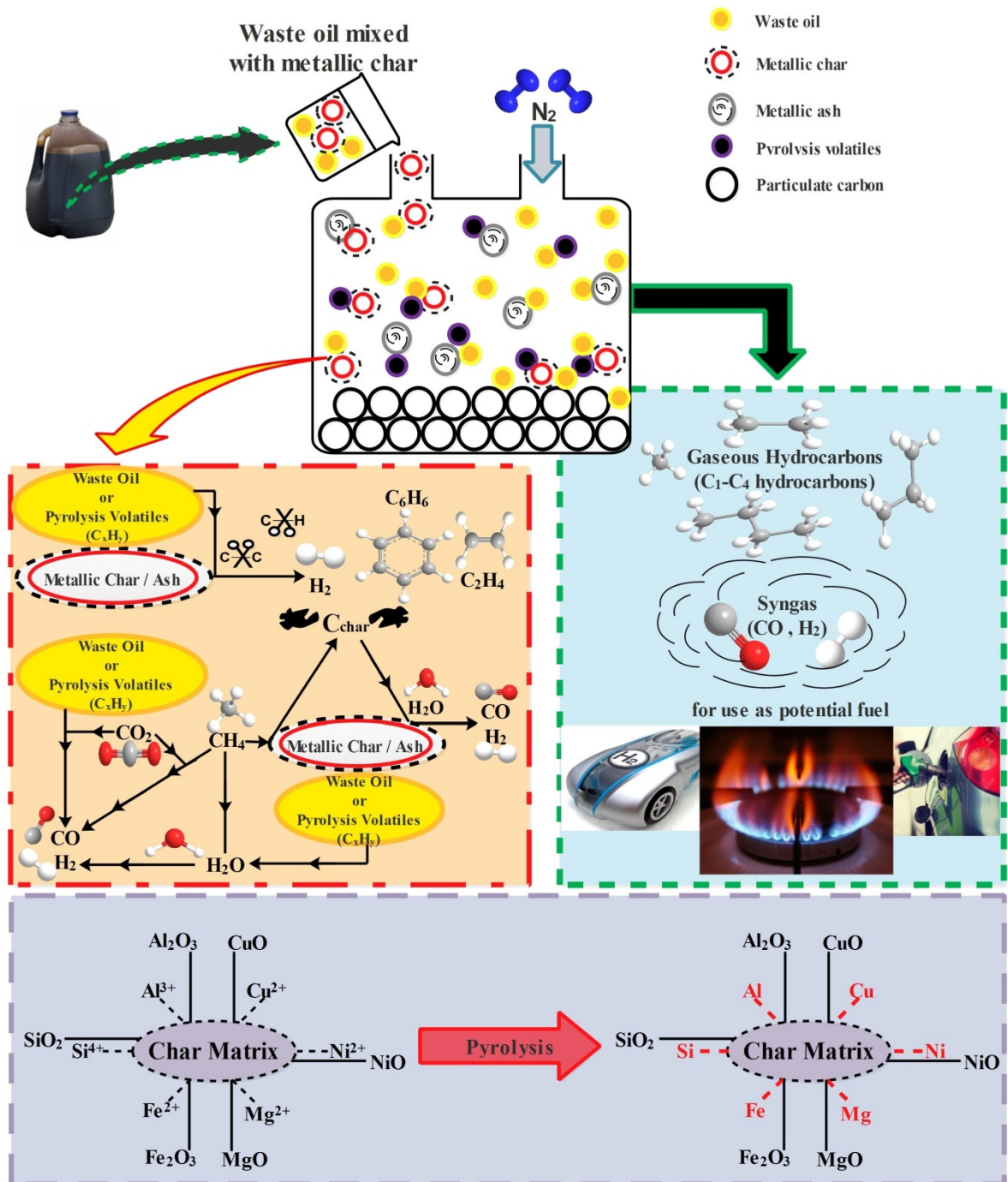
789 Th waste oil used in this study was found to contain a certain amount of water (about 20  
790 wt%); the presence of water in the waste oil has been reported in previous work [8]. The  
791 water could vaporise as steam during the pyrolysis process by the microwave heating. This  
792 could lead to the occurrence of steam reforming reaction of hydrocarbons (R5, R6) and the  
793 steam gasification of chars (R7), resulting in higher production of H<sub>2</sub> and CO in the pyrolysis  
794 gases (Table 4). It has been reported that catalysts containing Mg could enhance  
795 heterogeneous reactions such as steam gasification and reforming reactions [53]; the use of  
796 metallic-char containing Mg (see Table 3 and Fig. 5) supports the proposed occurrence of  
797 these reactions.

798 CO<sub>2</sub> was only detected in less than 0.6 vol% (Table 4), whereas higher quantities of CO  
799 were detected in the pyrolysis-gases (up to 13 vol%), suggesting that a significant portion of  
800 the CO<sub>2</sub> might be converted to form H<sub>2</sub> and CO by heterogeneous reactions such as  
801 dehydrogenation (R8) and dry-reforming (R9) reactions that have been reported to be  
802 promoted under microwave pyrolysis environment [14, 15]. Both the concentrations of CO<sub>2</sub>  
803 and aliphatic hydrocarbons (particularly CH<sub>4</sub>) were found to decrease when using increased  
804 amounts of the metallic-char (Table 4). This supports the proposed increased occurrence of  
805 these heterogeneous reactions that had resulted in higher productions of H<sub>2</sub> and CO in the  
806 pyrolysis-gases.

807 The results revealed that the increase in the amount of metallic-char added to the waste oil

808 led to a reduction in the subsequent yield of additional char product (Fig. 9), suggesting that a  
809 portion of the char product (generated by the decomposition of hydrocarbons, R1 and R4)  
810 was converted to H<sub>2</sub> and CO by gasification reactions (R7). These gasification reactions were  
811 likely to occur due to the ability of the metallic-char to absorb the microwave energy and heat  
812 up, transforming into hot spots and in turn promoting the occurrence of these reactions. These  
813 gasification reactions are a few of the heterogeneous reactions that were reported to be highly  
814 promoted in microwave pyrolysis systems [14, 25], and they were found to occur in  
815 microwave pyrolysis systems even at low reaction temperatures of 400 and 500 °C [42], thus  
816 the yield of char product was reduced in favour of H<sub>2</sub> and CO formation.

817 In this study, the addition of metallic-char to the waste oil was found to have a catalytic  
818 effect on both the cracking and the heterogeneous reactions that occurred during the  
819 pyrolysis, converting the waste oil (or the evolved pyrolysis-volatiles) into light  
820 hydrocarbons, H<sub>2</sub> and CO gases; this helps to explain the higher production of H<sub>2</sub> and CO  
821 gases, and also the higher yields of smaller hydrocarbon chains (C<sub>5</sub>-C<sub>10</sub> hydrocarbons, CH<sub>4</sub>,  
822 C<sub>2</sub>H<sub>4</sub>) observed in both the pyrolysis-oil and pyrolysis-gases. The results suggest that the  
823 reactions in catalytic microwave pyrolysis of waste oil are a combination of primary and  
824 secondary pyrolysis cracking, and serial and parallel secondary reactions occurring  
825 homogeneously or heterogeneously as described by R1 – R11, with the pyrolysis cracking and  
826 catalytic heterogeneous reactions dominating as metallic-char is incorporated into the  
827 pyrolysis process, resulting in a relatively high reaction selectivity toward H<sub>2</sub>, CO, and a  
828 desirable lighter hydrocarbon fraction in the pyrolysis products



829  
830  
831  
832  
833

Fig. 10. Reaction mechanisms accounting for microwave pyrolysis conversion of waste oil using the metallic char catalyst.

834 Fig. 10 summarizes the mechanisms involved in the microwave pyrolysis conversion of  
835 waste oil through the use of the metallic-char as a catalyst. In this microwave pyrolysis  
836 process, the metallic-char initially acted as an adsorptive-support to adsorb metals, metal  
837 oxides and waste oil. Then, the char became a microwave absorbent that absorbed microwave



838 energy and heated up to high temperature in a short time and in turn transformed into hot  
839 spots (high temperature sites) under the influence of microwave heating. The presence of this  
840 high temperature metallic-char had provided a reducing chemical environment in which the  
841 metallic-char acted an intermediate reductant to reduce the adsorbed metals or metal oxides  
842 into metallic states (R10, R11) which then functioned as a catalyst to provide more reaction  
843 sites that enhanced the cracking and heterogeneous reactions that occurred during the  
844 pyrolysis to convert the waste oil into producing higher yields of light hydrocarbons, H<sub>2</sub> and  
845 CO gases in the pyrolysis products. It should be noted that the metals contained in the  
846 metallic-char could be regenerated by gasification or thermal regeneration of the metallic-  
847 char since the metals should remain in solid states considering their high sublimation  
848 temperatures ( $\geq 1000$  °C, e.g. 2732 °C for Ni and 1535 °C for Fe) [38].

849 The results in this study have indicated that the use of metallic-char obtained from the  
850 previous pyrolysis of waste oil as a catalyst showed a significant influence on the product  
851 distribution in this pyrolysis process and led to the production of useful light hydrocarbons,  
852 H<sub>2</sub> and CO gases in the pyrolysis products. The use of metallic-char combined with  
853 microwave pyrolysis showed advantages in enhancing the reaction rates and the selectivities  
854 of the products. This presents new information on the use of metallic-char as a catalyst in  
855 microwave pyrolysis treatment of problematic waste oils. It can also be inferred from these  
856 results that if the microwave pyrolysis of waste oil were performed in a continuous operation  
857 over a long period of time, the increased amount of metallic-char that would be generated and  
858 trapped within the particulate-carbon bed would exert a similar catalytic influence and  
859 promote altering product compositions due to enhanced cracking and heterogeneous reactions  
860 occurring as a result of the formation of hot spots within the reactor.

861

862

#### 863 **4. Conclusion**

864 The metallic-char catalyst demonstrated a highly porous structure and was found to contain  
865 phases of metals and metal oxides. Combined with the results showing high surface area and  
866 thermal stability in a N<sub>2</sub> atmosphere, this makes the metallic-char a potentially suitable  
867 catalyst to be used in pyrolysis cracking process. The use of the metallic-char as a catalyst in  
868 the microwave pyrolysis of waste oil was found to have strong influence on the fraction of  
869 waste oil converted to pyrolysis-oil and pyrolysis-gases. The addition of the metallic-char  
870 also influenced the concentrations and molecular nature of the wide variety of compounds  
871 formed in the pyrolysis-oil and pyrolysis-gases. An increase in the amount of metallic-char  
872 catalyst resulted in the formation of hot spots within the reactor in which the high  
873 temperature metallic-char provided a reducing chemical environment to reduce the adsorbed  
874 metals or metal oxides into metallic states, which appear to act catalytically in providing  
875 more reactions sites in order for cracking and heterogeneous reactions to occur during the  
876 pyrolysis process. Higher yields of light hydrocarbons, H<sub>2</sub> and CO gases were obtained in the  
877 pyrolysis products in the presence of higher amounts of metallic-char. The addition of  
878 metallic-char catalyst equivalent to 20 wt% of the amount of waste oil added to the reactor  
879 generated a 65 wt% yield of pyrolysis-oil containing C<sub>5</sub>-C<sub>20</sub> hydrocarbons in addition to a 33  
880 wt% yield of pyrolysis-gases comprising 58 vol% of C<sub>1</sub>-C<sub>6</sub> hydrocarbons and 42 vol% of H<sub>2</sub>  
881 and CO gases, representing a potential source of high-value fuel and syngas. These results  
882 demonstrate that the metallic-char catalyst showed advantages in transforming the waste oil  
883 into potential fuel products, and thus showing excellent potential for use as a catalyst in  
884 microwave pyrolysis treatment of problematic waste oils.

885

#### 886 **Acknowledgements**

887 The authors acknowledges the financial support by the Ministry of Science, Technology,

888 and Innovation Malaysia (MOSTI), Ministry of Higher Education Malaysia (MOHE), and  
889 University Malaysia Terengganu for the conduct of the research under the E-Science fund  
890 (UMT/RMC/SF/13/52072(5), Vot No: 52072), the Fundamental Research Grant Scheme  
891 (Project No: FRGS/1/2013/TK05/UMT/02/2, Vot No: 59296), and the Research  
892 Acculturation Grant Scheme (Project No: RAGS/2012/UMT/TK07/3, Vot No: 57085).

893

#### 894 **References**

- 895 [1] M.a.F. Gómez-Rico, I. Martín-Gullón, A. Fullana, J.A. Conesa, R. Font, *J. Anal. Appl.*  
896 *Pyrolysis* 68-69 (2003) 527-546.
- 897 [2] M.J. Fuentes, R. Font, M.F. Gómez-Rico, I. Martín-Gullón, *J. Anal. Appl. Pyrolysis* 79  
898 (2007) 215-226.
- 899 [3] F. Audibert, *Waste engine oils: rerefining and energy recovery*, 1st ed., Elsevier B.V.,  
900 Amsterdam, 2006.
- 901 [4] D.W. Brinkman, J.R. Dickson, *Environ. Sci. Technol.* 29 (1995) 81-86.
- 902 [5] S.S. Lam, A.D. Russell, H.A. Chase, *Energy* 35 (2010) 2985-2991.
- 903 [6] S.S. Lam, A.D. Russell, H.A. Chase, *Ind. Eng. Chem. Res.* 49 (2010) 10845-10851.
- 904 [7] M.-A. Franco-Nava, J.-P. Blancheton, G. Deviller, J.-Y. Le-Gall, *Aquacult. Eng.* 31  
905 (2004) 135-155.
- 906 [8] S.S. Lam, A.D. Russell, C.L. Lee, S.K. Lam, H.A. Chase, *Int. J. Hydrog. Energy* 37  
907 (2012) 5011-5021.
- 908 [9] S.S. Lam, A.D. Russell, C.L. Lee, H.A. Chase, *Fuel* 92 (2012) 327-339.
- 909 [10] F.O. Rice, *J. Am. Chem. Soc.* 55 (1933) 3035-3040.
- 910 [11] F.O. Rice, K.F. Herzfeld, *J. Am. Chem. Soc.* 56 (1934) 284-289.
- 911 [12] F.O. Rice, M.D. Dooley, *J. Am. Chem. Soc.* 55 (1933) 4245-4247.
- 912 [13] D.A. Jones, T.P. Lelyveld, S.D. Mavrofidis, S.W. Kingman, N.J. Miles, *Resour.*  
913 *Conserv. Recycl.* 34 (2002) 75-90.
- 914 [14] Y. Fernández, A. Arenillas, J.M. Bermúdez, J.A. Menéndez, *J. Anal. Appl. Pyrolysis* 88  
915 (2010) 155-159.
- 916 [15] Y. Fernández, A. Arenillas, M.A. Díez, J.J. Pis, J.A. Menéndez, *J. Anal. Appl. Pyrolysis*  
917 84 (2009) 145-150.

- 918 [16] W. Zuo, Y. Tian, N. Ren, *Waste Manage.* 31 (2011) 1321-1326.
- 919 [17] S.S. Lam, H.A. Chase, *Energies* 5 (2012) 4209-4232.
- 920 [18] A.D. Russell, E.I. Antreou, S.S. Lam, C. Ludlow-Palafox, H.A. Chase, *RSC Advances* 2  
921 (2012) 6756-6760.
- 922 [19] E. Udalov, V. Bolotov, Y. Tanashev, Y. Chernousov, V. Parmon, *Theoretical and*  
923 *Experimental Chemistry* 46 (2011) 384-392.
- 924 [20] A. Domínguez, J.A. Menéndez, M. Inguanzo, J.J. Pis, *Bioresource Technol.* 97 (2006)  
925 1185-1193.
- 926 [21] N. Muradov, F. Smith, A. T-Raissi, *Catal. Today* 102-103 (2005) 225-233.
- 927 [22] L.B. Avdeeva, T.V. Reshetenko, Z.R. Ismagilov, V.A. Likholobov, *Applied Catalysis*  
928 *A: General* 228 (2002) 53-63.
- 929 [23] J.A. Menéndez, A. Domínguez, Y. Fernández, J.J. Pis, *Energ. Fuel.* 21 (2007) 373-378.
- 930 [24] A. Domínguez, J.A. Menéndez, Y. Fernández, J.J. Pis, J.M.V. Nabais, P.J.M. Carrott,  
931 M.M.L.R. Carrott, *J. Anal. Appl. Pyrolysis* 79 (2007) 128-135.
- 932 [25] A. Domínguez, Y. Fernández, B. Fidalgo, J.J. Pis, J.A. Menéndez, *Chemosphere* 70  
933 (2008) 397-403.
- 934 [26] O. Arpa, R. Yumrutas, *Fuel Process. Technol.* 91 (2010) 197-204.
- 935 [27] A. Sinağ, S. Gülbay, B. Uskan, S. Uçar, S.B. Özgürler, *J. Hazard. Mater.* 173 (2010)  
936 420-426.
- 937 [28] G.-J. Song, Y.-C. Seo, D. Pudasainee, I.-T. Kim, *Waste Manage.* 30 (2010) 1230-1237.
- 938 [29] A. Lea-Langton, N. Giannakeas, G. Rickett, V. Dupont, M. Twigg, *SAE International*  
939 *Journal of Fuels and Lubricants* 3 (2010) 810-818.
- 940 [30] ASTM Standard E1131-08, Standard Test Method for Compositional Analysis by  
941 Thermogravimetry, ASTM International, West Conshohocken, PA, 2008.
- 942 [31] M.J. Lázaro, R. Moliner, C. Domeño, C. Nerín, *J. Anal. Appl. Pyrolysis* 57 (2001) 119-  
943 131.
- 944 [32] Q. Xie, P. Peng, S. Liu, M. Min, Y. Cheng, Y. Wan, Y. Li, X. Lin, Y. Liu, P. Chen, R.  
945 Ruan, *Bioresource Technol.* 172 (2014) 162-168.
- 946 [33] J.A. Menéndez, E.M. Menéndez, A. Garcia, J.B. Parra, J.J. Pis, *J. Microwave. Power.*  
947 *EE.* 34 (1999) 137-143.
- 948 [34] P.H. Blanco, C. Wu, J.A. Onwudili, P.T. Williams, *Applied Catalysis B: Environmental*  
949 134-135 (2013) 238-250.
- 950 [35] I.F. Elbaba, P.T. Williams, *Applied Catalysis B: Environmental* 125 (2012) 136-143.

- 951 [36] A. López, I. de Marco, B.M. Caballero, M.F. Laresgoiti, A. Adrados, A. Aranzabal,  
952 Applied Catalysis B: Environmental 104 (2011) 211-219.
- 953 [37] S. Brunauer, L. Deming, W. Deming, E. Teller, J. Am. Chem. Soc 62 (1940) 1723.
- 954 [38] Y. Shen, P. Zhao, Q. Shao, D. Ma, F. Takahashi, K. Yoshikawa, Applied Catalysis B:  
955 Environmental 152–153 (2014) 140-151.
- 956 [39] J.C. Acomb, C. Wu, P.T. Williams, Applied Catalysis B: Environmental 147 (2014)  
957 571-584.
- 958 [40] C. Wu, P.T. Williams, Applied Catalysis B: Environmental 90 (2009) 147-156.
- 959 [41] X. Zhang, D.O. Hayward, Inorg. Chim. Acta 359 (2006) 3421-3433.
- 960 [42] T. Karayildirim, J. Yanik, M. Yuksel, H. Bockhorn, Fuel 85 (2006) 1498-1508.
- 961 [43] J.A. Menéndez, A. Domínguez, M. Inguanzo, J.J. Pis, J. Anal. Appl. Pyrolysis 71 (2004)  
962 657-667.
- 963 [44] H.P. Kuo, S.M. Pan, H.T. Hsu, Biomass Bioenergy 35 (2011) 3025-3031.
- 964 [45] E.A. Dawson, G.M.B. Parkes, P.A. Barnes, G. Bond, R. Mao, Carbon 46 (2008) 220-  
965 228.
- 966 [46] A. Domínguez, B. Fidalgo, Y. Fernández, J.J. Pis, J.A. Menéndez, Int. J. Hydrog.  
967 Energy 32 (2007) 4792-4799.
- 968 [47] T.P. Wampler, Applied Pyrolysis Handbook, CRC Press, New York, 1995.
- 969 [48] M. Seeger, R.J. Gritter, Journal of Polymer Science: Polymer Chemistry Edition 15  
970 (1977) 1393-1402.
- 971 [49] R.W.J. Westerhout, J. Waanders, J.A.M. Kuipers, W.P.M. van Swaaij, Industrial &  
972 Engineering Chemistry Research 37 (1998) 2293-2300.
- 973 [50] J.A. Onwudili, N. Insura, P.T. Williams, J. Anal. Appl. Pyrolysis 86 (2009) 293-303.
- 974 [51] D.B. Miller, I&EC Product Research and Development 2 (1963) 220-223.
- 975 [52] S. Boxiong, W. Chunfei, G. Binbin, W. Rui, Liangcai, Applied Catalysis B:  
976 Environmental 73 (2007) 150-157.
- 977 [53] C. Wu, P.T. Williams, Applied Catalysis B: Environmental 96 (2010) 198-207.
- 978
- 979
- 980

981

## Appendix

---

982

983

### **Catalytic microwave pyrolysis of waste engine oil using**

984

### **metallic pyrolysis char**

985

Su Shiung Lam <sup>a,c,\*</sup>, Rock Keey Liew <sup>a</sup>, Chin Kui Cheng <sup>b</sup>, Howard A. Chase <sup>c</sup>

986

<sup>a</sup> Eastern Corridor Renewable Energy Group (ECRE), School of Ocean Engineering,

987

University Malaysia Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia

988

<sup>b</sup> Faculty of Chemical and Natural Resources Engineering, University Malaysia Pahang,

989

Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang, Malaysia

990

<sup>c</sup> Department of Chemical Engineering and Biotechnology, University of Cambridge,

991

New Museums Site, Pembroke Street, Cambridge CB2 3RA, United Kingdom

992

lam@umt.edu.my, lrklrk1991@gmail.com, chinkui@ump.edu.my, hac1000@cam.ac.uk

993

\* Corresponding author. Tel: +609 6683844; fax: +609 6683991; E-mail address:

994

lam@umt.edu.my, sushiung@gmail.com (S.S. Lam); Postal address: Eastern Corridor

995

Renewable Energy Group (ECRE), School of Ocean Engineering, University Malaysia

996

Terengganu, 21030 Kuala Terengganu, Terengganu, Malaysia.

997

## 998 **Appendix A. Temperature measurement and limitation**

999 The temperature of the carbon bed in the system was monitored using a thermocouple that  
1000 was ducted into the middle layer of the carbon bed through the center of the shaft that  
1001 protrudes from the bottom of the stainless steel stirrer shaft. The thermocouple probe is in  
1002 direct contact with both the samples and the carbon in the reactor during experiment, and the  
1003 temperature measured is logged for subsequent analysis. In addition, ferrite core  
1004 thermocouple connectors and cable clamps were used to reduce the electromagnetic  
1005 interference caused by the microwaves on the temperature measurement.

1006 Accurate measurement of the evolution of the temperature of the carbon bed was difficult  
1007 during the heating process - firstly, there are inherent difficulties involved in measuring this  
1008 parameter in microwave devices [1]; secondly, it should be noted that the temperature is not  
1009 uniform throughout the carbon bed during the initial heating to the target temperature;  
1010 electrical arcing was found to occur for a relatively short period at the beginning of the  
1011 heating process, but it stopped when the carbon bed had been heated to the target  
1012 temperature. A stirred bed reactor is used in this study in which the physical movement and  
1013 mixing of carbon particles by the stirring system creates a uniform temperature distribution,  
1014 independent of the penetration depth of the microwaves into the bed of particulate-carbon.  
1015 Provided the temperature is kept consistent and uniform in this system, once the thermal  
1016 equilibration and steady state temperature were reached, the temperature shown by the  
1017 thermocouples are assumed to give a reliable reading of the average temperature of the bulk  
1018 carbon bed.

1019 [1] Menéndez JA, Menéndez EM, Garcia A, Parra JB, Pis JJ. Thermal treatment of active  
1020 carbons: a comparison between microwave and electrical heating. *J Microwave Power EE*  
1021 *1999;34:137-43.*  
1022

1023

1024 **Appendix B. Elemental analysis**

1025 Samples were analyzed on a dry or moisture-free basis by pre-heating at 200°C to remove  
1026 any moisture (residual water) and other remaining low boiling point compounds. They were  
1027 then burned at 1000°C in a flowing stream of oxygen. The products of combustion (CO<sub>2</sub>,  
1028 H<sub>2</sub>O, N<sub>2</sub> and SO<sub>2</sub>) then passed through the system with He as the carrier gas, and their content  
1029 of carbon, hydrogen, and sulphur were measured quantitatively by selective IR absorption  
1030 detectors, except for the nitrogen, which was measured by a thermal conductivity detector.  
1031 Oxygen content was measured by pyrolyzing a separate sample at 1300°C in a VTF-900  
1032 pyrolysis furnace (LECO Corporation, Michigan, USA). The oxygen released in the pyrolysis  
1033 reaction then reacted with activated charcoal to form CO, which was converted to CO<sub>2</sub> by  
1034 passing through an oxidation tube with He as the carrier gas. The CO<sub>2</sub> generated was then  
1035 measured as above by an IR detector.

1036

1037 **Appendix C. Thermogravimetric analysis**

1038 The sample (~20 mg) was heated from ambient temperature to 600 °C at a heating rate of  
1039 25 °C/min with high purity N<sub>2</sub> as the carrier gas, which then switched to O<sub>2</sub> gas and the  
1040 thermo balance was ramped to 950 °C with a final holding time of 20 min; the carrier gases  
1041 were vented through the apparatus at a flow rate of 0.1 L/min. The fraction decomposed  
1042 between 100 and 600 °C refers to the volatile matter content of the sample, and fixed carbon  
1043 refers to the fraction between 600 and 900 °C, and the fraction above 900 °C refers to the ash  
1044 content of the sample.

1045