



Catalytic microwave pyrolysis of waste engine oil using metallic pyrolysis char



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ARTICLE INFO

Article history:

Received 8 December 2013
Received in revised form 6 April 2015
Accepted 7 April 2015
Available online 9 April 2015

Keywords:

Pyrolysis
Char
Catalyst
Waste
Oil

ABSTRACT

Microwave pyrolysis was performed on waste engine oil pre-mixed with different amounts of metallic-char catalyst produced previously from a similar microwave pyrolysis process. The metallic-char catalyst was first prepared by pretreatment with calcination followed by analyses to determine its various properties. The heating characteristics of the mixture of waste oil and metallic-char during the pyrolysis were investigated, and the catalytic influence of the metallic-char on the yield and characteristics of the pyrolysis products are discussed with emphasis on the composition of oil and gaseous products. The metallic-char, detected to have a porous structure and high surface area (124 m²/g), showed high thermal stability in a N₂ atmosphere and it was also found to have phases of metals and metal oxides attached or adsorbed onto the char, representing a potentially suitable catalyst to be used in pyrolysis cracking process. The metallic-char initially acted as an adsorptive-support to adsorb metals, metal oxides and waste oil. Then, the char became a microwave absorbent that absorbed microwave energy and heated up to a high temperature in a short time and it was found to generate arcing and sparks during microwave pyrolysis of the waste oil, resulting in the formation of hot spots (high temperature sites with temperature up to 650 °C) within the reactor under the influence of microwave heating. The presence of this high temperature metallic-char, the amounts of which are likely to increase when increasing amounts of metallic-char were added to the waste oil (5, 10, and 20 wt% of the amount of waste oil added to the reactor), had provided a reducing chemical environment in which the metallic-char acted as an intermediate reductant to reduce the adsorbed metals or metal oxides into metallic states, which then functioned as a catalyst to provide more reaction sites that enhanced the cracking and heterogeneous reactions that occurred during the pyrolysis to convert the waste oil to produce higher yields of light hydrocarbons, H₂ and CO gases in the pyrolysis products, recording a yield of up to 74 wt% of light C₅–C₁₀ hydrocarbons and 42 vol% of H₂ and CO gases. The catalytic microwave pyrolysis produced 65–85 wt% yield of pyrolysis-oil containing C₅–C₂₀ hydrocarbons that can potentially be upgraded to produce transport-grade fuels. In addition, the recovered pyrolysis-gases (up to 33 wt%) were dominated by aliphatic hydrocarbons (up to 78 vol% of C₁–C₆ hydrocarbons) and significant amounts of valuable syngas (up to 42 vol% of H₂ and CO in total) with low heating values (LHV) ranging from 4.7 to 5.5 MJ/m³, indicating that the pyrolysis-gases could also be used as a gaseous fuel or upgraded to produce more hydrogen as a second-generation fuel. The results indicate that the metallic-char shows advantages for use as a catalyst in microwave pyrolysis treatment of problematic waste oils.

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1. Introduction

Waste engine oil is an environmentally hazardous waste that is difficult to dispose off due to the presence of undesirable species, such as soot and metals. On a global basis, nearly 24 million metric tons (Mt) of the waste oil are generated each year [1]. In particular, nearly 7.6 Mt are produced in the United States in addition

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to the approximately 2.2 Mt produced in the European Union [2]. Existing treatment processes, such as incineration, combustion, and catalytic hydro-treatment, are becoming increasingly impracticable due to concerns of environmental pollution and the difficulties of disposing of the sludge generated by these processes [3,4].

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

The main processes occurring during microwave pyrolysis of waste oil have been described in previous works [8,9] and can be summarized in Fig. 1. During the pyrolysis process, the waste oil ($\approx C_{40}$ hydrocarbons) is pyrolyzed through a primary pyrolysis stage in which the waste oil undergoes primary cracking and transforms into pyrolysis volatiles formed by a mixture of hydrocarbon gases and liquid oils existing in a vapor phase. The pyrolysis volatiles are generated from the primary cracking of waste oil that proceeds via a free-radical-induced random scission mechanism as predicted by Rice's theory [10–12], consisting of permanent gas species (e.g., H_2 , CO, CO_2), non-condensable gaseous hydrocarbons (C_1 – C_4 hydrocarbons), and condensable light hydrocarbons ($\approx C_{25}$ hydrocarbons). The pyrolysis volatiles then undergo a **secondary** pyrolysis stage whereby serial and parallel secondary reactions could occur and this results in the formation of products consisting of even lighter condensable hydrocarbons ($\approx C_6$ – C_{18} hydrocarbons) collected as liquid hydrocarbon oil) and higher amounts of non-

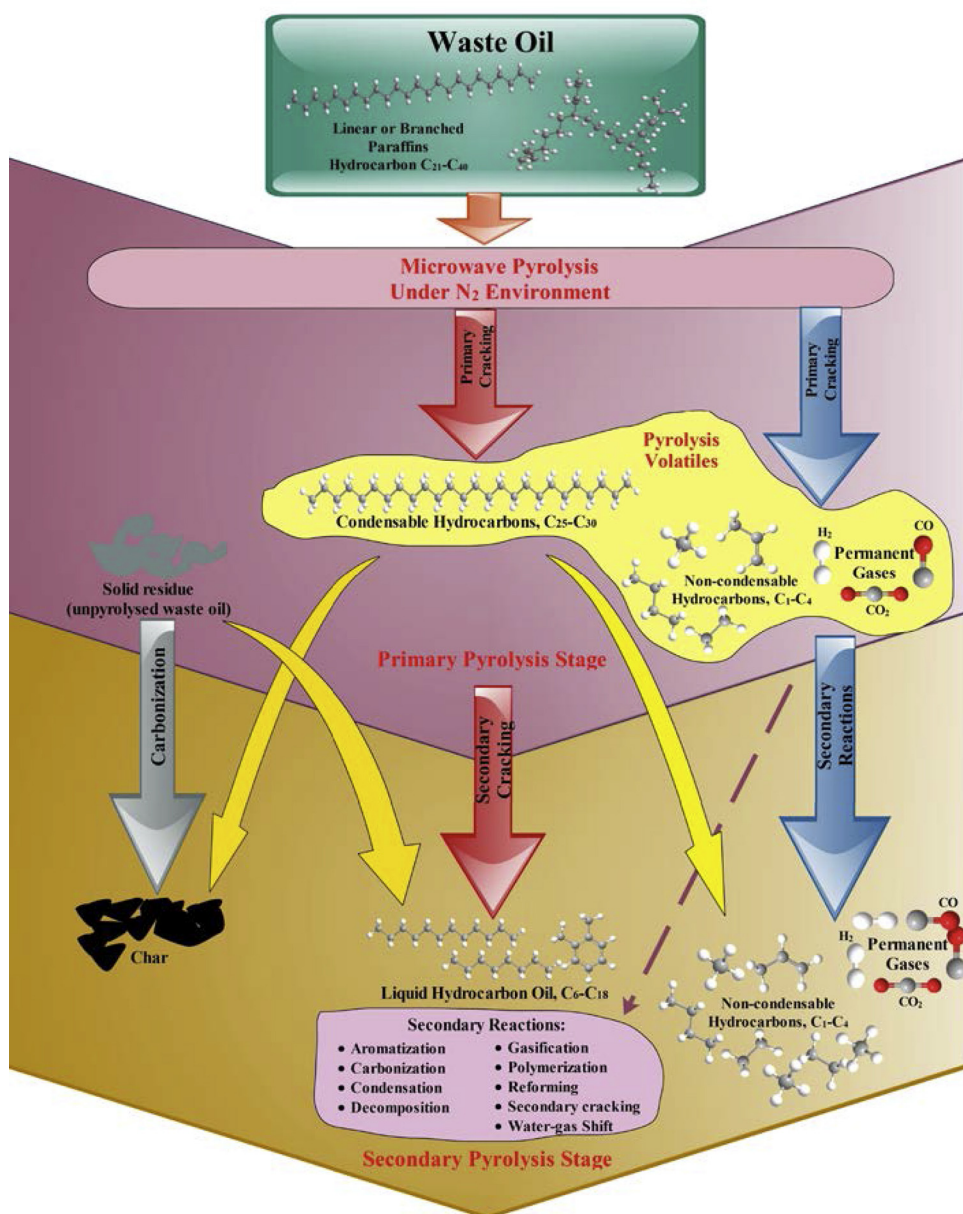


Fig. 1. Main processes occurring during microwave pyrolysis of waste oil: primary pyrolysis consisting of primary cracking, and secondary pyrolysis consisting of serial and parallel secondary reactions occurring either homogeneously or heterogeneously.

condensable gaseous hydrocarbons (C₁–C₄ hydrocarbons), and permanent gas species (e.g. H₂, CO, CO₂) in addition to the production of a char product. Homogenous or heterogeneous secondary reactions could occur such as secondary cracking, aromatization, reforming, deoxygenation, dehydrogenation, condensation, and carbonization [8] (Fig. 1).

The use of microwave radiation as a heat source is known to offer additional advantages over traditional thermal heat sources [13,14], and the combination of carbon-based material and the novel use of microwave heating in pyrolysis processes is of increasing interest as reflected by considerable recent research reported in the literature [15–18]. Microwave systems show a distinct advantage in providing a rapid, energy-efficient, and targeted heating process compared to conventional technologies, thus facilitating increased production rates and decreased production costs. Moreover, thermal energy is targeted only to microwave receptive materials and not to gases within the heating chamber or to the chamber itself. It can promote certain chemical reactions by selectively heating the reactants, leading to a more uniform temperature profile and improved yield of desirable products [16,19].

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

It can also be inferred that if the microwave pyrolysis is to be performed in a continuous operation over a long period of time, the amount of the char product trapped within the particulate-carbon bed in the reactor would increase as a result of the prolonged period of operation. The presence of increasing amounts of this char is likely to have an influence on the product distribution in this pyrolysis process. This carbonaceous char, likely to contain involatile metals originally present in waste oil, could act as a microwave-absorbent and heat up by microwave radiation, and in turn pyrolyze the waste oil added into the reactor. It could also promote certain heterogeneous reactions by heating the pyrolysis-volatiles evolved from the pyrolysis of waste oil, leading to a different product composition observed in the pyrolysis products. It has been reported that the metal-containing char product could potentially be used as an inorganic catalyst in thermal cracking processes [20]; the presence of some metals (e.g., Fe, Ni) in the char could have a catalytic effect on some of the heterogeneous reactions (e.g., methane decomposition reaction) that occurred as have been reported by others in pyrolysis studies of other materials [19,21,22]. In addition, the use of char produced from pyrolysis processes as a catalyst has recently shown advantages in transforming biomass materials (e.g., sewage sludge, coffee hulls) into valuable gases such as H₂ and syngas in microwave pyrolysis process [16,23–25]; the waste materials were mixed with small amounts of the char and subjected to pyrolysis treatment.

In this study, microwave pyrolysis using a reactor bed of particulate-carbon was performed on waste oil in the additional presence of different amounts of metallic-char produced previously from the pyrolysis process as the catalyst in order to understand the influence of the chemical nature and amount of the metallic-char on the yield of pyrolysis products and with an emphasis on the chemical composition of the oil and gaseous products. The metallic-char catalyst was pre-treated by calcination and characterized by

Table 1
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	C ₇ –C ₄₁
Aromatics	1.2
Others ^a	7.5

^a Unknown compounds due to unidentified peaks.

different analytical methods before and after being subjected to pyrolysis. In addition, a study was performed to examine the heating characteristics of the mixture of waste oil and metallic-char in the presence of a microwave-heated bed of particulate-carbon through monitoring its temperature profile during the pyrolysis. These evaluations are important to examine if the metallic-char could act as a microwave-absorbent and heat up by microwave radiation, and if the metallic-char could be used as a catalyst in the pyrolysis of waste oil. Most existing waste oil pyrolysis studies focus on conventional electric-resistance-heated and electric-arc-heated pyrolysis [26–28], and there are very few studies about the pyrolysis products generated from microwave pyrolysis of waste oil, and in particular no similar studies have been reported on the application of metallic-char as a catalyst in microwave pyrolysis of waste oil; this study aims to rectify these deficiencies.

2. Experimental

2.1. Materials

Shell 10W-40 motor oil was used throughout the experiments. The waste oil was sampled from the crankcase of diesel engines run on unleaded fuel. Before pyrolysis, the oil samples were filtered such that the size of any remaining particulates (i.e. metal particles, carbon soot, and other impurities) was less than 100 μm. The oil samples were then examined for hydrocarbon composition by gas chromatography-mass spectrometry (GC-MS), metal composition by atomic-absorption spectrometry (AAS), phosphorus content by X-ray Fluorescence (XRF) analyzer, and sulfur content by elemental analysis. The GC-MS analysis (Table 1) revealed that the waste oil is formed from a mixture of low and high molecular weight aliphatic and aromatic hydrocarbons, and the majority of the hydrocarbon compounds were detected in the range of C₇–C₄₁. Phosphorus and sulfur were detected in very low concentrations (phosphorus: <0.1 wt%; sulfur: <0.8 wt%); the sulfur content of the waste oil has been reported and discussed in previous work [7]. The low concentrations of sulfur and phosphorus could be explained by the removal of some oil additives containing sulfur and phosphorus during the pre-filtration treatment of the waste oil, and also possibly due to the transport of some additives into the vehicle exhaust system during engine operation [29].

Particulate-carbon (TIMREX FC250 Coke, TIMCAL Ltd Bodio, Switzerland) with a particle size ranging from 90 to 250 μm was used as a microwave-absorbent to heat the waste oil. The specifica-

Table 2
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%
sulfur	1.3 wt%
Sieve size	<250 μm (2% >250 μm, 75% >125 μm, 85% >90 μm)
Density	0.80–0.91 g/cm ³

tions of the carbon are presented in Table 2. The particulate-carbon was pre-heated to 800 °C for 50 min to remove any water and sulfur-containing compounds. The sulfur content of the particulate-carbon was vaporized as sulfur-containing gases (e.g., H₂S, SO_x), which were then passed through a closed chamber filled with activated carbon that acted as a sorbent to clean and retain sulfur from the gas streams. The pre-heated carbon was then analyzed for its sulfur content by elemental analysis and that analysis showed that the sulfur content had been reduced to ≤0.05 wt% after the heat treatment at 800 °C.

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

Particles of metallic-char were obtained from the previous pyrolysis of waste oil at 550 °C. These chars with a particle size of <30 μm were separated from the particulate-carbon particles (90–250 μm in size) that formed the bed that was used to conduct the pyrolysis using sieves. Then, the char with a particle size ranging

from 20–30 μm was separated from this previously sieved batch of chars (<30 μm in size) using a narrow-range sieve, and used for this study. The metallic-char was calcined at 600 °C in air atmosphere for 1 h and then stored in a desiccator until further use as a catalyst. The preparation of the metallic-char for use as a catalyst is briefly summarized in Fig. 2. The metallic-char was then examined for use as a microwave-absorbent to heat the waste oil and also tested as a catalyst in the microwave pyrolysis treatment of waste oil.

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

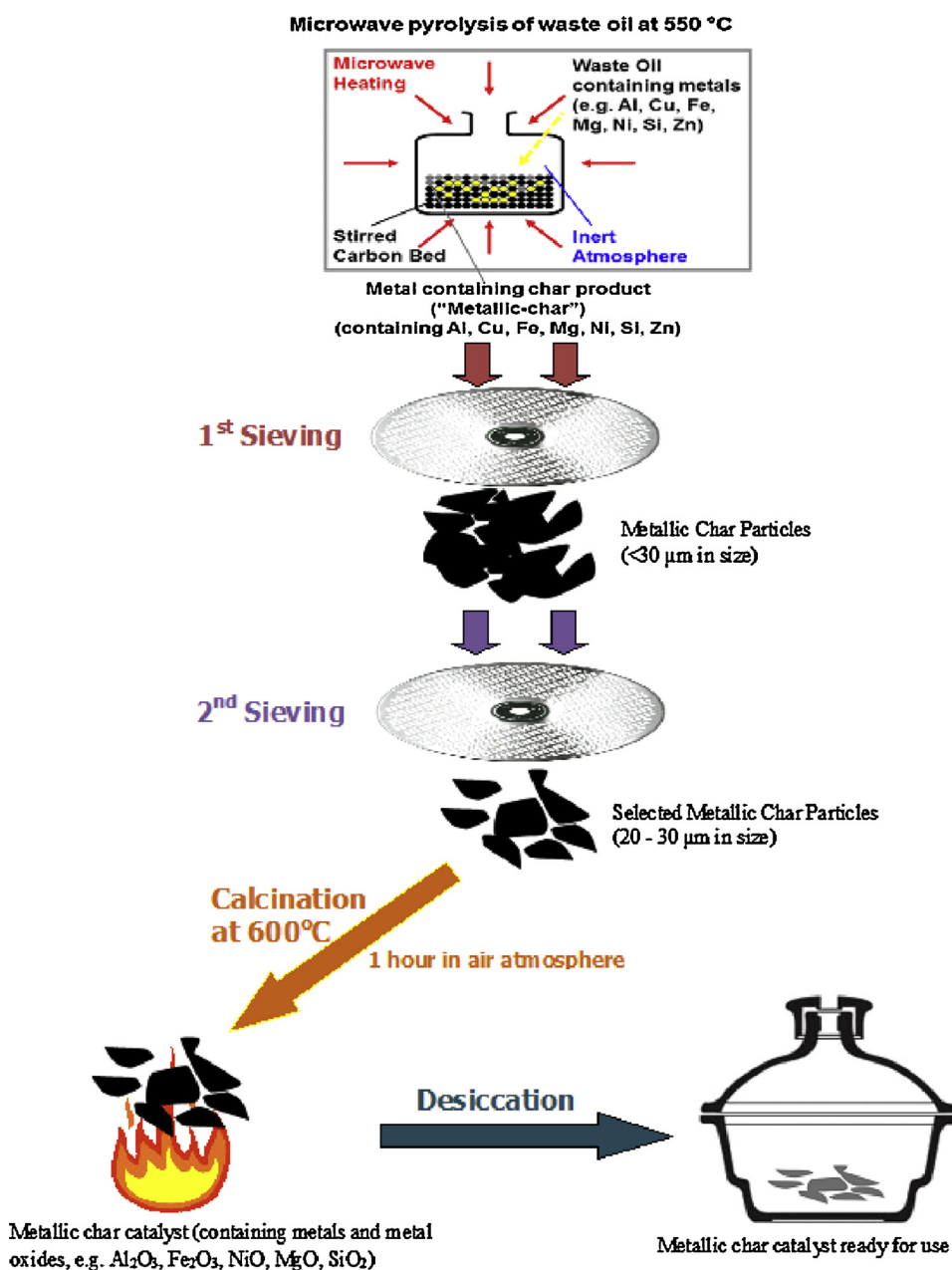


Fig. 2. Preparation of metallic pyrolysis char for use as a catalyst.

X-ray diffraction (XRD) analyses using a X-Ray diffractometer (Rigaku Corporation, Japan) were also performed on the catalyst before and after being subjected to pyrolysis to investigate its chemical composition. SEM/EDX was also performed on both the fresh and used catalyst to investigate the size, morphology, presence of metals, and coke deposition on the particles present in the catalyst. In addition, TGA was performed on the catalyst in an N₂ atmosphere to evaluate its thermal stability, whereas temperature programmed oxidation (TPO) was performed on the used catalyst in an air atmosphere to investigate the reactivity of the used catalyst with oxygen and also the oxidation of coked carbons deposited on the surface of the used catalyst; these analyses were performed using a Q500 thermogravimetric analyzer (TA Instruments UK Ltd., Crawley, West Sussex) in which the catalyst sample (~20 mg) was heated from ambient temperature to a final temperature at 950 °C at a heating rate of 15 °C/min with a final holding time of 15 min.

2.2. Experimental details

The experimental apparatus and method developed for this investigation have been described in detail in previous work [6,8]. The only change from this description is the addition of a Type-K metallic thermocouple to measure the evolution of the temperature of the gases and pyrolysis-volatiles (evolved from the waste oil being pyrolyzed) present in the vapor zone before they are driven out of the reactor into the product collection system by the N₂ purge gas. The thermocouple enters the reaction chamber through a side port on the top of the reactor and is positioned in the space above the carbon bed. In addition, a thermocouple was used to monitor the temperature of the carbon load in the system; temperature measurement in the reactor and its limitations are not the main focus of this paper and thus are presented in (Appendix A).

In outline, microwave pyrolysis was performed in a bell-shaped quartz reactor on waste oil pre-mixed with small amounts of the metallic-char catalyst. The reactor was initially filled with 1 kg of particulate-carbon as the reaction bed, which was then heated to 550 °C by microwave radiation (1). The particulate-carbon, added initially into the reactor in one batch, was stirred (3) to ensure a uniform temperature distribution throughout the reactor and to maximize heat transfer during pyrolysis. N₂ purge-gas at a flow rate of 0.25 L/min was vented through the system to maintain the apparatus in an inert atmosphere. The microwave generator was initially turned on to heat the carbon bed to the target pyrolysis temperature of 550 °C; the oven was then left for 5 min to ensure complete thermal equilibrium. The waste oil was blended with different amounts of metallic-char (5, 10, and 20 wt% of the amount of waste oil added to the reactor, i.e., 5, 10, and 20 g of metallic-char/100 g of waste oil) to create a waste oil-char mixture, which was then continuously added to the reactor (4) at a constant feeding rate of 1 kg/h when the temperature of the carbon bed had reached 550 °C. Products generated during pyrolysis, termed generally as pyrolysis volatiles (consisting of a mixture of hydrocarbon gases, liquids, and suspended solids existing in a vapor phase), leave the reactor and pass through a condensation system (6–9). The heavier volatiles are condensed into pyrolysis-oil (10, 11), and the lighter volatiles are collected as incondensable pyrolysis-gases (13, 14), which can be sampled before being vented from the system. The same procedure was repeated with the particulate-carbon as a control and all these results were compared to the microwave pyrolysis experiments performed on waste oil in the presence of only the particulate-carbon bed in the reactor. All the pyrolysis experiments were performed under ambient atmospheric pressure.

The amount of additional residue material not converted to gaseous or liquid products (both of which leave the reactor) was determined by measurement of the weight change in the reactor and its contents before and after pyrolysis. The residue materials

are likely to be chars produced from tertiary cracking reactions of the pyrolysis process [5]. The char particles in the reactor consisted of the char residues (i.e., the new char produced in this round of pyrolysis, termed generally as “char product”) together with the metallic-char catalyst added in combination with the waste oil into the reactor. These char particles mostly accumulated on the surface of the carbon bed and they were separated from the particulate-carbon particles (90–250 μm in size) using 90 and 250 μm sieves. Then, the new char product, consisting of char particles with the majority of particles present being ≤10 μm, was separated from the original pyrolysis-char (20–30 μm in size) using a 20 μm sieve. It should be noted that the new char product contained a relatively small amount of char particles larger than 10 μm but these larger char particles could not be analyzed due to the limitations involved in separating them from 20 to 30 μm metallic-char that had been added in combination with the waste oil into the reactor.

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

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

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

2.3. Analytical methods

Oil samples were analyzed using a 6890/5973 GC-MS instrument (Agilent Technologies, Palo Alto, CA), allowing the quantification of compounds by both species and size; the detailed description of this analytical method has been reported in previous work [5,7]. Gases such as H₂, CH₄, CO, CO₂, were analyzed using a Varian 3380 gas chromatograph (Varian Inc., Palo Alto, CA) fitted with two thermal conductivity detectors (GC-TCD), whereas gaseous hydrocarbons from C₁ to C₄ were analyzed using a 6890 GC (Agilent Technologies, Palo Alto, CA) coupled with a flame ionization detector (GC-FID); the detailed description of these analytical methods have been reported in previous work [8]. Compounds were identified using the NIST 2005 mass spectral library using

similarity indices of >70%, or by comparison with published GC–MS data for similar products, and quantification of compounds was obtained by external standard method and relative retention times once the component has been identified.

Elemental analyses of solid samples were performed using a LECO CHNS-932 elemental analyzer (LECO Corporation, Michigan, USA); the detailed description of this analytical method is presented in (Appendix B). TGA analysis of solid samples was performed using a Q500 Thermogravimetric Analyzer (TA Instruments UK Ltd., Crawley, West Sussex), allowing the proximate quantification of moisture, volatile matter, fixed carbon, and ash content of compounds. Detailed analysis (Appendix C) was performed according to ASTM Standard E1131-08 [30]. The oil and solid samples were also analyzed using a Varian Spectr AAS instrument; the detailed description of this analytical method, and the sample preparation, has been reported in previous work [6]. Experimental analysis of each metal was performed according to Lázaro et al. [31] and the standard working conditions specified in the Varian AAS instruction manual for metal determination. The samples were analyzed for their content of Al, As, Ba, Ca, Cd, Cu, Cr, Fe, Mg, Mo, Ni, Pb, Si, V and Zn.

ASA analysis of the solid samples was performed using a Micromeritics ASAP 2010 Automatic Sorption Analyzer (Micromeritics UK Ltd., Dunstable, Bedfordshire) to characterize their porous structure and to determine their surface area. 90 mg of sample was degassed at 120 °C for 2 h prior to analysis. Then, the sample was exposed to varying pressures of N₂ gas at a temperature of 77 K, and the volume of N₂ adsorbed onto the sample's surface at different pressures was recorded. The data were used to plot the N₂ adsorption and desorption isotherms that allow

the characterization of porous structure and calculation of surface area of the sample using the Multipoint Brunauer, Emmett, and Teller (BET) equation [32,33]. External surface area and micropore volume were calculated based on the *t*-plot method, and the total pore volume was determined at *P/P*₀ of 0.99.

3. Results and discussion

Microwave pyrolysis of waste oil was performed in order to convert the waste oil into potentially valuable products suitable for use as a fuel. The pyrolysis was performed in a continuous operation using the apparatus described, which is fitted with magnetrons capable of delivering 5 kW of microwave power and capable of sustaining a waste oil feed rate of 5 kg/h with a positive energy ratio of 11 (energy content of hydrocarbon products/ electrical energy supplied for microwave heating) and a net energy output of 170 MJ/h.

3.1. Characteristics of metallic-char catalyst

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

The results from elemental analysis show that carbon (~86 wt%) and oxygen (9 wt%) represented the main elements present in the metallic-char, whereas hydrogen (4 wt%), nitrogen (0.2 wt%), and sulfur (0.5 wt%) were detected in very low concentrations. The

Table 3
Characteristics of the metallic-char and metallic-ash.

	Metallic-char ^a		Metallic-ash ^b	
Elemental composition (wt%)				
C		86.3		n.p. ^c
H		4		n.p.
N		0.2		n.p.
S		0.5		n.p.
O		9		n.p.
Proximate composition (wt%)				
Moisture		– ^d		–
Volatile matter		5		2
Fixed carbon		85		4
Ash		10		94
Particle size		20–30 μm		n.p.
Surface area		124 m ² /g		n.p.
External surface area (m ² /g)		28		n.p.
Micropore area (m ² /g)		97		n.p.
Micropore volume (cm ³ /g)		0.065		n.p.
Total pore volume (cm ³ /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 ₂	5.2		MgO	15.1
Al ₂ O ₃	4.3		ZnO	16.7
Fe ₂ O ₃	7.3		CuO	1.1
CaO	21.0		NiO	3.2
K ₂ O	0.3		PbO	0.3
Na ₂ O	0.5			

^a Obtained from microwave pyrolysis of waste oil at 550 °C followed by calcination at 600 °C in air atmosphere for 1 h.

^b Ash collected from heating the metallic-char at 950 °C in air atmosphere for 20 min.

^c n.p.– Analysis not performed.

^d Not detectable.

detection of oxygen in the metallic-char indicates that char oxidation had occurred to some extent to form possibly metal oxides during the preparation of the metallic-char for use as a catalyst by calcination the char at 600 °C in air for 1 h (see Section 2.1.1, Fig. 2).

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

The metallic-ash was further analyzed and examined for its chemical composition by proximate and XRF analysis. As expected, ash represented the main elements (94 wt%) present in the metallic-ash as demonstrated by proximate analysis, whereas volatile matter and fixed carbon were detected in very low concentrations (2 wt% and 4 wt%, respectively). XRF analysis revealed that the metallic-char contained metal oxides comprising mainly of CaO, ZnO, MgO, Fe₂O₃, SiO₂, Al₂O₃, and NiO. The detection of these metal oxides suggests that some of the metals originally attached or adsorbed onto the metallic-char were likely to have reacted with oxygen to form metal oxides that were retained within the metallic-char during the preparation of the metallic-char as a catalyst by calcination.

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

Fig. 3 shows the N₂ adsorption and desorption isotherms plotted from the volume of N₂ adsorbed onto the surface of metallic-char and particulate-carbon at different pressures of N₂ gas. The adsorption–desorption isotherm obtained for the metallic-char indicates a combination between the isotherms of Type I and Type IV according to the classification of adsorption isotherms by International Union of Pure and Applied Chemistry (IUPAC) and Brunauer, Deming, Deming, and Teller (BDDT system) [37]. The plot at lower relative pressures ($P_i/P_o \leq 0.5$) shows a Type I adsorption isotherm indicative of a microporous structure whereas the plot at higher relative pressures ($P_i/P_o > 0.5$) indicates a Type IV adsorption isotherm in which capillary or pore condensation occurred and this generated a hysteresis loop indicating the presence of mesoporosity. These observations suggest that the metallic-char had both microporous and mesoporous structure; porous solid is classified as microporous with a pore size of up to 2 nm and mesoporous with a pore size of 2–50 nm by IUPAC.

The metallic-char showed a type H1 hysteresis loop according to the classification of hysteresis loops by IUPAC as indicated by adsorption and desorption branches that are nearly vertical and parallel, indicating the presence of a porous structure

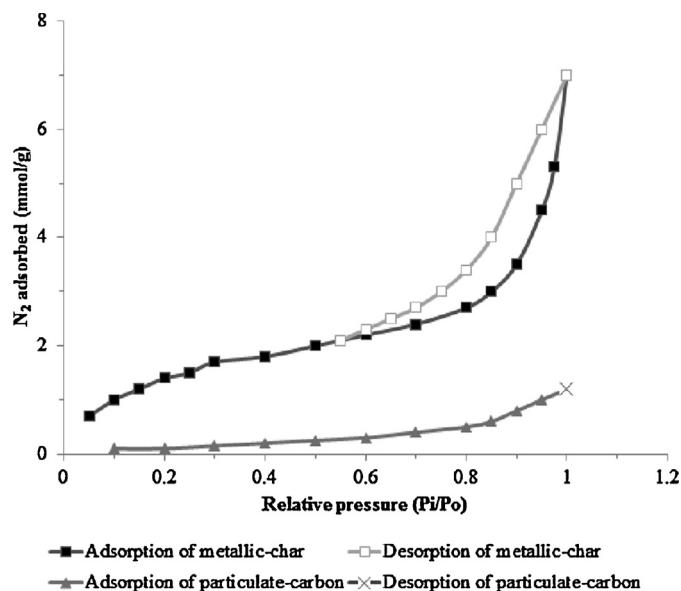


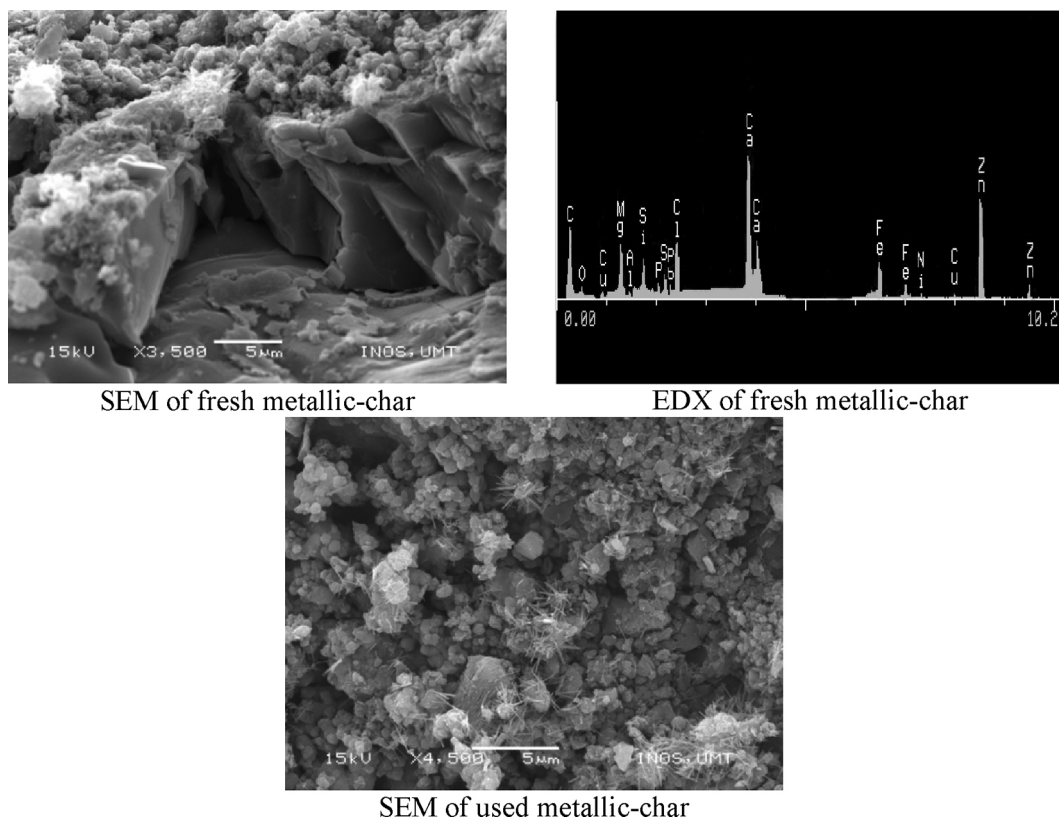
Fig. 3. N₂ adsorption and desorption isotherms of metallic-char and particulate-carbon.

containing relatively uniform cylindrical pores with a narrow distribution of pore size. The presence of type H1 hysteresis loop is also indicative of both delayed condensation and little hold-up of percolation, showing a characteristic of good adsorption capacity by the metallic-char, particularly for adsorbing metal ions [38]. The data from the N₂ adsorption and desorption isotherms were calculated for determination of the surface area and the metallic-char was found to have a surface area of 124 m²/g, the majority of which was comprised of micropores (97 m²/g), and a micropore volume of 0.065 cm³/g, indicating that this char had a relatively high internal porosity (Table 3). These results support the highly porous structure with many cavities observed in the SEM/EDX scans of the metallic-char (Fig. 4).

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

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

Fig. 4 presents the SEM-micrograph and EDX-spectrum of the fresh metallic-char. The SEM/EDX scans demonstrated that the metallic-char had a porous structure nearly comparable to activated char with most of the particles having a nearly spherical shape. The presence of highly porous structure indicates that the metallic-char can be a suitable candidate for use as a catalyst support or adsorbent as has been reported by Y. Shen et al. [38]. Cavities and particles having a particle size of about 1–5 μm were found distributed over the metallic-char, indicating the presence of a porous network with a high surface area. The small particles were likely to



SEM of fresh metallic-char

EDX of fresh metallic-char

SEM of used metallic-char

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

be formed by smaller char and metallic particles either attached or adsorbed onto the metallic-char.

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

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

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

The metallic-char was analyzed by XRD to investigate the presence and change of crystalline phases on the metallic-char structure before and after pyrolysis. Fig. 5 shows the XRD plots of the fresh and used metallic-char from microwave pyrolysis experiments performed on waste oil. The XRD of the fresh metallic-char showed the presence of metal phases containing Al, Ca, Fe, Mg, Ni, Si, and Zn, and also phases of metal oxides comprising SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , ZnO , and NiO . Although other metals (e.g., Cd, Cu, Pb) and metal oxides (e.g., K_2O , Na_2O , CuO , PbO) were detected in the metallic-char by XRF and AAS analyses, their peaks were not detectable by XRD analysis, probably due to their low concentrations in the metallic-char (Table 3).

For used metallic-char, lower peaks were observed for the metal oxides and relatively higher peaks identified as Al, Fe, Mg, Zn, and Ni phase were detected compared to those observed in the

fresh metallic-char (Fig. 5). This suggests that some of the metal oxides (originally attached to the metallic-char) had been reduced to form their metal elements through the reductive and heterogeneous reactions (e.g., steam reforming) that occurred between the waste oil (or the evolved pyrolysis-volatiles) and the carbon and metal oxides in the metallic-char during the pyrolysis at a high temperature of 550°C . It was likely that the metallic-char, being a carbonaceous material that can be heated and transformed into a high temperature site under the influence of microwave heating, had provided a reducing chemical environment in which the metallic-char acted as an intermediate reductant to reduce the adsorbed metal oxides into its metallic states ((R10), (R11); see Section 3.5). In addition, sintering of metal particles such as Ni could occur as a result of the high temperature provided under the microwave pyrolysis condition [39].

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

The metallic-char before pyrolysis was analyzed by TGA as an evaluation of its thermal stability under pyrolysis environment in an N_2 atmosphere, and the resulting plot is presented in Fig. 6. It was revealed that the metallic-char showed high thermal stability in a N_2 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_2 atmosphere.

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

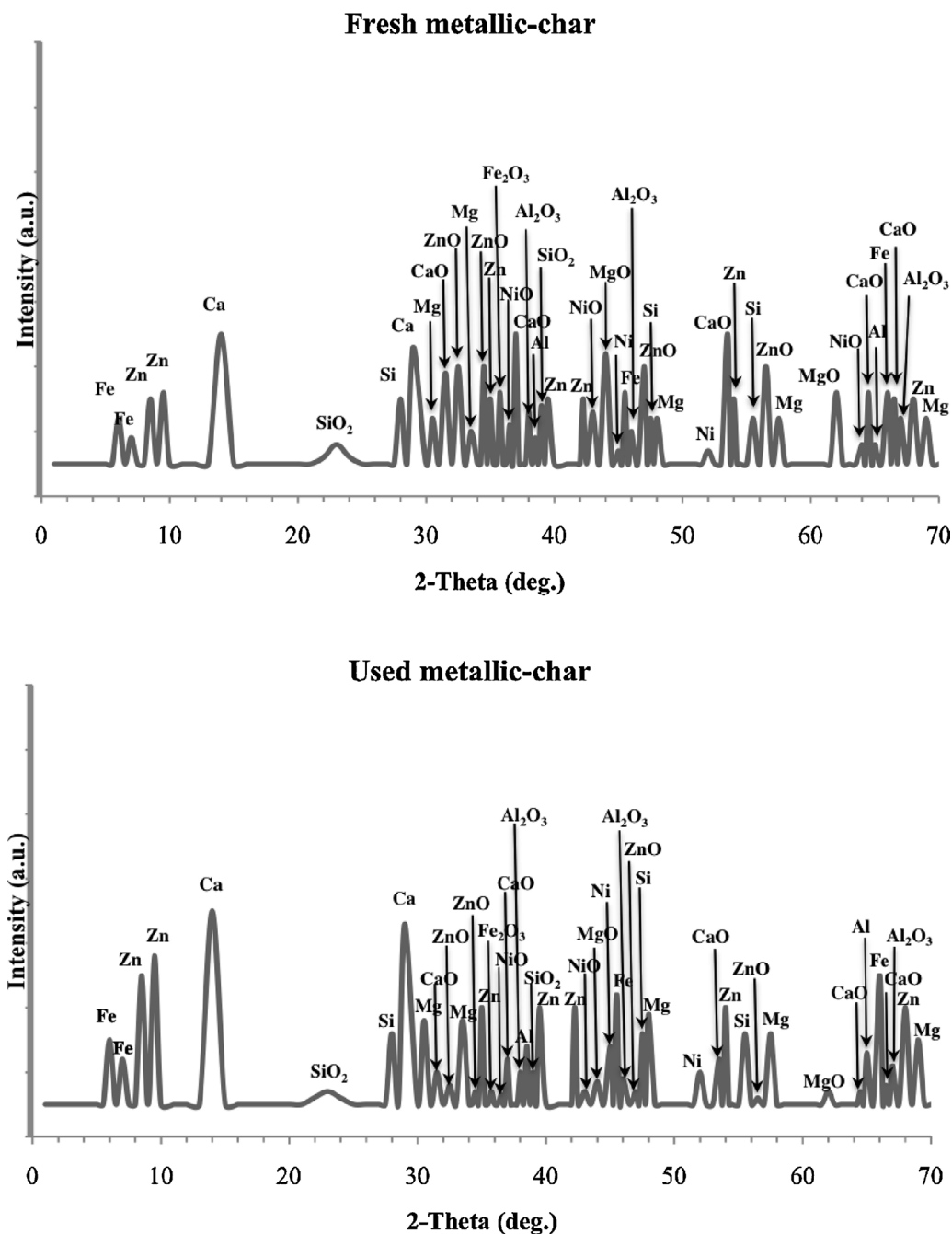


Fig. 5. XRD analysis of fresh and used metallic-char.

200 °C, which was likely due to the evaporation of water present in the char. The weight of the char then increased slightly for about 9% from 200 to 400 °C, which could possibly be attributed to the oxidation of metallic elements present in the used char (see Fig. 5 for the metallic phase observed in the used metallic-char from XRD analysis), e.g., oxidation of metallic Ni as has been reported by Wu and Williams [40]. After 400 °C, the used metallic-char showed a reduction in weight for about 13% when it was heated to 560 °C, and the weight remained at about 90% until 600 °C. The reduction in weight between 400 °C and 600 °C could be explained by the oxidation of the coke carbons deposited on the used metallic-char. This result is in agreement with the findings of other workers in which the authors have reported that the oxidation or combustion of carbon deposited on the surface of a catalyst normally happens at temperatures between 400 and 600 °C [34,35]. The metallic-char

then showed a dramatic reduction of about 80% of weight when it was heated from 600 to 900 °C in air, and the weight remained at 10% through the remaining heating period. The dramatic reduction of weight at this temperature range suggests that the fixed carbon originally present in the metallic-char (Table 3) was likely to have reacted with the oxygen present in the air to form carbon oxides at temperature above 600 °C. It can also be inferred from these results that a temperature of 600 °C can be selected for thermal regeneration of the metallic-char in order to extend its service life since this temperature represents the optimum balance between sufficiently high temperature needed to remove the coked carbon deposited on the used metallic-char, while not being so high as to promoting the oxidation of the fixed carbon in the metallic-char that would result in weight reduction of the char.

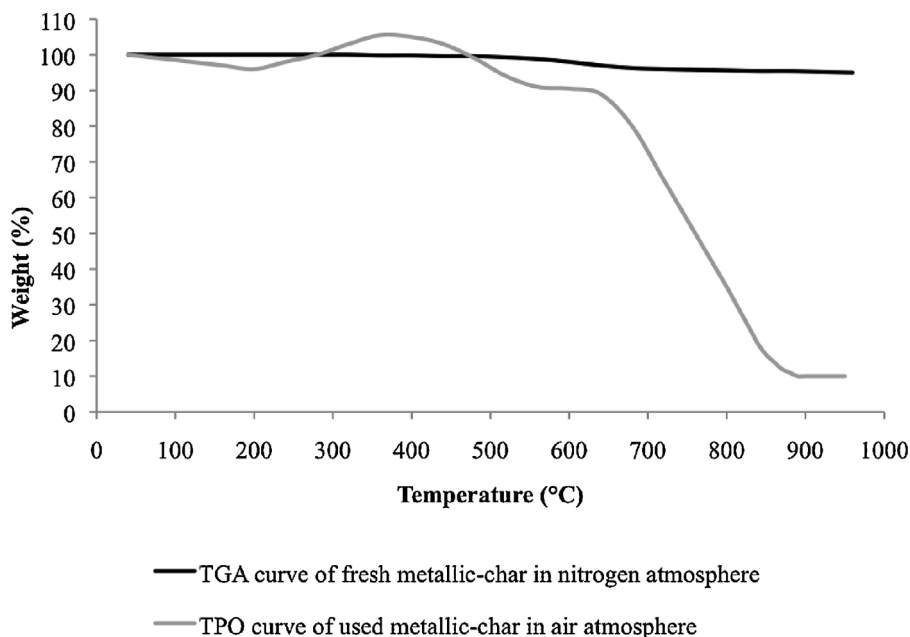


Fig. 6. TGA and TPO analysis of metallic-char.

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

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

The waste oil-char mixture (80:20 wt%) was continuously added to the reactor containing a bed of particulate-carbon maintained at the target temperature of 550 °C by microwave heating. This initiated the pyrolysis process and the waste oil was pyrolyzed and transformed into pyrolysis-volatiles, which then left the reactor and passed through the product collection system. Electrical arcing was found to occur and sparks were observed 3 min after the initial injection of the waste oil-char mixture into the hot carbon bed. Such a phenomenon was found to occur intermittently within and on the surface of the carbon bed and this resulted in a series

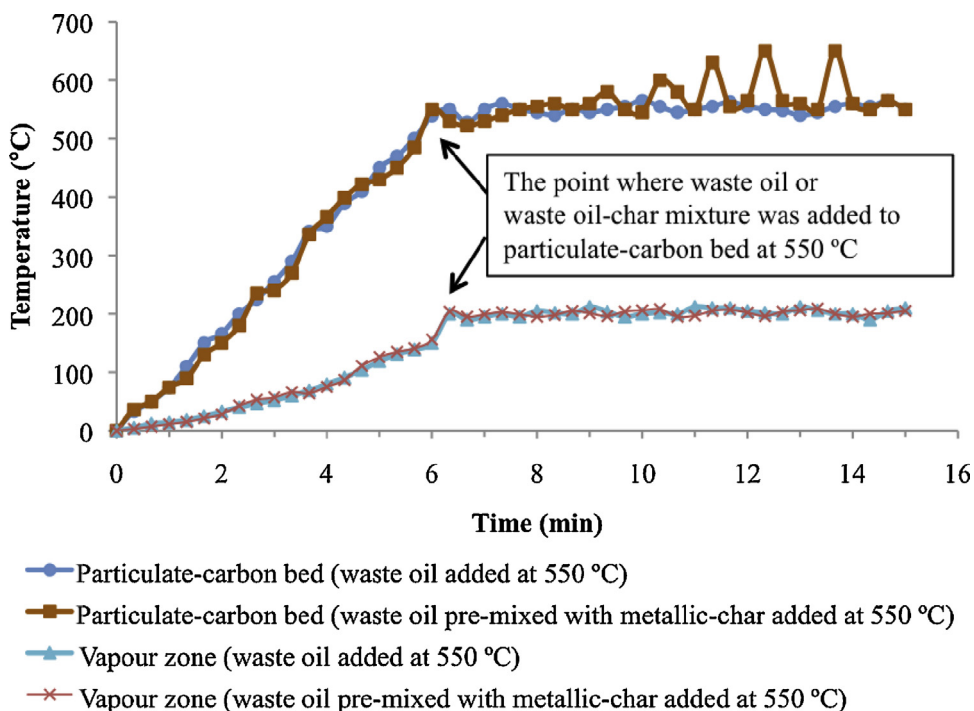


Fig. 7. Temperature profiles during microwave pyrolysis of waste oil by contact with a bed of particulate-carbon (1 kg) in the additional presence of a small amount of metallic-char pre-added to the waste oil (20 wt% of the amount of waste oil added to the reactor). The data presented show typical results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

of transient rises of temperature readings to a maximum of 650 °C during the pyrolysis of the waste oil-char mixture. Nevertheless, the temperature of the carbon bed was able to be maintained predominantly at the desired target pyrolysis temperature (550 °C) by the magnetron control system, except with some intermittent rises to 650 °C during pyrolysis in the presence of metallic-char.

The sparks and the intermittent rises of temperature were likely to have been caused by electrical arcing that occurred as a result of the metals present in the waste oil and those metallic elements that were retained within the metallic-char (Table 3); the presence of metals in the waste oil has been reported in previous works [6]. It has also been reported in other microwave pyrolysis studies [23] that sparks (regarded as “microplasmas”) were observed during the heating of pyrolysis-char and they also exhibited a very high temperature. In addition, the particles of metallic-char were observed to be incandescent (exhibiting a bright-red color) against the background of dark waste oil within a dark particulate-carbon bed, suggesting that they were transformed into hot spots (high temperature sites) during the pyrolysis, probably due to their being more rapidly heated by microwave radiation. These observations suggest that hot spots were formed during the pyrolysis of the waste oil-char mixture, and they were most likely created as a result of the addition of metallic-char to the reactor. The addition of metallic-char is thought to have an effect on the pyrolysis of waste oil as the resulting hot spots could promote heterogeneous reactions between the metallic-char and the waste oil (or the evolved pyrolysis-volatiles) and lead to a different product composition. This is consistent with results from microwave pyrolysis studies of other materials, where the formation of H₂ was observed even at a low pyrolysis temperature of 500 °C [23,41,42]. It can also be inferred from these results that hot spots would form in the reactor if the microwave pyrolysis of waste oil (with no added metallic-char) is performed in a continuous operation over a long period of time due to the increased amount of metallic-char that is generated and remained trapped within the particulate-carbon bed over a prolonged period of operation.

The temperature measured in the vapor zone (the space above the carbon bed in the reactor) showed interesting results (Fig. 7). There was a slow increase of temperature to ~150 °C as the particulate-carbon bed was heated to the target temperature at

550 °C, and this was probably due to a convective heating effect resulting from the heating of the carbon bed by microwave radiation and also the associated radiative heat transfer between the carbon bed and the thermocouple. When the waste oil or the 80:20 wt% mixture of waste oil and metallic-char was added to reactor for pyrolysis treatment in a carbon bed at 550 °C, there was a sudden increase of temperature in the vapor zone from 150 to 200 °C, and the temperature remained at around this level throughout the remaining pyrolysis period. The sudden rise of temperature was likely due to the evolution of hot pyrolysis-volatiles from the waste oil that entered the vapor zone. The lower temperature in the vapor zone (~200 °C) compared to the temperature in the particulate-carbon bed (≥550 °C) showed that different temperature distributions are present within the reactor during the microwave pyrolysis and this may be partly due to the continuous addition of cold N₂ purge gas into the reactor. The different heat distributions in different sections of the reactor may have effects on the reaction pathways that occur in this pyrolysis process.

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

Figs. 8 and 9 outline the effect of the amount of metallic-char on the fraction of waste oil converted to pyrolysis-gases, pyrolysis-oil, and char product. The study showed that the waste oils were thermally cracked to pyrolysis products dominated by pyrolysis-oil (65–85 wt%) and smaller amounts of pyrolysis-gases (8–33 wt%) and char product (2–7 wt%). The amount of metallic-char was found to have a significant influence on the yields of pyrolysis product. The yield of pyrolysis-gases was found to increase with increasing amounts of metallic-char fed together with the waste oil into the reactor. Hot spots were observed on addition of the waste oil-char mixture into the particulate-carbon bed during the pyrolysis process (see Section 3.2). The formation of hot spots was likely to have promoted the heterogeneous reactions between the metallic-char and the waste oil (or the evolved pyrolysis-volatiles) to produce greater quantities of gases such as H₂ and CO as reported by others in microwave pyrolysis studies of other wastes [25,43]. Thus, the presence of higher amounts of metallic-char was likely to enhance the heterogeneous reactions that occurred during the pyrolysis and this resulted in a higher yield of pyrolysis-gases and a lower

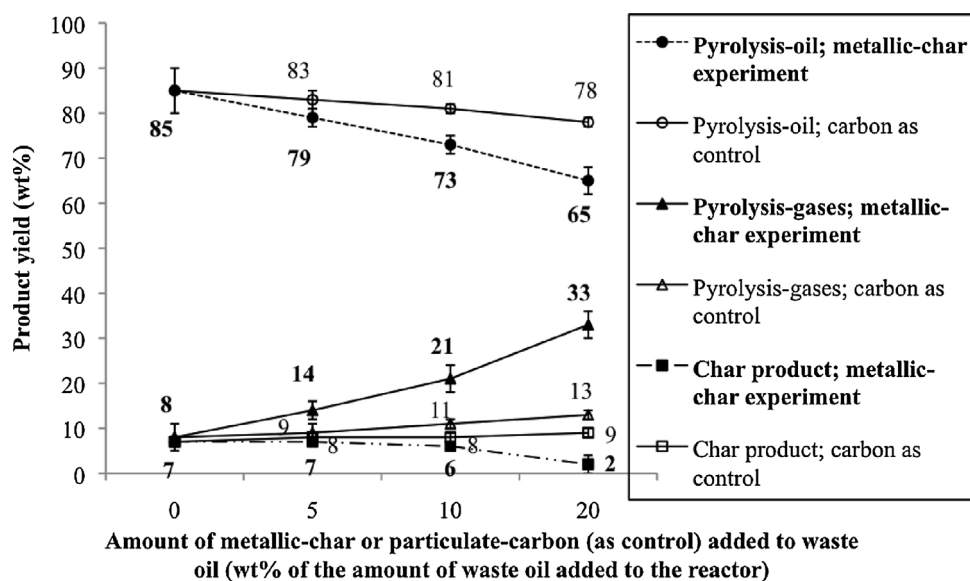


Fig. 8. Product yields (wt%) as a function of the amount of metallic-char or particulate-carbon (as control) added to waste oil. Process conditions: pyrolysis was performed on waste oil by contact with 1 kg of particulate-carbon bed when the effects of varying the amount of metallic-char added to the 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 N₂ purge rate of 250 ml/min.

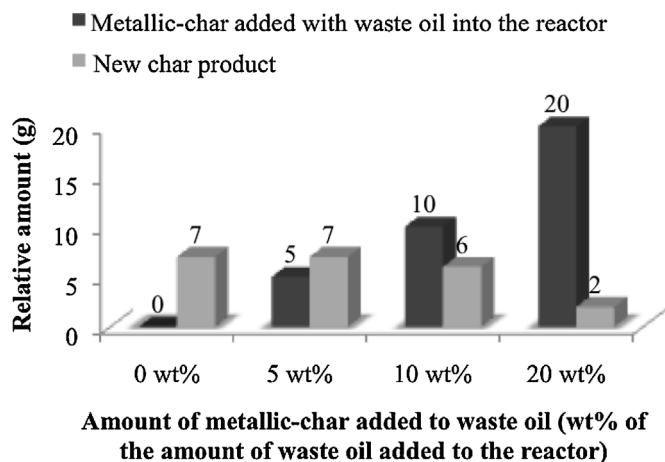


Fig. 9. The relative amounts of metallic-char and char product as a function of the amount of metallic-char added to waste oil.

corresponding yield of pyrolysis-oil. However, the amount of new char production was found to decrease with increasing amounts of metallic-char added to the waste oil (Fig. 4). This could be explained by the gasification of the chars to produce H_2 and CO , this being one of the heterogeneous reactions that have been reported to be highly promoted in microwave pyrolysis systems [14,15,20,24]; this is likely to have contributed to the lower yield of the new char product. The results show that the addition of metallic-char to the waste oil could promote different product compositions due to additional heterogeneous reactions that occurred during the pyrolysis in the presence of metallic-char.

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

Table 4 demonstrates the main chemical components identified in the pyrolysis-oil and pyrolysis-gases obtained from the experiments performed with different amounts of metallic-char. The pyrolysis-oil comprised mainly of C_5 – C_{30} hydrocarbons, which were dominated by aliphatic hydrocarbons (58–65 wt%) and significant amounts of aromatic hydrocarbons (29–38 wt%). The composition of the pyrolysis-gases was dominated by aliphatic hydrocarbons (58–78 vol%) and significant amounts of permanent gases (i.e., H_2 , CO , CO_2 , H_2S , 23–42 vol%). These results indicate the cracking of waste oil (C_7 – C_{41} hydrocarbons; see Table 1) to small hydrocarbon components (C_1 – C_{30} hydrocarbons; see Table 4), and the subsequent formation of aromatics and permanent gases (H_2 , CO , CO_2 , H_2S) through cracking, aromatization, and heterogeneous reactions that were likely to have occurred during pyrolysis. The production of pyrolysis-oil (comprising C_5 to C_{20} aliphatic hydrocarbons) and valuable gases, such as CH_4 , C_2H_4 , H_2 , and CO represents a potentially high-value chemical feedstock or fuel source. The alkanes in the pyrolysis-oil could be upgraded to produce transport-grade fuels, whereas the alkenes and aromatics constitute a feedstock that is highly desired in the petrochemical industry, especially in plastic manufacture. The low heating values (LHV) of the pyrolysis-gases was estimated based on the concentration of CO , H_2 , and CH_4 in the pyrolysis-gases [44]. The pyrolysis-gases show a LHV ranging from 4.7 to 5.5 MJ/m^3 , suggesting that the pyrolysis-gases could be used as a gaseous fuel and burned directly in gas engines or fuel cells, or upgraded to produce hydrogen and synthetic fuel (via a Fischer–Tropsch process). In particular, the hydrogen obtained can potentially be used as a second-generation fuel or as a synthesis chemical, and the CO could be steam-reformed to produce more hydrogen.

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

In this study, the increase in the amount of metallic-char added to the waste oil was thought to have led to the formation of hot spots within the reactor (see Section 3.2), and in turn promoted heterogeneous reactions between the metallic-char and the waste oil (or the evolved pyrolysis-volatiles) to produce greater yields of H_2 and CO and lower yields of CO_2 and CH_4 . In addition, the hot spots created by the metallic-char (homogeneously mixed with the waste oil) appeared to promote cracking reactions during the pyrolysis and resulted in the observed formation of higher amounts of lighter hydrocarbons in both the pyrolysis-oil (i.e., C_5 – C_{10} hydrocarbons) and pyrolysis-gases (i.e., $\leq C_3$ hydrocarbons). This agrees with the findings reported by other researchers working on microwave pyrolysis studies of other materials [15,25,43], which propose that char particles may absorb microwave energy and heat up, then transform into hot spots, which in turn act in a catalytic manner to promote the cracking and heterogeneous reactions during the microwave pyrolysis process, e.g., the decomposition reactions of hydrocarbons to produce H_2 , and the aromatization reactions to generate H_2 and benzene [8].

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

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

Table 4
Main chemical components identified in the pyrolysis-oil and pyrolysis-gases produced under various conditions.^a

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

^a 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 N₂ purge rate of 250 mL/min.

^b Particulate-carbon was used as a control.

^c Aliphatics – alkanes, naphthenes, alkenes, dialkenes.

^d Aromatics – benzene, toluene, xylene, alkyl-benzenes.

^e C₅ and C₆ compounds detected in the pyrolysis-gases are grouped and presented in a total value.

^f The sum of C₁–C₆ aliphatic hydrocarbons.

^g Low heating value (LHV) of the gas product (kJ/m³) is calculated based on the concentration of CO, H₂, and CH₄ in the pyrolysis-gases [44], i.e., [(30 × CO) + (25.7 × H₂) + (85.4 × CH₄)] × 4.2.

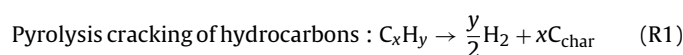
3.5. Possible chemical reaction mechanisms accounting for the catalytic conversion of waste oil using the metallic-char catalyst coupled with microwave pyrolysis.

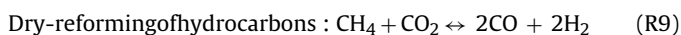
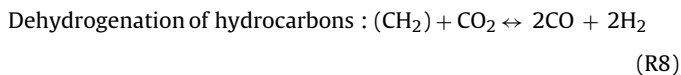
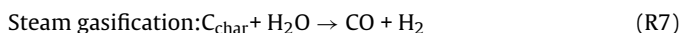
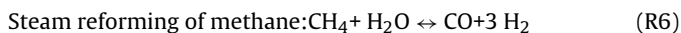
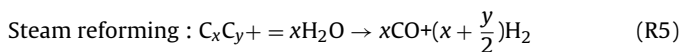
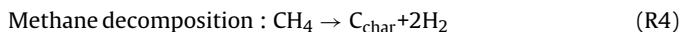
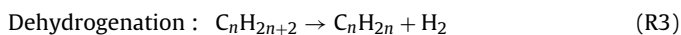
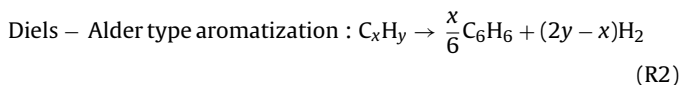
The results have shown that microwave pyrolysis in the presence of the metallic-char as the catalyst cracked the waste oil to produce a unique product distribution of compounds comprising predominantly light hydrocarbons, H₂ and CO gases, and char product in the pyrolysis products. The production of these compounds could derive mainly from the primary and secondary pyrolysis cracking reactions occurring via a free-radical-induced mechanism [10–12], and secondary reactions comprising both homogenous and heterogeneous reactions, such as Diels–Alder type aromatization reactions (i.e., condensation, dehydrogenation), reforming, dehydrogenation, decomposition, gasification, carbon reduction, and carbonization.

The wide distribution of aliphatic chains in the pyrolysis products supports the proposed free-radical-induced random scission mechanism for the catalytic pyrolytic cracking of waste oil; the reaction mechanism, comprising random scission reaction, H-atom-abstraction reactions, β-scission reaction, and termination reactions, has also been proposed for the pyrolysis of polyolefins based on the wide distribution of aliphatic chains found in the pyrolysis products [47–50]. Hydrocarbon radicals were likely to be generated from this mechanism through which the radicals were then stabilized by the capture of hydrogen atoms from the molecules nearby and this resulted in the conversion of heavy

hydrocarbons in the waste oil into lighter hydrocarbons by H-atom abstraction and β-scission reactions; this accounts for the light aliphatic hydrocarbons detected in both the pyrolysis-oil and pyrolysis-gases. The free-radical mechanism could proceed further during the pyrolysis cracking of waste oil whereby the large aliphatic hydrocarbons (e.g., large alkenes) might undergo secondary pyrolysis cracking and decompose to form aliphatic hydrocarbons of shorter chains as proposed by Miller [51]. The short-chained aliphatic hydrocarbons (e.g., alkenes and dialkenes) produced from the free-radical-induced random scission mechanism could then proceed to form aromatic hydrocarbons observed in the pyrolysis products by Diels–Alder type aromatization reactions, which involve condensation of alkenes followed by dehydrogenation to form aromatic hydrocarbons. Depending on the extent of these secondary actions and the amount of thermal energy generated by the microwave radiation at the pyrolysis temperature, carbonization could occur and lead to the production of carbonaceous char as the char product.

The production of permanent gases species (e.g., H₂, CO, CO₂) and char product could be attributed to the secondary reactions occurring either homogeneously or heterogeneously in the presence of the metallic-char as the catalyst during the pyrolysis process. The proposed secondary reactions are termed as (R1)–(R11) as below:





Reduction of metal ions (Me^{2+}) and metallic oxides (Me_mO_n) to metal (Me) by carbon:



H_2 gas was likely to be generated via the catalytic heterogeneous Reactions (R1) and (R2) occurring between the metallic-char and the waste oil or the evolved pyrolysis-volatiles [14,15,24,41], since significant amount of H_2 (up to 29 vol%) was detected in the pyrolysis-gases (Table 4). In addition, the decreasing yield of aliphatic hydrocarbons with increasing amount of metallic-char added to the pyrolysis process (Table 4) suggest that it was the increased occurrence of the (R1) and (R2) Reactions that had converted some of the aliphatic hydrocarbons into H_2 and aromatics, resulting in higher yields of these compounds detected in the pyrolysis products; this supports the occurrence of the proposed catalytic heterogeneous Reactions (R1) and (R2) for H_2 formation. Al-containing catalyst has been reported to have the ability to enhance aromatization Reaction (R2) in producing aromatics [52], thus the increasing amount of metallic-char containing Al (Table 3) was likely to have promoted the (R2) Reaction to generate higher yield of aromatics as observed in the pyrolysis-oil.

The high yield of ethylene observed in the pyrolysis-gases (up to 34 vol%, Table 4) was likely to arise from the dehydrogenation of ethane to ethylene (R3) during the catalytic microwave pyrolysis of the waste oil. This reaction was found to be promoted under the influence of microwave heating within microwave pyrolysis systems [14,16,24]; this also contributes to the higher yield of H_2 and lower yield of ethane observed in the pyrolysis-gases (Table 4). In addition, the presence of metals and metal oxides, such as Al and Al_2O_3 were reported to have a catalytic effect on this reaction [19]. The increase in the amount of metallic-char added to the waste oil led to the presence of higher amounts of these metal elements in the reactor, thus promoting the occurrence of dehydrogenation reactions and resulting in the increased yields of ethylene observed in the pyrolysis-gases; this also contributes to the increased yield of H_2 and lower yield of ethane.

A reduction in CH_4 content was observed with an increase in the amount of metallic-char added to the waste oil (Table 4), suggesting that a portion of the CH_4 was transformed into H_2 by the methane decomposition Reaction (R4) that occurred during the pyrolysis; this also contributes to the production of char product and the increased yield of H_2 during the pyrolysis. This reaction was found to be promoted under the influence of microwave heating and the

formation of hot spots within the microwave pyrolysis system [43]. In addition, carbon materials and metal-containing catalysts (e.g., Fe- Al_2O_3 , Ni, Al) were reported to show catalytic effects on this reaction [21,22]. The use of metallic-char as a catalyst followed by the formation of hot spots by the addition of the carbonaceous metallic-char containing Fe, Ni, Al_2O_3 , (see Table 3 and Fig. 5) support the proposed occurrence of methane decomposition reactions for the formation of char product and H_2 .

The waste oil used in this study was found to contain a certain amount of water (about 20 wt%); the presence of water in the waste oil has been reported in previous work [8]. The water could vaporize as steam during the pyrolysis process by the microwave heating. This could lead to the occurrence of steam reforming reaction of hydrocarbons ((R5) and (R6)) and the steam gasification of chars (R7), resulting in higher production of H_2 and CO in the pyrolysis gases (Table 4). It has been reported that catalysts containing Mg could enhance heterogeneous reactions, such as steam gasification and reforming reactions [53]; the use of metallic-char containing Mg (see Table 3 and Fig. 5) supports the proposed occurrence of these reactions.

CO_2 was only detected in less than 0.6 vol% (Table 4), whereas higher quantities of CO were detected in the pyrolysis-gases (up to 13 vol%), suggesting that a significant portion of the CO_2 might be converted to form H_2 and CO by heterogeneous reactions, such as dehydrogenation (R8) and dry-reforming (R9) reactions that have been reported to be promoted under microwave pyrolysis environment [14,15]. Both the concentrations of CO_2 and aliphatic hydrocarbons (particularly CH_4) were found to decrease when using increased amounts of the metallic-char (Table 4). This supports the proposed increased occurrence of these heterogeneous reactions that had resulted in higher productions of H_2 and CO in the pyrolysis-gases.

The results revealed that the increase in the amount of metallic-char added to the waste oil led to a reduction in the subsequent yield of additional char product (Fig. 9), suggesting that a portion of the char product (generated by the decomposition of hydrocarbons, (R1) and (R4)) was converted to H_2 and CO by gasification Reaction (R7). These gasification reactions were likely to occur due to the ability of the metallic-char to absorb the microwave energy and heat up, transforming into hot spots and in turn promoting the occurrence of these reactions. These gasification reactions are a few of the heterogeneous reactions that were reported to be highly promoted in microwave pyrolysis systems [14,25], and they were found to occur in microwave pyrolysis systems even at low reaction temperatures of 400 and 500 °C [42], thus the yield of char product was reduced in favor of H_2 and CO formation.

In this study, the addition of metallic-char to the waste oil was found to have a catalytic effect on both the cracking and the heterogeneous reactions that occurred during the pyrolysis, converting the waste oil (or the evolved pyrolysis-volatiles) into light hydrocarbons, H_2 and CO gases; this helps to explain the higher production of H_2 and CO gases, and also the higher yields of smaller hydrocarbon chains (C_5 – C_{10} hydrocarbons, CH_4 , C_2H_4) observed in both the pyrolysis-oil and pyrolysis-gases. The results suggest that the reactions in catalytic microwave pyrolysis of waste oil are a combination of primary and secondary pyrolysis cracking, and serial and parallel secondary reactions occurring homogeneously or heterogeneously as described by (R1)–(R11), with the pyrolysis cracking and catalytic heterogeneous reactions dominating as metallic-char is incorporated into the pyrolysis process, resulting in a relatively high reaction selectivity toward H_2 , CO, and a desirable lighter hydrocarbon fraction in the pyrolysis products

Fig. 10 summarizes the mechanisms involved in the microwave pyrolysis conversion of waste oil through the use of the metallic-char as a catalyst. In this microwave pyrolysis process, the metallic-char initially acted as an adsorptive-support to adsorb

metals, metal oxides and waste oil. Then, the char became a microwave absorbent that absorbed microwave energy and heated up to high temperature in a short time and in turn transformed into hot spots (high temperature sites) under the influence of microwave heating. The presence of this high temperature metallic-char had provided a reducing chemical environment in which the metallic-char acted an intermediate reductant to reduce the adsorbed metals or metal oxides into metallic states ((R10)

and (R11)) which then functioned as a catalyst to provide more reaction sites that enhanced the cracking and heterogeneous reactions that occurred during the pyrolysis to convert the waste oil into producing higher yields of light hydrocarbons, H₂ and CO gases in the pyrolysis products. It should be noted that the metals contained in the metallic-char could be regenerated by gasification or thermal regeneration of the metallic-char since the metals should

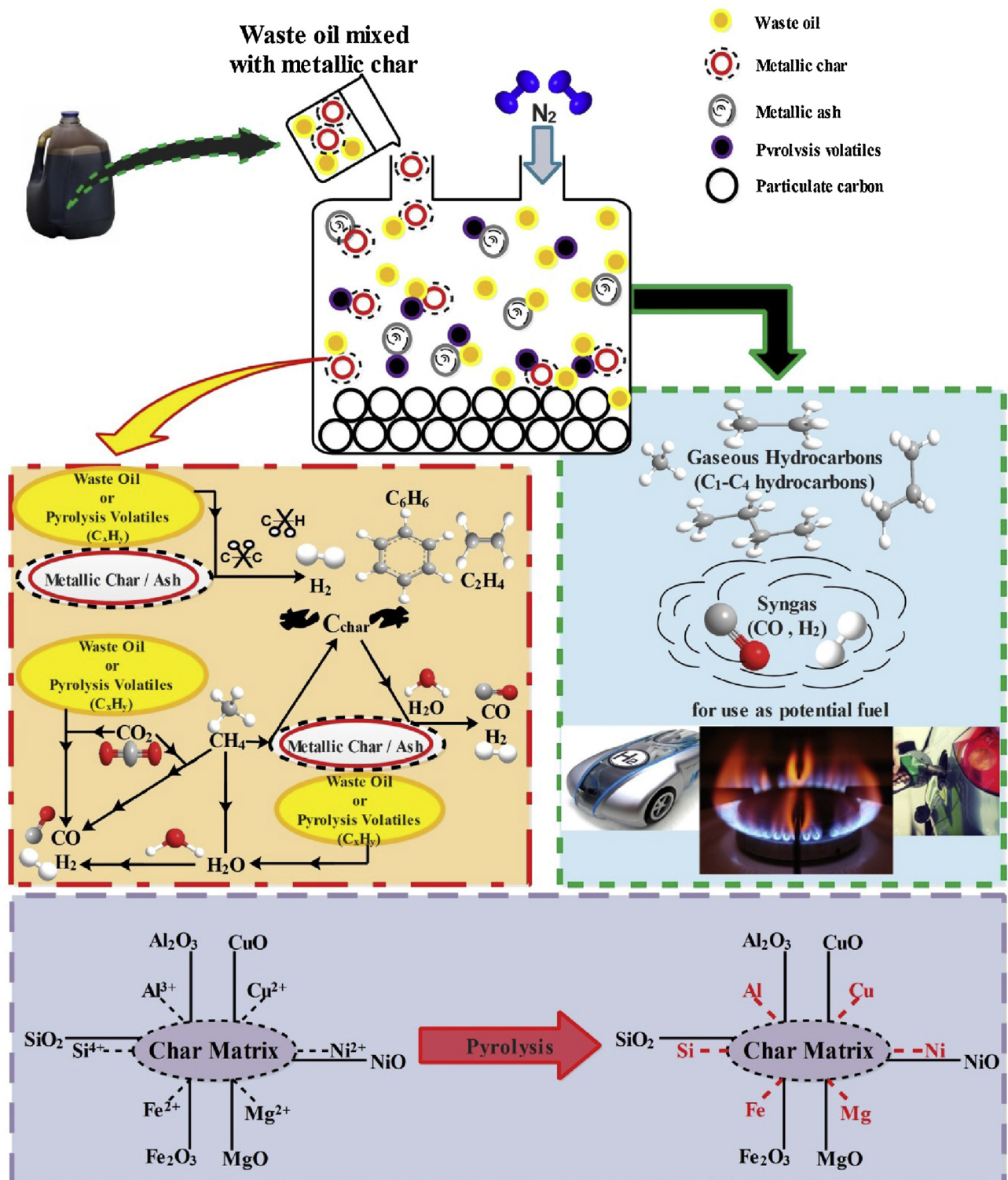


Fig. 10. Reaction mechanisms accounting for microwave pyrolysis conversion of waste oil using the metallic char catalyst.

remain in solid states considering their high sublimation temperatures (≥ 1000 °C, e.g., 2732 °C for Ni and 1535 °C for Fe) [38].

The results in this study have indicated that the use of metallic-char obtained from the previous pyrolysis of waste oil as a catalyst showed a significant influence on the product distribution in this pyrolysis process and led to the production of useful light hydrocarbons, H₂ and CO gases in the pyrolysis products. The use of metallic-char combined with microwave pyrolysis showed advantages in enhancing the reaction rates and the selectivities of the products. This presents new information on the use of metallic-char as a catalyst in microwave pyrolysis treatment of problematic waste oils. It can also be inferred from these results that if the microwave pyrolysis of waste oil were performed in a continuous operation over a long period of time, the increased amount of metallic-char that would be generated and trapped within the particulate-carbon bed would exert a similar catalytic influence and promote altering product compositions due to enhanced cracking and heterogeneous reactions occurring as a result of the formation of hot spots within the reactor.

4. Conclusion

The metallic-char catalyst demonstrated a highly porous structure and was found to contain phases of metals and metal oxides. Combined with the results showing high surface area and thermal stability in a N₂ atmosphere, this makes the metallic-char a potentially suitable catalyst to be used in pyrolysis cracking process. The use of the metallic-char as a catalyst in the microwave pyrolysis of waste oil was found to have strong influence on the fraction of waste oil converted to pyrolysis-oil and pyrolysis-gases. The addition of the metallic-char also influenced the concentrations and molecular nature of the wide variety of compounds formed in the pyrolysis-oil and pyrolysis-gases. An increase in the amount of metallic-char catalyst resulted in the formation of hot spots within the reactor in which the high temperature metallic-char provided a reducing chemical environment to reduce the adsorbed metals or metal oxides into metallic states, which appear to act catalytically in providing more reactions sites in order for cracking and heterogeneous reactions to occur during the pyrolysis process. Higher yields of light hydrocarbons, H₂ and CO gases were obtained in the pyrolysis products in the presence of higher amounts of metallic-char. The addition of metallic-char catalyst equivalent to 20 wt% of the amount of waste oil added to the reactor generated a 65 wt% yield of pyrolysis-oil containing C₅–C₂₀ hydrocarbons in addition to a 33 wt% yield of pyrolysis-gases comprising 58 vol% of C₁–C₆ hydrocarbons and 42 vol% of H₂ and CO gases, representing a potential source of high-value fuel and syngas. These results demonstrate that the metallic-char catalyst showed advantages in transforming the waste oil into potential fuel products, and thus showing excellent potential for use as a catalyst in microwave pyrolysis treatment of problematic waste oils.

Acknowledgements

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

Appendix A.

Temperature measurement and limitation

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

Accurate measurement of the evolution of the temperature of the carbon bed was difficult during the heating process – firstly, there are inherent difficulties involved in measuring this parameter in microwave devices [54]; secondly, it should be noted that the temperature is not uniform throughout the carbon bed during the initial heating to the target temperature; electrical arcing was found to occur for a relatively short period at the beginning of the heating process, but it stopped when the carbon bed had been heated to the target temperature. A stirred bed reactor is used in this study in which the physical movement and mixing of carbon particles by the stirring system creates a uniform temperature distribution, independent of the penetration depth of the microwaves into the bed of particulate-carbon. Provided the temperature is kept consistent and uniform in this system, once the thermal equilibration and steady state temperature were reached, the temperature shown by the thermocouples are assumed to give a reliable reading of the average temperature of the bulk carbon bed.

Appendix B.

Elemental analysis

Samples were analyzed on a dry or moisture-free basis by pre-heating at 200 °C to remove any moisture (residual water) and other remaining low boiling point compounds. They were then burned at 1000 °C in a flowing stream of oxygen. The products of combustion (CO₂, H₂O, N₂ and SO₂) then passed through the system with He as the carrier gas, and their content of carbon, hydrogen, and sulfur were measured quantitatively by selective IR absorption detectors, except for the nitrogen, which was measured by a thermal conductivity detector. Oxygen content was measured by pyrolyzing a separate sample at 1300 °C in a VTF-900 pyrolysis furnace (LECO Corporation, Michigan, USA). The oxygen released in the pyrolysis reaction then reacted with activated charcoal to form CO, which was converted to CO₂ by passing through an oxidation tube with He as the carrier gas. The CO₂ generated was then measured as above by an IR detector.

Appendix C.

Thermogravimetric analysis

The sample (~20 mg) was heated from ambient temperature to 600 °C at a heating rate of 25 °C/min with high purity N₂ as the carrier gas, which then switched to O₂ gas and the thermo balance was ramped to 950 °C with a final holding time of 20 min; the carrier gases were vented through the apparatus at a flow rate of 0.1 L/min. The fraction decomposed between 100 and 600 °C refers to the volatile matter content of the sample, and fixed carbon refers to the fraction between 600 and 900 °C, and the fraction above 900 °C refers to the ash content of the sample.

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