



Recovery of diesel-like fuel from waste palm oil by pyrolysis using a microwave heated bed of activated carbon



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ABSTRACT

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

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1. Introduction

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

of waste cooking oil generated annually, the disposal of waste cooking oil has become a challenge and concern to the modern society.

Recently, pyrolysis techniques have been reported to show increased efficiency in transforming biomass and waste materials into potential fuel products [3–8]. Pyrolysis is a thermal degradation process that can be used to treat waste materials in an oxygen-free atmosphere to produce liquid oil, gases and char. It has been reported that the liquid oil and gases can be utilized as a chemical feedstock or they can be upgraded to obtain light hydrocarbons for use as a fuel, and the char produced can also be

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used as a substitute for activated carbon [9]. There has been further development in the conversion of triglyceride-based vegetable oil into biofuel by pyrolysis techniques [10]. Waste cooking oil, containing significant amounts of triglycerides, represents a potential feedstock to be converted into a biofuel. The waste oil is readily available in large quantity, do not contend with other food crops, and presents a cost effective resource for biofuel production by pyrolysis techniques.

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

Most pyrolysis studies on biomass conversion have focused on processes heated by a conventional heating source (e.g. furnace, oven). There have been limited reports on the application of pyrolysis to the treatment and recycling of waste cooking oil, except for a study performed by Omar and Robinson [12] on conventional and microwave-assisted pyrolysis of rapeseed oil in which the authors had focused on the effects of temperature and microwave power. These microwave pyrolysis experiments were performed in the absence of specifically added microwave absorber, and it was shown that low amounts microwave energy were absorbed by the waste oil and this resulted in low yields of pyrolysis products. This indicates that waste cooking oil requires heating by contact with materials of high microwave absorbency to achieve higher temperatures in order for extensive pyrolysis to occur.

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

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

2. Materials and methods

2.1. Preparation of WPCO and AC

WPCO was collected from a fried chicken restaurant in Kuala Terengganu, Malaysia. The WPCO was filtered by Whatman No. 4 filter paper to remove unwanted suspended food particles. The filtered oil was collected and stored in glass bottles wrapped with aluminium foil. The glass bottles were filled up completely to prevent oxidation of the oil during storage. The WPCO was analyzed for its characteristics and these are presented in Table 1.

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

2.2. Microwave pyrolysis experiments on WPCO

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

Pyrolysis products in gaseous form (termed 'pyrolysis volatiles') were generated during the pyrolysis process and these gases then left the reactor and passed through a condensation system consisting of Vigreux and Liebig condensers in addition to an ice bath. The gases were either collected as non-condensable pyrolysis gases

Table 1
Characteristics of WPCO.

Elemental composition (wt%)	
C	71.2
H	13.3
N	0.8
S	0
O ^a	14.7
Calorific value (CV) (MJ/kg)	
	39.2
Fatty acid composition (wt%)	
Palmitic acid (C ₁₆ H ₃₂ O ₂)	25
Stearic acid (C ₁₈ H ₃₆ O ₂)	8
Oleic acid (C ₁₈ H ₃₄ O ₂)	29
Linoleic acid (C ₁₈ H ₃₂ O ₂)	12

^a Oxygen calculated by mass difference.

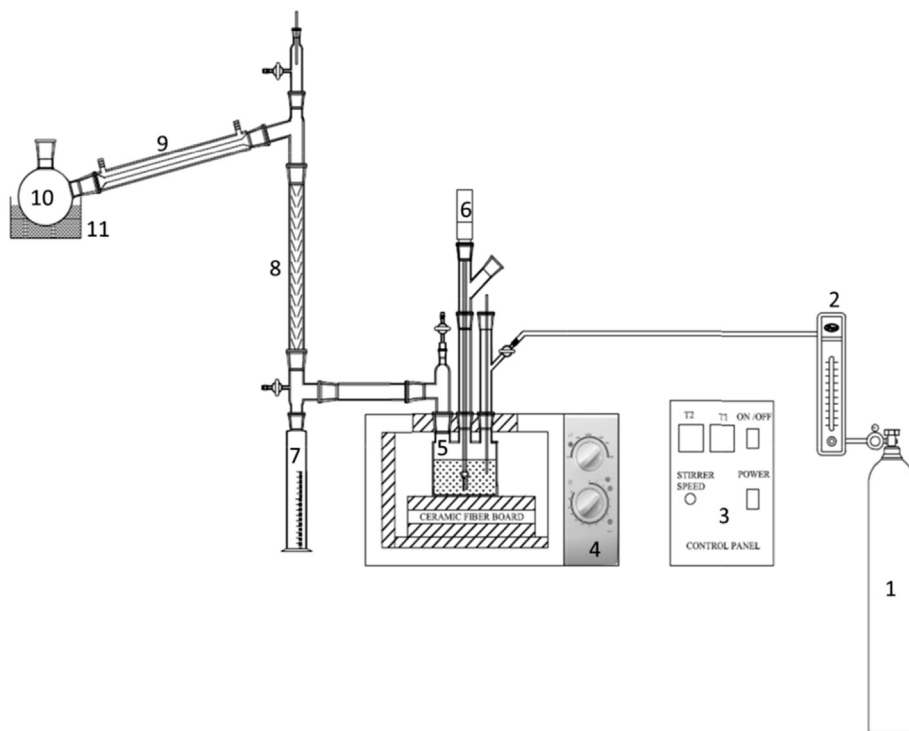


Fig. 1. Schematic drawing of the microwave pyrolysis system. (1) Nitrogen gas, (2) Flowmeter, (3) Temperature controller, (4) Modified microwave oven, (5) Pyrolysis reactor, (6) Stirrer, (7) 1st collecting vessel, (8) Vigreux column, (9) Liebig condenser, (10) 2nd collecting vessel, (11) Ice bath.

or condensed within the collecting vessels and collected as a liquid biofuel product, whereas any solid char residues were collected after the reactor was cooled to the room temperature.

The weight increase in the 1st and 2nd collecting vessels were measured to obtain the yield of biofuel. It was previously found that a small amount of biofuel was obtained in the 2nd collecting vessel (<1 wt%), thus the collected biofuel was mixed with the biofuel obtained in 1st collecting vessel for further analysis. The yield of char residue was obtained by calculating the weight of reactor and its content before and after pyrolysis process, and the gas yield was determined by resulting mass difference. The biofuel was then transferred into glass bottles and stored for further analysis. All the pyrolysis experiments were repeated for three times to ensure good reproducibility of the data.

2.3. Analytical methods

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

3. Results and discussion

3.1. Characteristics of WPCO

Table 1 shows the characteristics of the WPCO. The high calorific

value of the waste oil (39 MJ/kg) suggests that the WPCO can be a suitable feedstock for conversion into a fuel source by exploiting the potential of pyrolysis to recover the energy value of the waste oil. It was found that the WPCO is dominated by palmitic acid and oleic acid, which are considered as carboxylic acids with long hydrocarbon chains. These carboxylic acids are normally attached to a glycerol molecule to form triglycerides that contribute to the majority of the composition of WPCO, thus the overall size of these triglycerides is either C_{51} equivalent (i.e. $3 \times \text{C}_{16} + 3$) or C_{57} equivalent (i.e. $3 \times \text{C}_{18} + 3$), indicating the presence of very large hydrocarbon molecules that are unsuited for use as a biofuel. However, the WPCO can be a suitable pyrolysis feedstock since the very large hydrocarbon molecules (i.e. C_{51} or C_{57} hydrocarbons) could be pyrolyzed and converted into light hydrocarbons for potential use as a fuel.

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

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

The microwave-heated bed of AC showed considerable advantages in providing a rapid heating process ($\sim 16\text{--}18$ $^{\circ}\text{C}/\text{min}$) to heat and pyrolyze the WPCO at a desirable high temperature (up to 550 $^{\circ}\text{C}$) in which the process time taken for the heating and pyrolysis cracking of the WPCO at 450 $^{\circ}\text{C}$ was fully completed in less than 25 min (Fig. 2). In contrast, it has been reported that a longer process time ranging from 60 to 120 min was needed for the conventional fixed-bed pyrolysis of rapeseed oil [12] and palm oil [10] that used furnace as the heat source, albeit in completely different apparatus. The rapid heating represents a favorable feature in

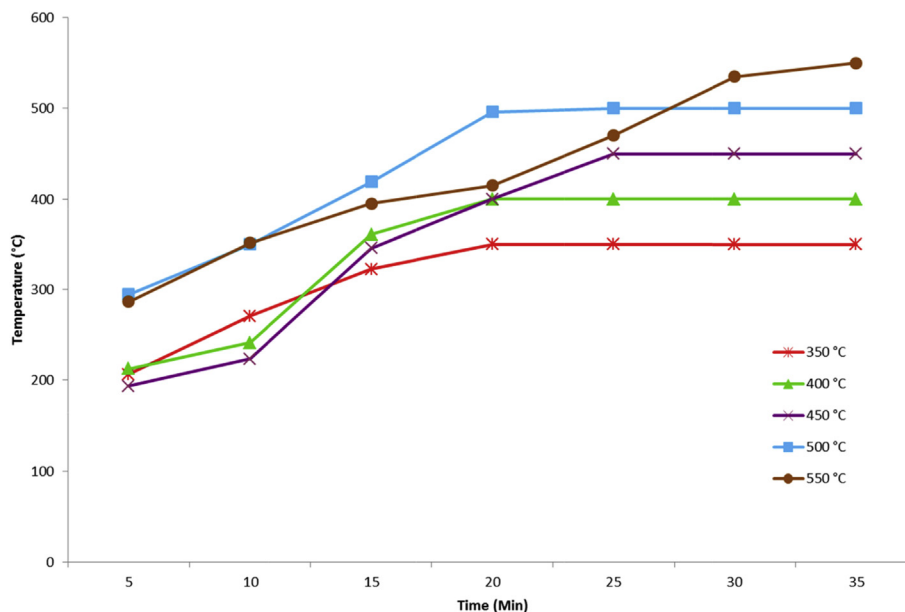


Fig. 2. Temperature profiles shown by microwave pyrolysis of WPCO at different process temperature.

providing an energy-efficient pyrolysis process to reduce the power consumption when compared with pyrolysis processes heated by a conventional heating source (e.g. furnace, oven). Conventional pyrolysis processes usually employ an external heating source that needs to heat all the substances in the heating chamber including the evolved pyrolysis-volatiles, the surrounding N_2 gas, and the chamber itself, thus energy is not fully targeted to the material being heated and this results in significant energy losses and in turn leads to a long process time. On the contrary, the use of a well-mixed bed of AC in microwave pyrolysis process provides a localized reaction ‘hot zone’ in contact with the added WPCO. The intimate contact of the WPCO with the AC particles in the stirred bed ensures minimal distances for the heat to be transferred to the WPCO rapidly in order for pyrolysis cracking to occur more quickly and extensively. Furthermore, energy is efficiently targeted only to microwave receptive AC bed and not to gases within the heating chamber or to the walls of the chamber itself.

3.3. Product yields

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

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

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

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

3.3.1. Chemical composition of the biofuel product

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

3.3.1.1. Elemental composition and calorific value (CV). Table 2

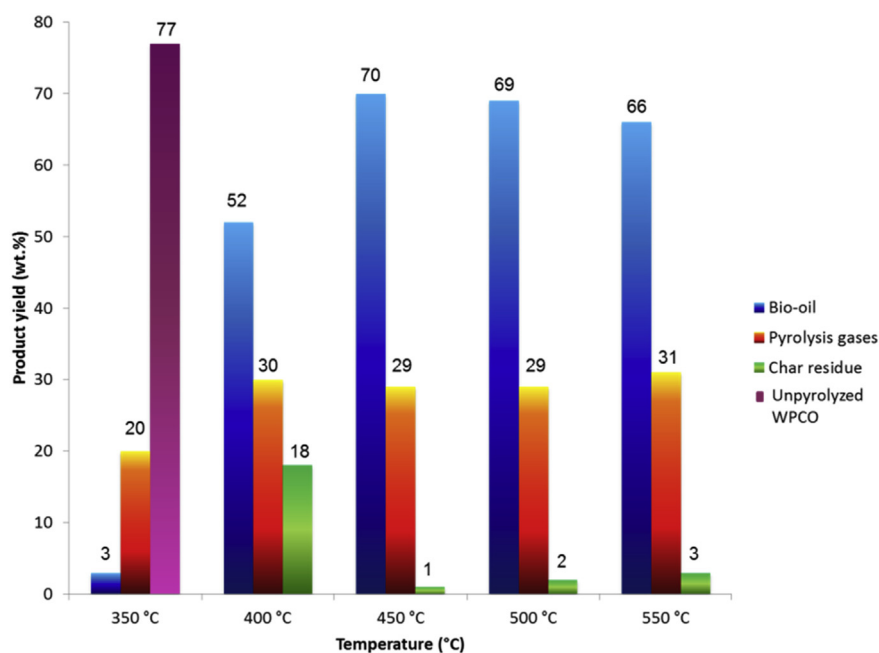


Fig. 3. Product yield (wt%) from microwave pyrolysis of WPCO performed at different process temperatures.

Table 2
Elemental composition and CV of biofuel obtained at different process temperatures.

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

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

The biofuels showed a H/C ratio of about 2, indicating the presence of aliphatic hydrocarbons (C_xH_y) such as alkanes, naphthenes, alkenes, dialkenes in the oil products. The detection of low oxygen content (4–10 wt%) in the biofuels indicates the presence of low amounts of oxidized species in the biofuel (Table 2). This could be attributed to the use of a bed of activated carbon that also provided a reducing chemical environment at the process temperatures. The bed of activated carbon acted as a reductant to remove oxygen functionalities from the feed oil and to decrease the formation of undesirable oxidized species during the pyrolysis, thus leading to the low oxygen content in the biofuel; the mass loss of activated carbon was regarded as negligible as it was found to be less than 1 wt% after the pyrolysis operation. In addition, the oxygenated compound that initially present in WPCO might form gaseous compound such as carbon dioxide or light hydrocarbons as a result of deoxygenation reactions (e.g. dehydration, decarboxylation, decarboxylation) during pyrolysis cracking of WPCO [20,21], and these compounds would remain in the gaseous phase and escape from the reactor, thus leading to the reduction in the

oxygen content of the biofuel. Interestingly, sulphur was not detected in the biofuels (Table 2). This indicates the potential of the liquid products to be used as a fuel since their zero sulphur content will result in no SO_x emissions compared to the use of traditional liquid fuels derived from fossil fuels. Nitrogen was detected in low concentrations in the biofuel, recording a concentration of about 1 wt%. It was likely that the nitrogen was obtained from the distillation or evaporation of some of the nitrogen-containing components in the WPCO that occurred during the pyrolysis process; the nitrogen-containing components was likely to derive from the heterocyclic aroma compounds originally present as flavor enhancer in the food and which had been transferred and trapped within the oil during the frying of the food. These processes transferred the nitrogen-containing compounds from the WPCO in the reactor to the condensation system and then into the recovered biofuel. Although the biofuel contains relatively low concentration of nitrogen, given its likely future uses as a fuel in engine operation and if the concentration assessed to pose too great a risk, the nitrogen content can be removed via catalytic upgrading through the use of zeolite catalyst (e.g. ZSM-5, USY). The biofuel obtained showed a CV ranging from 41 to 46 MJ/kg (Table 2), which is higher than the original WPCO before pyrolysis (39.2 MJ/kg; Table 1).

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

This study showed that WPCO was thermally cracked to a liquid hydrocarbon product dominated by aliphatic hydrocarbons (alkanes, alkenes). The aliphatic hydrocarbons were mostly alkanes (~50%), and alkanes from decane (C₁₀H₂₂) to tridecane (C₁₃H₂₈) showed the highest concentration. Alkenes (~34%) with carbon chain lengths ranging from C₉–C₁₈ were also present with 5-

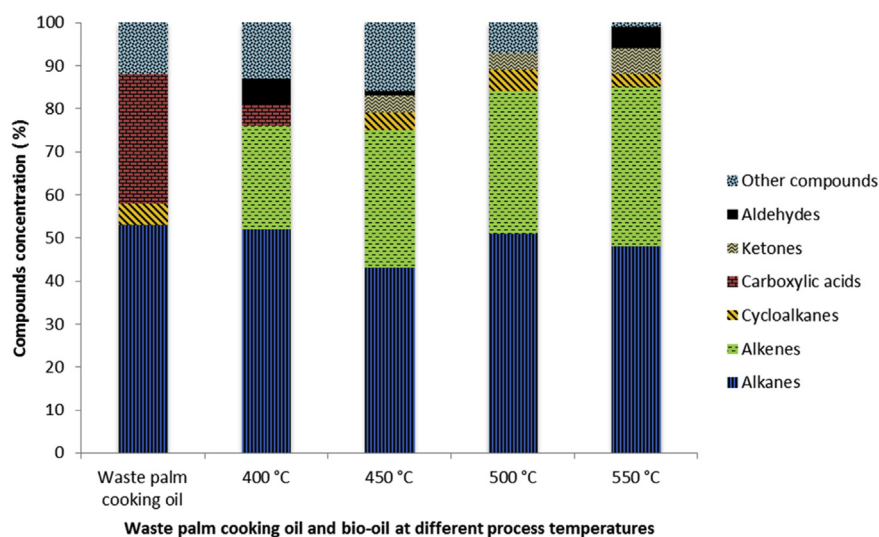


Fig. 4. Main compounds (peak area%) detected in WPCO and the biofuel obtained at different process temperatures.

octadecene ($C_{18}H_{36}$) and 8-heptadecene ($C_{17}H_{34}$) being the most abundant. The biofuel obtained at 500 °C contains the highest concentration of aliphatic hydrocarbons, accounting for 89% of its composition. The aliphatic hydrocarbons accounts for 79% of the liquid obtained at 450 °C, whereas only 76% was recorded at 400 °C. The production of liquid products comprising mainly of aliphatic hydrocarbons represents a potentially high-value chemical feedstock or fuel source. In particular, the C_{10} – C_{15} alkanes (43–49%; Table S1) is within the hydrocarbon range of diesel fuel (C_{10} – C_{15}) [22] and thus could be upgraded to produce transport-grade diesel, whereas the alkenes are highly desired chemicals that can be used in plastic manufacture [9].

Process temperature was found to have an influence on the chemical composition of the biofuel generated. Increasing the temperature from 450 °C to 550 °C led to an increase in the content of alkanes in the biofuel, and the alkanes content improved towards the presence of smaller hydrocarbon chains (C_{10} – C_{12}) (Table S1). The increase in the process temperature also resulted in greater production of alkenes in the biofuel (up to 37%) with the size of the alkenes being improved towards the presence of smaller hydrocarbon chains ($\leq C_{13}$; Table S1). In addition, the biofuel obtained at 550 °C showed a higher concentration of light hydrocarbons (C_5 – C_{13}) (72%) compared to the biofuel obtained at 500 °C (60%), 450 °C (45%) and 400 °C (4%) (Table S1). These results indicate the increased occurrence of the cracking of heavier hydrocarbons in the WPCO at higher process temperatures to produce lighter hydrocarbons. The higher thermal energy at higher process temperatures enhances secondary cracking of the pyrolysis volatiles evolved from the WPCO being pyrolyzed, thus enhancing the cleavage of larger hydrocarbon chains present in the pyrolyzed volatiles into smaller hydrocarbon chains and this leads to a higher corresponding yield of light hydrocarbons in the biofuel. Overall, increasing process temperature leads to higher production of light hydrocarbons in the biofuel.

Interestingly, there was no carboxylic acid detected in the biofuel during the pyrolysis at the process temperature of 450 °C, 500 °C, and 550 °C, suggesting that carboxylic acids, particularly the fatty acids attached to triglycerides in the WPCO (Table 1), had been converted to other compounds during the pyrolysis at these process temperatures. The carboxylic acids were likely to be split during the pyrolysis and from which the carboxyl group was converted to an alkane and the remaining bits of the hydrocarbon chain were converted to alkenes; these types of deoxygenation

reactions (e.g. decarbonylation, decarboxylation) have been reported to commonly occur during thermal treatment processes like pyrolysis [20,21]. The production of a biofuel with no carboxylic acids and triglycerides represents a desirable feature because their presence could lead to the occurrence of undesired polymerization reactions during the storage and upgrading in which the carboxylic acids may react to form acidic tar or sludge and this could lead to increased viscosity of the oil and furthermore the tar or sludge could cause problems such as filter plugging and system fouling [9].

The hydrocarbons produced in the biofuel (C_{10} – C_{15} hydrocarbons) are of fundamentally much smaller length (less than one third) than those present in original WPCO (the presence of triglycerides that is equivalent to C_{51} or C_{57} hydrocarbons). The production of a biofuel with short hydrocarbon chains and that is also free of carboxylic acids by this pyrolysis approach represents a favorable feature in producing a hydrocarbon product that is much more suited to be used as a fuel, particularly as a diesel fuel considering that the hydrocarbons with short chains are within the hydrocarbon range of diesel fuel (C_{10} – C_{15}) [22].

Oxygenated compounds such as aldehydes and ketones were found to be present only in minor quantities in the biofuel ($\leq 6\%$) compared to that present in the biofuel (53%) obtained by conventional pyrolysis of palm oil using a furnace [10]. Combined with the results of no carboxylic acids being detected in the biofuel, this provides useful information as to the extent of oxidation that had occurred and resulted in the formation of oxygenated by-products such as aldehydes, ketones, and carboxylic acids in the biofuel during pyrolysis. The presence of only small amounts of aldehydes and ketones with no detection of carboxylic acids indicates little occurrence of such oxidation reactions in this pyrolysis process, since the AC bed had acted as a reductant to convert some of the oxygen present in the feedstock to CO or CO_2 which then leaves the system in the gas phase, thus reducing the amount of oxygen that is transformed into oxygenated by-products in the biofuel. This corroborates the low oxygen contents found in the biofuel by elemental analysis (Table 2), and the beneficial effects of the activated carbon bed (acting as a reducing reaction environment) in decreasing both the extent of oil oxidation and the resulting formation of oxygenated by-products that could generate undesirable acidic tar or sludge in the biofuel.

3.3.1.3. *Chemical composition of biofuel compared to transport-grade diesel and biodiesel.* The biofuel obtained from this pyrolysis

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

Our biofuel shows lower oxygen content (5 wt%) than that of biodiesel (11 wt%), and represents a favorable feature in producing a fuel with improved stability and higher heating value compared to conventional biodiesel that shows a higher oxygen content. However, the biofuel was found to have a higher oxygen content compared to fossil transport-grade diesel, which is oxygen-free. This suggests that additional steps are needed to eliminate oxygen from the biofuel if it is to be used as a diesel fuel. Although the biofuel contains a relatively low level of oxygen given their likely future uses as a fuel (e.g. diesel), were the concentration of oxygen assessed to pose too great a risk, or if complete removal of oxygen was required, one potential route would be to perform deoxygenation or decarboxylation to convert the oxygenated compounds that remained in the biofuel to alkanes or aromatics.

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

It is clear that the pyrolysis approach offers a promising alternative to transesterification and produces a biofuel that may have advantages over conventional biodiesel. This approach also offers advantages over transesterification in avoiding the use of solvents and catalysts such as the methanol and acid or base catalyst required to perform transesterification. In addition, there is no need to remove oxygenated compounds (particularly glycerol and any

non-esterified fatty acids) from the products formed during transesterification. The use of catalyst and the presence of free fatty acid and glycerol as by-products in the resulting biodiesel are common problems associated with transesterification that could lead to many drawbacks such as slow reaction rate, corrosion, and difficulty in separating catalyst from the biodiesel [29,30], and also the formation of undesired soap that can lead to reduction in biodiesel yield, decreased catalyst efficiency, and increased formation of gel and viscosity of biodiesel [31].

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

3.3.2. Energy balance

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

1. The energy consumption is assumed to derive mainly from the usage of electricity to generate the microwave radiation for pyrolysis to occur. The electrical consumption is based on the electrical power input (1.12 kW) during the pyrolysis treatment, which is estimated to be approximately 1.5 times the nominal power output of the magnetron (0.75 kW) for the sum of the periods when they are switched on during the pyrolysis operation, assuming that the energy conversion efficiency of electricity into microwave energy is about 0.67 as reported by others in the literature [33–35]. It should be mentioned that the 1.12 kW of electrical input is an overestimate of the actual electrical consumption, considering the simplicity of the pyrolysis reactor and the fact that the actual amount of absorbed microwave power is not measured in this operation. Adding a

Table 3
Chemical composition of the biofuel compared to transport-grade diesel and biodiesel.

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

(–) not available.

^a Process conditions: Pyrolysis was performed at a process temperature of 450 °C.

^b ASTM D6751 specifications of biodiesel [23,24].

^c ASTM D975 specifications of diesel [23,24].

^d Calculated by mass difference.

^e Carbon range of biodiesel (C₁₄–C₂₄) [27].

^f Hydrocarbon range of diesel fuel (C₁₀–C₁₅) [22].

^g CV of biodiesel derived from palm oil and waste cooking oil from previous studies [25,26].

- device to record the absorbed power would improve the estimate of the energy consumption in the process, and would further increase the apparent energy conversion efficiency.
- Heat losses from the pyrolysis reactor are substantial and would not be representative of the losses that would occur at pilot or industrial scale. No attempt has been made to fully insulate the pyrolysis reactor and fittings nor to recover energy during the condensation of the pyrolysis products.
 - The CV of the pyrolysis gases and char are ignored in this assessment since only the biofuel is of particular interest in this study.

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

The microwave pyrolysis process showed a positive energy ratio ranging from 1.96 to 2.73 and a net energy output (E_{balance}) of 22480–29200 kJ/kg. This demonstrates that this pyrolysis approach is capable of recovering an oil product with an energy content much greater than the amount of electrical energy used for operating the pyrolysis process. These results suggest that the setup of a pyrolysis equipment using the apparatus described from this pyrolysis approach with an electrical power input of 1.12 kW is capable of processing WPCO at a process temperature of 450 °C to produce a biofuel product with an energy content equivalent to about 3.06 kW (i.e. 1.12 kW \times energy ratio of 2.73).

Despite the fact that there was energy loss occurred during the pyrolysis operation (18–27% of E_{input}), the pyrolysis process still showed significantly high recovery ($\geq 73\%$) of the energy input to the system. It should however be noted that the high energy recovery observed in this study involve the assumption that the only energy input of the process is the electrical energy used to operate the pyrolysis operation. In practice lower energy recovery would be realized in which additional energy inputs have been considered, including the energy needed for the collection and transport of WPCO to the processing plant, and for the refining or upgrading of the biofuel if it needs to be further processed to produce a transport-grade diesel fuel. However, it is envisaged that inclusion

of heat integration and recovery systems to recover energy loss from the prototype reactor, which are normally implemented during pilot or industrial scale operation, could further increase the amount of energy that can be recovered from the pyrolysis system. In addition, the CV of the pyrolysis gases and char have been ignored in this assessment. Inclusion of the energy content from these pyrolysis products would further increase the energy recovery.

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

4. Conclusion

Pyrolysis using a microwave-heated bed of activated carbon provided rapid heating (~ 18 °C/min) which heated and pyrolyzed the waste oil at 450 °C in a process taking less than 25 min. It also showed advantages in providing a localized reaction hot zone that thermally promoted extensive cracking to produce higher yield of a biofuel product, while simultaneously created a reducing environment that prevented the formation of undesirable oxidized compounds in the biofuel.

The pyrolysis produced a biofuel product that is low in oxygen, free of sulphur, carboxylic acid and triglycerides, and which also contains light C_{10} – C_{15} hydrocarbons and a high calorific value nearly comparable to diesel fuel. The biofuel shows lower oxygen content, lighter hydrocarbon content, and a higher calorific value than that reported for biodiesel derived from transesterification of waste cooking oil.

The pyrolysis apparatus operated with an electrical power input

Table 4
Energy recovery and consumption in microwave pyrolysis of WPCO.

Process temperature	E_{WO}^a (kJ/kg)	E_{BO}^b (kJ/kg)	$E_{\text{pyrolysis}}^c$ (kJ/kg)	$E_{\text{pyrolysis}}/E_{\text{WO}}^d$ (%)	E_{ratio}^e	E_{balance}^f (kJ/kg)
450 °C	39200	46000	16800	43	2.73	29200
500 °C	39200	46000	20160	51	2.28	25840
550 °C	39200	46000	23520	60	1.96	22480
E_{input}^g (kJ/kg)			E_{loss}^h (kJ/kg)			E_{recovery}^i (kJ/kg)
56000			10000			46000
59360			13360			46000
62720			16720			46000

^a Energy content or CV of WPCO.

^b Energy content of biofuel, i.e. CV of biofuel \times amount of biofuel obtained/amount of WPCO.

^c Electrical energy consumed during the pyrolysis treatment, i.e. 1.12 kW of electrical power input \times duration of pyrolysis treatment/amount of WPCO.

^d Amount of energy (from E_{WO}) consumed by $E_{\text{pyrolysis}}$.

^e Energy ratio, defined as the energy content of the biofuel divided by the electrical energy input needed to operate the system, i.e. $E_{\text{BO}}/E_{\text{pyrolysis}}$.

^f Energy balance, defined as the energy content of the biofuel minus the electrical energy input needed to operate the system, i.e. $E_{\text{BO}} - E_{\text{pyrolysis}}$.

^g Energy input of the system, defined as the sum of the total CV of the WPCO (E_{WO}) and the electrical energy input needed to operate the system ($E_{\text{pyrolysis}}$), i.e. $E_{\text{WO}} + E_{\text{pyrolysis}}$.

^h Energy losses from the system, includes the heat losses from the prototype reactor, the energy loss from the conversion of microwave energy into thermal energy, and the CV of the pyrolysis-gases and the char, i.e. $(E_{\text{WO}} + E_{\text{pyrolysis}}) - E_{\text{BO}}$.

ⁱ Energy recovered from the system, i.e. $(E_{\text{WO}} + E_{\text{pyrolysis}}) - E_{\text{loss}}$.

of 1.12 kW was capable of producing a biofuel with an energy content equivalent to about 3 kW, showing a positive energy ratio of 2.7 and $\geq 73\%$ recovery of the energy input to the system.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.energy.2016.09.076>.

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