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PYROLYSIS OF OIL PALM BIOMASS USING PALM SHELL CHAR AS MICROWAVE ABSORBER

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ABSTRACT

The main aim of this research was to reveal the heating characteristics of palm shell char (PSC) acting as a microwave absorber (MA) for the pyrolysis of oil palm biomass (shell and fibre). This was done by mixing oil palm biomass with PSC-MA and subjecting it to microwave irradiation. A domestic microwave oven with a maximum power of 1000 W and 2.45 GHz frequency was used. Prior to pyrolysis, the heating characteristic of PSC-MA in terms of its temperature profile (through batch and continuous temperature measurements) was examined. It was found that PSC-MA could act as very good microwave receptor. However, the method of temperature measurement played an important role in the heating and pyrolysis behaviour. A minimum microwave power of 450 W was needed to carry out the pyrolysis process in the present work. Results of the microwave pyrolysis show that the ratio of biomass to PSC-MA has a significant influence on the product yield. A synergistic effect between PSC-MA and the biomass can reduce the consumption of energy, time and cost of the thermo-chemical process.

Keywords: oil palm biomass, microwave pyrolysis, palm shell char, temperature profiles, bio-oil.

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INTRODUCTION

Pyrolysis is considered to be the most promising route for thermo-chemical treatment because it can be used as an independent process for the production of biofuels and other valuable chemical products, or as an initial step in gasification and combustion (Bridgwater and Kuester, 1988). A fast pyrolysis process has already been developed on a pilot scale in our laboratory to obtain bio-oil from various biomasses (Islam *et al*., 1999; Islam and Ani, 2000; Kawser and Ani, 2000; Ani *et al*., 2008). Besides this, others have attempted to pyrolyse oil palm biomass such as pressed fruit fibre (Khor *et al*., 2009) and empty fruit bunches (Sukiran *et al.,* 2009). Pyrolysis, being an endothermic process, requires continuous heat to sustain the process. In our previous work, this was achieved by using a conventional heating system such as an electrical heater. Typically, the heat is transferred to the feed materials by conduction and convection in conventional pyrolysis systems (Chen *et al.,* 2008). However, these techniques suffer from certain drawbacks. Primarily, a substantial amount of energy is consumed in the form of electricity. Other drawbacks include heat transfer resistance, heat losses to the surroundings, damage to the reactor wall due to continuous electric heating, *etc*. Furthermore, a lack of rapid heating results in a long heating duration and undesired or secondary reactions. These secondary reactions are responsible for low product quality due to the incessant cracking of the product. Finally, large sized biomass particles are not recommended for conventionally heated pyrolysis systems. This is because high heating rates, good bio-oil yield and quality may be difficult to achieve for such large-sized feed materials.

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Keeping in view the above problems, a new technique utilising microwaves (MW) as an alternative source of energy was developed. Recently, MW has gained much interest for waste destruction in terms of pyrolysis of plastic (Ludlow-Palafox and Chase, 2001), sewage sludge (Menéndez *et al.,* 2002; Domínguez *et al.,* 2008), and wood (Miura *et al.,* 2004). In addition to this, two excellent review articles offer an overview of the application of MW in different fields of waste and environmental engineering (Jones *et al.,* 2002; Appleton *et al.,* 2005). Various advantages in using MW are also reported in these two reviews. Largely, the process is the same, *i.e.* pyrolysis, but the energy supplied to carry out the process has been revolutionised. Rather than supplying energy indirectly via conduction, convection or other such means, it is supplied directly by MW into the material to create heat. The key merit of MW pyrolysis as stated by Miura *et al.* (2004) is to prevent an undesired secondary reaction that leads to the formation of impurities in the product, resulting in decreased yield of the desired compounds.

The heating characteristics of MW are unique when compared with those of conventional heating techniques. This is due to the volumetric heating nature of MW whereby the molecules go into rotation due to the high frequency, and thus create the heat, provided that the penetration depth of MW into the materials is sufficient. *Figure 1* illustrates the difference between conventional and MW heating temperature profiles in a particle. However, the heating characteristics of materials in bulk might be somewhat different and might depend on various factors, in particular the dielectric properties of the materials. For this reason, an investigation into the heating characteristics as determined by temperature measurements was necessary for new materials such as PSC-MA.

In recent times, pyrolysis of biomass using MW technology has received a great deal of attention. This includes the pyrolysis of fir pine wood sawdust (Chen *et al.,* 2008), corn stover (Yu *et al.,* 2007), rice straw (Huang *et al.,* 2008), fir sawdust (Guo *et al.,* 2006), aspen pellet and corn stover (Wan *et al.,* 2009), coffee hulls (Domínguez *et al.,* 2007) and wheat straw (Budarin *et al.,* 2009). Most of these researchers used MW receptors, MA, additives or catalysts to reach the desired pyrolysis temperature under MW irradiation. This is because of the poor MW-absorbing characteristics of the biomass materials (Kreiger-Brockett, 1994). Therefore, it is necessary to add inorganic additives such as NaOH, HCOONa, $NaHCO_3$, SiO_2 and $Ca(OH)_2$ to pyrolyse the biomass. However, few or none have conducted detailed studies into the temperature profiles of the MW-absorbing materials or of the susceptors such as char, additives, *etc*. Very recently a review on MW heating of carbon material was published by Menéndez *et al.* (2010a). According to them, carbonaceous materials including biomass char are very good MW absorbers leading to high

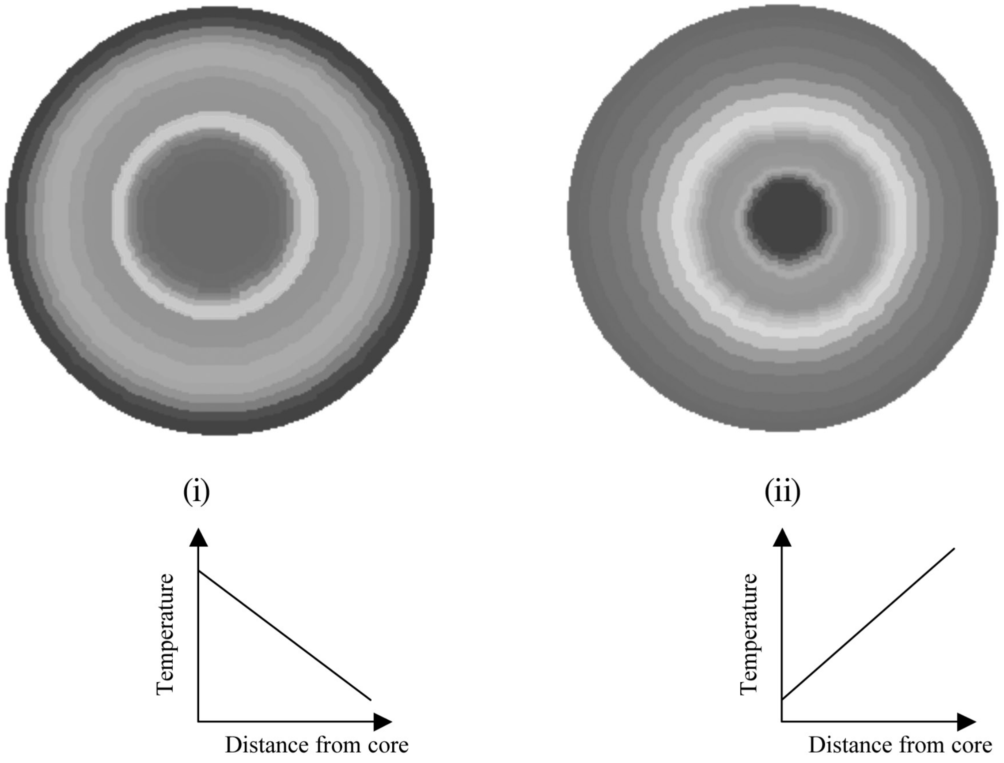


Figure 1. (i) Microwave heating and (ii) conventional heating profiles (for illustration purpose).

generation of heat. Hence, carbonaceous materials have been used as MW receptors or absorbers to indirectly heat poor MW-absorbing materials such as biomass, coal, oil shale, sewage sludge and other organic wastes. The rationale behind using biomass char or carbonaceous materials as MW receptors is not only because they have ready MW-absorbing properties but also because they are cheap, easily available, are environment- and process-friendly. However, this review article is limited to reports on previous work that used carbon as MA, and there are no details on investigations into the temperature profile. Several researchers (Menéndez *et al.*, 2010a, b) have also stated that MW irradiation of carbonaceous materials can lead to the formation of microplasma, where the temperature can reach a higher value than the surroundings. Menéndez *et al.* (2010b) in their recently published letter used a video facility to observe the MW heating of carbonaceous materials including biomass char, but without any study on temperature profiles. Moreover, several other researchers have attempted to measure the temperature at the end of the process or reaction which might delude them from the actual temperature profile of the materials. Indeed, a continuous temperature profile can provide better temperature history of the materials being irradiated.

From the above literature review, it is observed that a detailed investigation into the heating characteristics of biomass char particles under MW irradiation is still lacking. This is important in view of the fact that the individual heating characteristics of MA will offer some insight into the synergistic effect of mixing MA with poor MW-absorbing materials such as biomass. Explicitly, there has been no published reports on any attempt to depict the temperature profiles of palm shell char (PSC) obtained from oil palm shell biomass. The effect of such MA on the temperature profile and yield of bio-oil is also found to be lacking in the literature with the exception of a recently published article (Salema and Ani, 2011). Nevertheless, in this particular article, the work was focused more on the MW pyrolysis of oil palm biomass, while no attention was given to the heating characteristics of PSC-MA. Therefore, it would be interesting to identify the individual heating performance of PSC-MA, as well as of oil palm biomass under MW irradiation.

Hence, the objective of the present article is to reveal the heating characteristics of PSC-MA, and subsequently to utilise this char to pyrolyse oil palm biomass. Temperature profiles of PSC-MA and oil palm biomass were used to investigate the heating characteristics. Two types of temperature profiles were presented for PSC-MA. First, the temperature was measured in batches, and second, continuous temperature measurement was carried out under MW irradiation. Furthermore, the effect of biomass to PSC-MA ratio on the yield of bio-oil was also presented as evidence for PSC being an efficient MW-absorbing material.

EXPERIMENTAL DESIGN

Materials

Two types of oil palm biomass [oil palm fibre (OPF) and oil palm shell (OPS)], were obtained from FELDA Kulai palm oil mill situated in Johor state of Malaysia, and used as received. OPS was pyrolysed using a large particle size, *i.e.* without any grinding, ranging from 0.001 to 0.1 m. Conversely, OPF was ground to a smaller size of about 300 to 600 μm. The width of the OPS pieces was in the range of 0.0005 to 0.004 m and that of OPF was less than 0.001 m. In the present work, char obtained from conventional pyrolysis of OPS was used as MA, and was designated as PSC-MA (palm shell char-microwave absorber). The size of PSC-MA was in the range of 100 to 300 μm. Data from the proximate and ultimate analyses of the oil palm biomass in dry condition is shown in *Table 1*. Approximately 67% increase in carbon content was noticed in PSC after pyrolysis of OPS. In the present study, PSC was produced via a fast pyrolysis process at 500°C. Accordingly, to the Brunauer Emmett Teller (BET) surface area of PSC was about 150 m^2 g^{-1} at 500°C for a size of 850 μm, but this can be influenced by the carbonisation temperature as reported in previous studies (Hayashi *et al.*, 2002; Tan and Ani, 2004). For raw OPS, the BET surface area was reported to be about 1.6 m^2 g^{-1} while that for PSC was 194.3 m^2 g^{-1}, but in this case the char was prepared at 700°C (Guo and Lua, 2000). The moisture content of the samples of OPS and OPF as received was found to be about 8 and 10 wt %, respectively.

Experimental Set-up and Methods

PSC-MA heating. The PSC-MA heating experiments were carried out using a domestic MW system (as shown in *Figure 2*) having a frequency of 2450 MHz and a maximum power output of 1 kW. The

TABLE 1. PROXIMATE AND ULTIMATE ANALYSES OF OIL PALM BIOMASS

Biomass	Volatile matter, wt %	Fixed carbon, wt %	Ash content, wt %
Shell	78	20	2
Fibre	72.8	19.2	8
	C	H	O
Shell	50.1	6.85	41.15
Fibre	45.18	5.52	40.72

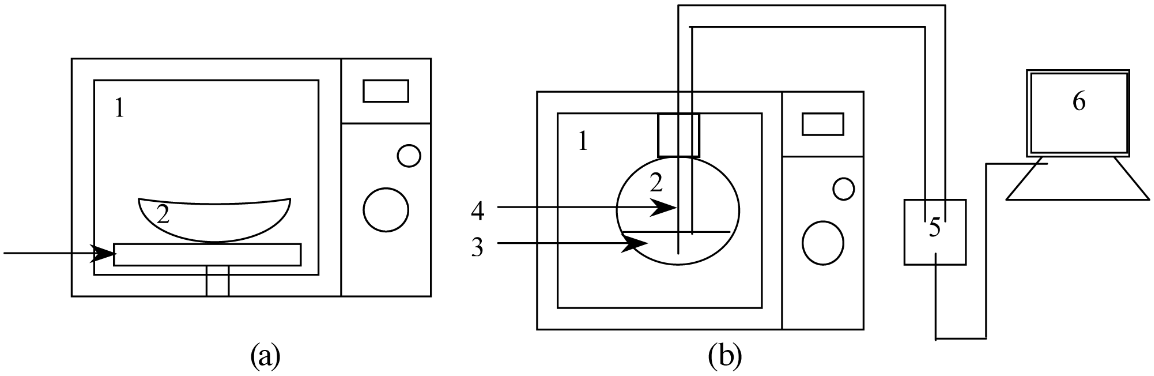


Figure 2. Schematic diagram of microwaves (MW) heating of palm shell char-microwave absorber (PSC-MA): (a) batch temperature measurement method: 1. microwave cavity, 2. ceramic dish, 3. turntable; (b) continuous temperature measurement method: 1. microwave cavity, 2. Pyrex round-bottomed glass reactor, 3. char bed, 4. thermocouples, 5. temperature data acquisition system, 6. personal computer.

turntable was used to measure batch temperature profiles at a rotational speed of 5 rpm (*Figure 2a*). However, this turntable option was detached in the latter part of the study, *i.e*. during continuous temperature measurements as shown in *Figure 2b*. The MW oven cavity was 336 × 241 × 349 mm with a volume of 28 litres. The MW system was equipped with a triple distribution system (TDS) as supplied by the manufacturer, which is supposed to evenly distribute MW throughout the interior of the oven because of the three antennae provided in such a system, consequently resulting in more uniform heating. This unique wave distribution system facilitates MW to penetrate into the materials from all sides.

To establish its batch temperature profile, PSC-MA was placed in a MW oven for varying time intervals ranging from 1 to 5 min and at various power outputs (100, 180, 300, 450, 600, 850 and 1000 W). Temperature was measured using an infrared pyrometer, model No. 08406-00 of Cole Parmer, Chicago, IL, USA, and the specifications of which are shown in *Table 2*. The temperature measured by this infrared pyrometer was cross-checked by a K-type thermocouple, and was found to be at almost the same value.

For the batch temperature measurement method, different amounts (10, 20 and 30 g) of PSC-MA were placed in a ceramic dish, and the dish was positioned in the centre of the turntable inside the MW cavity. This is because the MW energy was assumed to concentrate in the centre of the MW cavity as reported by Prosetya and Datta (1991). PSC-MA was heated under the set MW power and time. Temperature was measured immediately with the infrared pyrometer as soon as the MW irradiation ended. Heating time was limited to a maximum of 5 min. Experiments were done in triplicate, and the temperature readings were averaged. It should be noted that the infrared pyrometer could only read the PSC-MA surface temperature and not the core temperature of the material.

TABLE 2. INFRARED THERMOMETER SPECIFICATIONS

Temperature range	–18°C to 540°C
Accuracy	± 1% of reading or ± 1.0°C, whichever is greater at ambient operating temperature
Response time	350 m s

For the continuous temperature measurement method, the domestic MW system was modified to accommodate a round-bottomed Pyrex glass reactor of 2-litre capacity as shown in *Figure 2b*. In this case, the turntable was detached and removed. About 250 g of PSC-MA was placed inside the glass reactor. The heating was done without any stirring, *i.e*. the char bed was left static. Two K-type stainless steel thermocouples of about 2 mm thickness were positioned to measure the temperature continuously, T1 inside the char bed, and T2 just on the surface of the char bed. The vertical distance between the two thermocouples was about 0.02 m. PSC-MA was irradiated with MW power set at 180, 300 and 450 W for the desired time duration. In this experiment, it was not possible to exceed 450 W of MW power because the highest temperature recorded was about 1200°C, which was almost double the melting point of the Pyrex glass reactor (550°C). The experiments were conducted twice in this case, and the temperature profiles were found to be almost similar. It should be noted that the inside temperature refers to the interior of the bed region and not the particle core temperature, because in this study bulk temperature was measured rather than single particle temperature.

Pyrolysis of Oil Palm Biomass

The experiments on MW pyrolysis were carried out in a modified 1-kW domestic MW facility having a frequency of 2450 MHz. A schematic

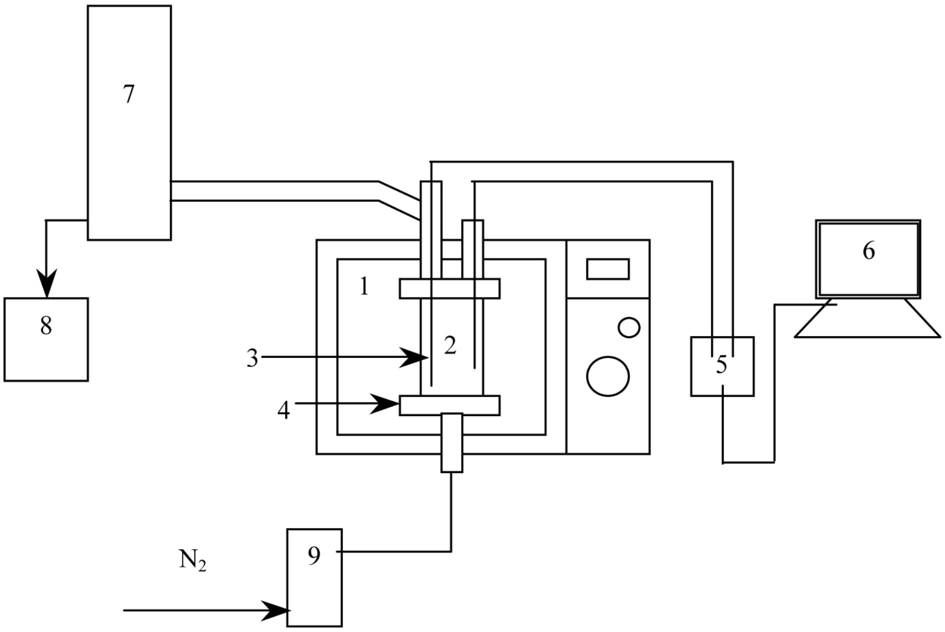


Figure 3. Schematic diagram of microwaves (MW) pyrolysis facility: 1. MW cavity, 2. quartz glass fluidised bed reactor, 3. thermocouples, 4. distributor plate, 5. temperature data acquisition system, 6. personal computer, 7. condensing unit, 8. bio-oil collector, 9. rotameter.

diagram of the experimental set-up for the modified MW pyrolysis system is shown in *Figure 3*. Different levels of MW power (100, 180, 300, 450, 600, 850 and 1000 W) could be selected for varying exposure times (1 to 90 min). The MW cavity was modified to accommodate a quartz glass reactor (0.1 m I.D. × 0.15 m height). This reactor was facilitated by a perforated steel distributor plate with 1-mm holes at the bottom. Both ends of the quartz reactor were closed with glass caps which were tightened by clips. These glass caps had suitable openings to facilitate the entrance of nitrogen gas from the bottom and the exit of pyrolysis vapors from the top. Measurements of the process temperature were done using two K-type metallic thermocouples connected to an 8-channel Pico data acquisition system (temperature accuracy of ±0.5°C, giving as many readings as possible per second) acquired from United Kingdom. This system was linked to a personal computer for continuous recording of data using the Picolog Software. Thermocouple T1 was inserted inside the bed region and T2 was held just above the bed surface, with a vertical distance of about 0.01 m between the thermocouples. The thermocouples were grounded to avoid any discrepancy in temperature readings or arcing due to the microwaves. However, for further reassurance, an infrared temperature pyrometer (temperature accuracy of ± 1°C) supplied by Cole-Parmer, Illinois, USA, was used. It was found that the metal thermocouple and infrared temperature detector readings were in close agreement with one another, having at most a difference of 3°C or 5°C when recorded at the end of the experiments. The surface temperature of the materials could be easily detected because the bed was static.

For each experiment, the amount of PSC-MA (25, 50, 100 wt %) in the oil palm biomass was varied and charged into the quartz reactor. Nitrogen gas at a flow rate of about 20 litres per minute (LPM) and at a purity of 99.96% was supplied before the initiation of the experiments to ensure an inert environment. During each experimental run, nitrogen gas was continuously supplied at a flow rate of about 10 LPM to maintain the inert environment as well as to sweep the vapour out of the reactor. The inert gas can also play an important role in preventing any possible explosion or hazard, thus taking care of safety issues during the experiments. MW power (450 W) and an irradiation time of 25 min were kept constant for each batch. The vapour generated out of the reactor was condensed into bio-oil (liquid) using a water-cooled condenser at a temperature of about 5°C to 8°C. The bio-oil remaining in the equipment was also determined via the weight difference of the equipment before and after the experiments. The remaining bio-oil was determined in the reactor, connecting tubes and condensing unit. All these equipment were made of glass and could be easily dismantled for weighing them individually, and could be reconnected for further experimental runs. Thus, total bio-oil and solid char residue were weighed at the end of the experiments to determine the yield. The yield of the flue gas was established by difference. All the experiments were repeated twice to verify the values obtained.

The temperature profiles were found to be more or less similar with small variations in the case of

OPF. Repeated determinations of the product yield showed variations of about 1 wt% to 2 wt%.

RESULTS AND DISCUSSION

Temperature Profiles

Figure 4 depicts the batch temperature profiles of PSC-MA during MW heating. It can be observed that the temperature depended on the duration of irradiation and the MW power applied. The temperature was also found to vary slightly with the weight of PSC-MA. From *Figure 4*, a MW power of 450 W and above was required to raise the temperature of PSC-MA more rapidly than with a lower MW power, *i.e.* 300 W and below. This was a significant finding in terms of revealing the operational power range of the microwaves. A gradual increase in temperature was found at a lower power input, *i.e.* below 450 W, which stabilised after certain time. Hence, irradiating the MA char at a low MW power even for longer time resulted in a plateauing temperature profile. The increase in the slope of the linear temperature profile at 450 W and above also proved that 450 W was the minimum MW power necessary to achieve the desired temperature. The present results show good agreement with those of previous researchers (Guo and Lua, 2000), who found that a power lower than 450 W increased the temperature slightly (~100°C) compared with a continual increase in temperature at a power of 450 W and higher. They also proved by proximate analysis of PSC subjected to different power and time that there was no weight loss found in the volatile matter and fixed carbon at MW powers of 80, 150 and 300 W regardless of the time duration. Therefore, it was confirmed that a minimum MW power of 450 W was required to increase the temperature rapidly. As reported by Ania *et al.* (2005), for carbonaceous materials to reach the desired temperature, the main factor to be modified or adjusted is the MW power output besides the dielectric properties of the carbon materials. *Figure 4* illustrates the sudden rise in temperature at a longer irradiation time (3 min and above) for a MW power of 450 W. This could be due to an increase in the absorbability of PSC-MA after a certain MW irradiation time, because irradiation time increased the specific surface area of the char (Miura *et al.*, 2004). Furthermore, this relates to the continuous carbonisation reaction taking place inside the char, thus providing new pores for reaction (Guo and Lua, 2000). Since the batch type of measurement recorded the temperature at the end of the MW irradiation, *i.e.* when MW was turned OFF, the temperature measured was at its lowest or after PSC-MA had cooled down. This

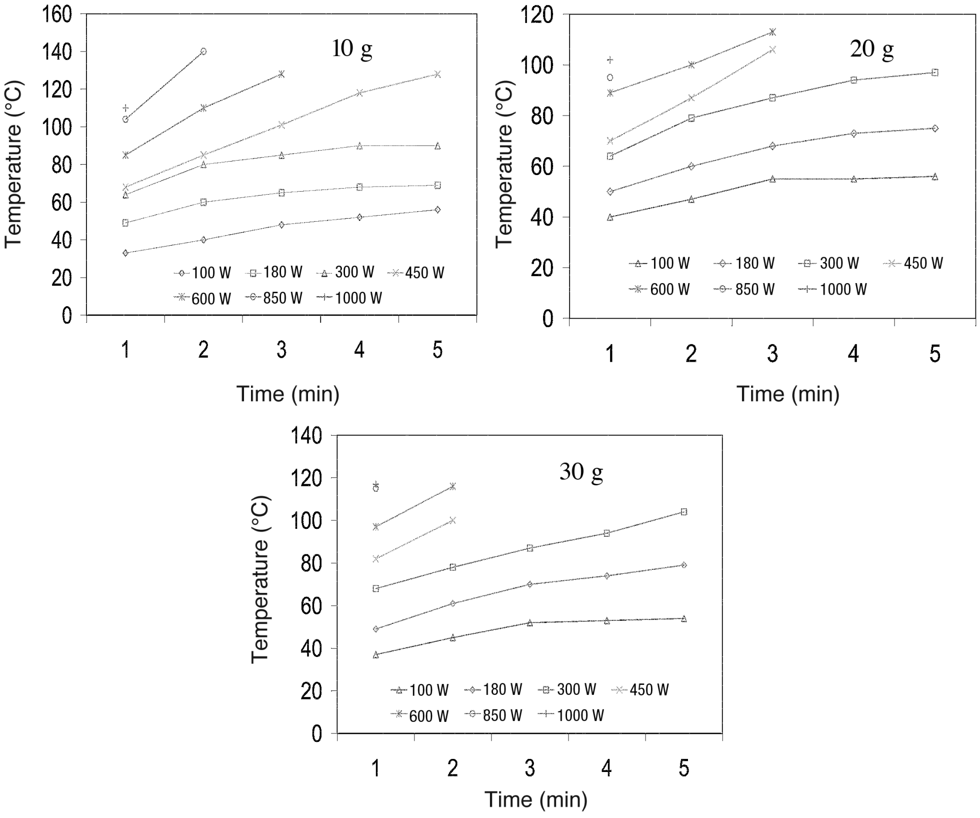


Figure 4. Batch temperature profiles of palm shell char-microwave absorber (PSC-MA) under microwaves (MW) heating at different power and weight of PSC-MA.

might provide misleading temperature profiles in a multimode domestic MW oven. PSC-MA might have reached a much higher temperature during the MW generation, *i.e*. in the ON mode or when MW were generated. Therefore, researchers should be cautious about the temperatures measured under such conditions. Hence, to investigate the real-time temperature profile of PSC-MA during MW irradiation, the continuous temperature measurement method should be implemented.

The temperature profile of PSC-MA at low MW power output was almost independent of the amount or weight of the char. However, some differences were shown at a higher power. Differences in heating rate (°C min^{-1}) of PSC-MA were observed at varying MW power and PSC-MA weight as shown in *Figure 5*. The heating rates of PSC-MA at low MW power input were nearly similar for all weights, but differed when the MW power output was increased from 450 W upwards. This could be related to the dielectric property of the char. It was reported by Challa *et al.* (1994) that the dielectric constant and loss factor of the char varied with temperature. Hence, an increase in dielectric property with temperature would have helped in improving the MW-absorbing capacity of the char with time. Another interesting finding was that the heating rate at 850 and 1000 W became almost stable as the PSC-MA weight was increased (*Figure 5*). This might have been due to saturation of the PSC MW-absorbing capacity at such high MW power.

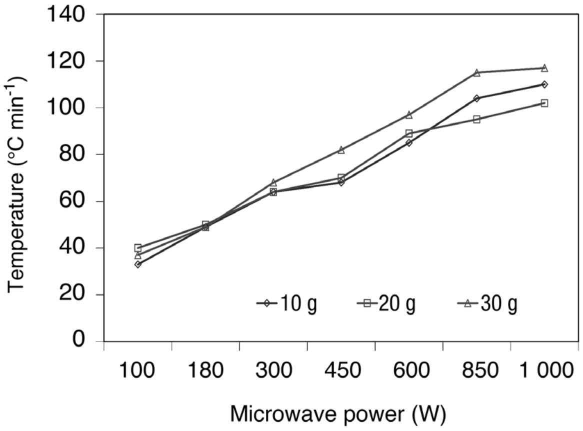


Figure 5. *Heating rate (°C min^{-1}) of palm shell char-microwave absorber (PSC-MA) during batch temperature measurements.*

During continuous temperature measurement, PSC-MA was subjected to MW irradiation at three different powers, *viz.* 180, 300 and 450 W, in a round-bottomed glass reactor. Such real-time continuous temperature profiles are depicted in *Figure 6*. This type of temperature profile was possible via the temperature data acquisition system using K-type metallic thermocouples (T1: temperature inside bed, T2: surface temperature of bed) positioned on the static material bed. The profile shows a

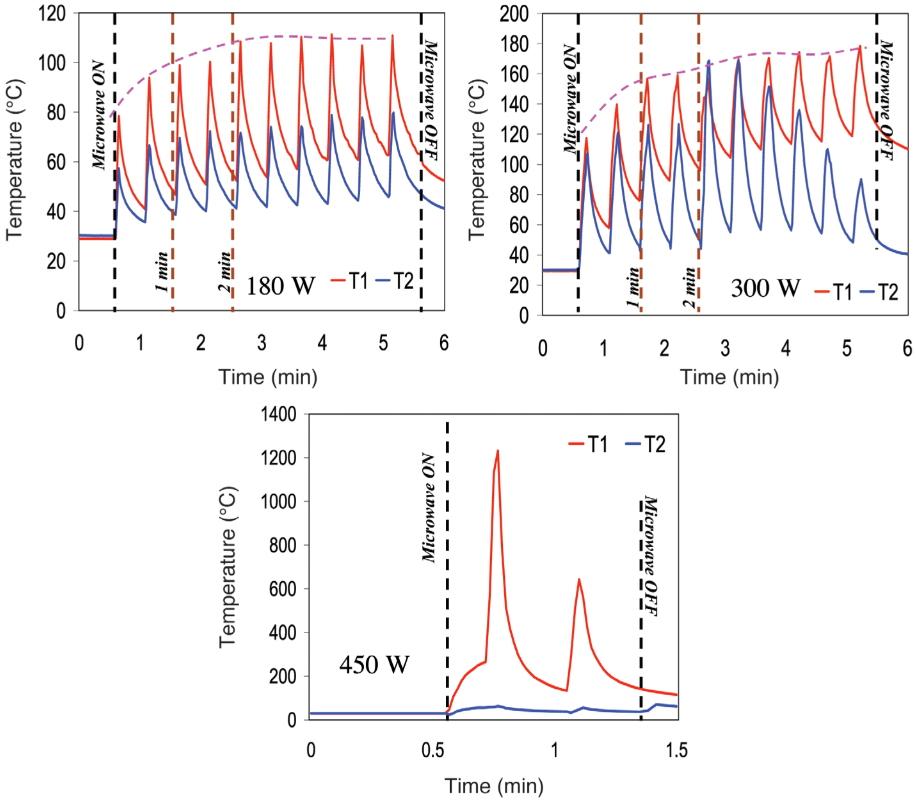


Figure 6. *Continuous temperature measured profiles of palm shell char-microwave absorber (PSC-MA) (weight of char = 250 g) T1: inside bed temperature, T2: bed surface temperature.*

sinusoidal wave pattern because of the cyclic (ON/OFF) operation of the magnetron (MW generator) as is commonly found in multimode domestic MW ovens. An almost similar temperature profile was reported by Will *et al*. (2004) for multimode MW ovens. The material showed the maximum temperature as a peak when the magnetron was ON (during the generation of MW). After this, the temperature of PSC-MA dropped instantly to a certain level as soon as the MW were OFF. This cyclic or variable power principle is found in all domestic multimode MW systems and is commonly known as duty cycle control (Thostenson and Chou, 1999). The molecules get excited only during interaction with MW (ON mode), leading to a sudden rise in temperature of the materials. Conversely, the rotational or vibration motion of the molecules ceases instantaneously when MW are turned off, thus leaving the molecules in random motion without any generation of heat. Interestingly, this cyclic type of temperature profile was observed for both the temperatures inside the bed (T1) and on the bed surface (T2). During the cyclic temperature profile, two peaks were normally observed after 1 min of irradiation as shown in *Figure 6*. Hence, this reveals that within 1 min the magnetron radiates the microwaves about two times. *Table 3* presents the temperatures at such peaks at intervals of 1 min duration. The peak temperature was observed to stabilise after 3 min of MW irradiation in the case of a MW power of 180 W (*Figure 6*). However, a gradual increase was found for a power of 300 W. In the case of 450 W, data on the temperatures were limited because the temperature had exceeded 550°C, which might have caused damage to the glass reactor if the experiment had been continued longer. Fortunately, the glass reactor was saved from damage because the temperature dropped immediately after MW were turned OFF. This study also confirmed the minimal MW power required to raise the temperature to a higher degree, and the result was also in total agreement with the batch measured temperature.

One of the important properties among the dielectric properties of materials is the penetration depth of MW into the materials. As penetration depth determines the heating characteristics of the materials, when the thickness of the materials is more than the penetration depth only the surface will be heated (Thostenson and Chou, 1999). As can be seen in *Figure 6*, the inside bed temperature T1 was higher compared to the bed surface temperature. This demonstrates that MW did penetrate the PSC-MA bed. This penetration depth was also reported to be dependent on the dielectric loss factor of the materials (Bradshaw *et al.*, 1998). It was also speculated that temperature uniformity might be affected by the MW penetration depth. Furthermore, non-homogeneity of the material cannot be ignored when there is a lack of temperature uniformity. For instance, the biomass char used in the present study consisted of numerous chemical entities, thus making them chemically inhomogeneous in nature.

Another significant effect found at the MW power of 450 W (*Figure 6*) was an abrupt increase in bed temperature T1 to about 1200°C in just 8 s. In contrast, to other power outputs such as 180 and 300 W, the maximum bed temperature T1 only reached about 110°C and 175°C, respectively. This large variation in temperature profile might be due to the presence of microplasma in the case of 450 W, particularly near the tip of the thermocouple T1. These microplasmas could be seen by the naked eye and were bluish in colour. No doubt the temperature at such a region might have been around 1500°C or even higher. Nevertheless, such microplasmas exist for only a few seconds. Hence, the results of this study concur with that of very latest observation furnished by Menéndez *et al.* (2010b). They examined the microplasmas while irradiating biomass char with MW. Hence, presence of microplasma could be the cause for the sudden increase in temperature at

TABLE 3. TEMPERATURES OF BIOMASS CHAR UNDER MICROWAVE IRRADIATION IN CONTINUOUS MODE

Microwave power, W	Time scale, min	Peak 1		Peak 2	
		T1	T2	T1	T2
180	0-1	78.44	57.20	93.82	66.52
	1-2	98.86	69.56	100.23	72.23
	2-3	108.34	71.59	107.71	74.04
	3-4	110.28	74.21	111.27	78.77
	4-5	106.83	77.85	110.84	78.94
300	0-1	117.38	104.97	139.58	115.96
	1-2	156.59	115.01	158.94	112.31
	2-3	157.13	167.76	169.47	168.81
	3-4	170.43	151.40	174.31	135.70
	4-5	171.61	102.03	178.39	87.02
450	0-1	1 231.57	62.75	642.36	48.07

450 W. According to the author's observations, the minerals and other inorganic constituents present in the char materials might have been responsible for creating such microplasma at the tips of the metallic thermocouples due to interaction with MW. However, such microplasmas were not observed at 180 and 300 W. The reason for such a discrepancy is not immediately known, but might be speculated upon. Certain minerals or inorganic compounds might be activated to a greater extent at higher MW power. The BET surface area of PSC-MA might also have played an important role in absorbing the microwaves.

Another important observation was that the inside bed temperature (T1) was higher than the bed surface temperature (T2) at all MW power outputs. This indicates that the temperature inside the PSC-MA bed was higher than its surface temperature. The batch temperature profiles corresponded to the PSC-MA surface temperatures because the former temperatures were measured using an infrared pyrometer which can only measure material surface temperature as mentioned before. However, in the continuous temperature measurements, two peaks were found in a 1-min cycle as discussed earlier. Therefore, the temperature measured at intervals of every minute in the batch method conferred the lowest temperature. In other words, the temperature determined by the batch method should be accepted with caution because it can mislead the temperature profile, specifically when measured in multimode domestic MW ovens. It is therefore important to observe and study the temperature profile of MA prior to the final pyrolysis process so that the pyrolysis temperature profiles can be accepted with confidence.

Oil Palm Biomass Pyrolysis

From the above PSC-MA temperature profiles and heating characteristics study, MW power of 450 W was selected to pyrolyse the oil palm biomass in order to obtain bio-oil. *Figure 7* exemplifies the temperature profiles of OPS and OPF biomass without any PSC-MA. It can be observed that the bed temperature (T1) reached a maximum of about 100°C and 80°C for OPS and OPF, respectively. Apparently, no pyrolysis or emission of vapour took place at this stage, although water vapour was noticed. This proved that these biomasses were poor MW-absorbers, a finding that agrees with those of a previous researcher, Kreiger-Brockett (1994). The increase in temperature at this stage was due to the presence of water in the form of moisture. As water is a good MW-absorber (Zhang and Datta, 2003) because of its dielectric property and polar nature (Kappe and Stadler, 2005), it can generate the heat within the biomass. Initially there was a sharp increase in temperature for OPS up to 4 min, thereafter almost stabilising. Once the water is evaporated from the biomass, other chemical constituents in the biomass do not absorb MW as readily. However, when the same biomass material converts into char form, the rate of MW absorption increases significantly, because carbon and other mineral or inorganic compounds (which are good MW absorbers) are formed. Therefore, only a marginal increase in temperature can be observed within the biomass. Interestingly, in case of OPS the bed surface temperature was higher than the temperature inside the bed (T2 > T1) which was in contrast to OPF where T1 > T2 (*Figure 7*). The temperature profile discussed here refers to the temperature of the bulk of particles, *i.e.* the bed region, and not that of a single particle. The distinction in temperature profiles between OPS and OPF as mentioned above could be due to a limited penetration depth of MW into the OPS biomass bed because of its physical properties. Basically, in its original form, OPS are hard nut shells. Another reason is that the BET surface area of raw biomass such as OPS was found to be much lower compared with that of PSC-MA. The surface area of PSC-MA increased drastically after its

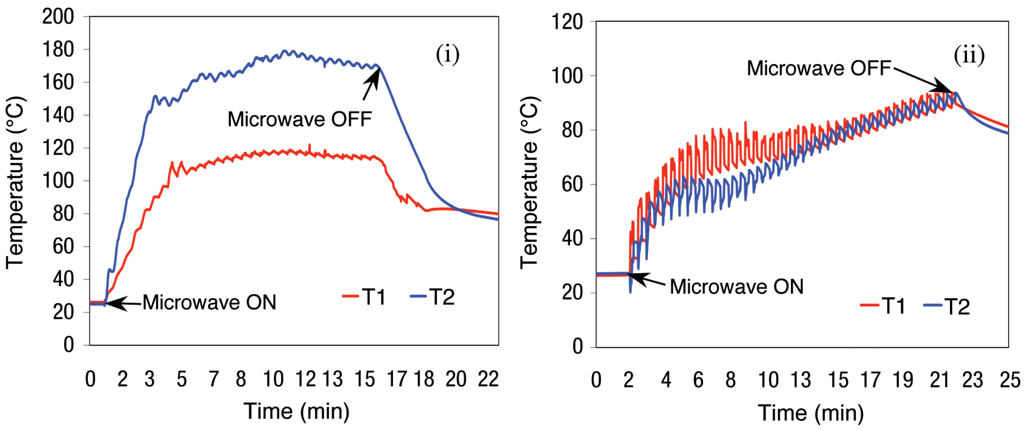
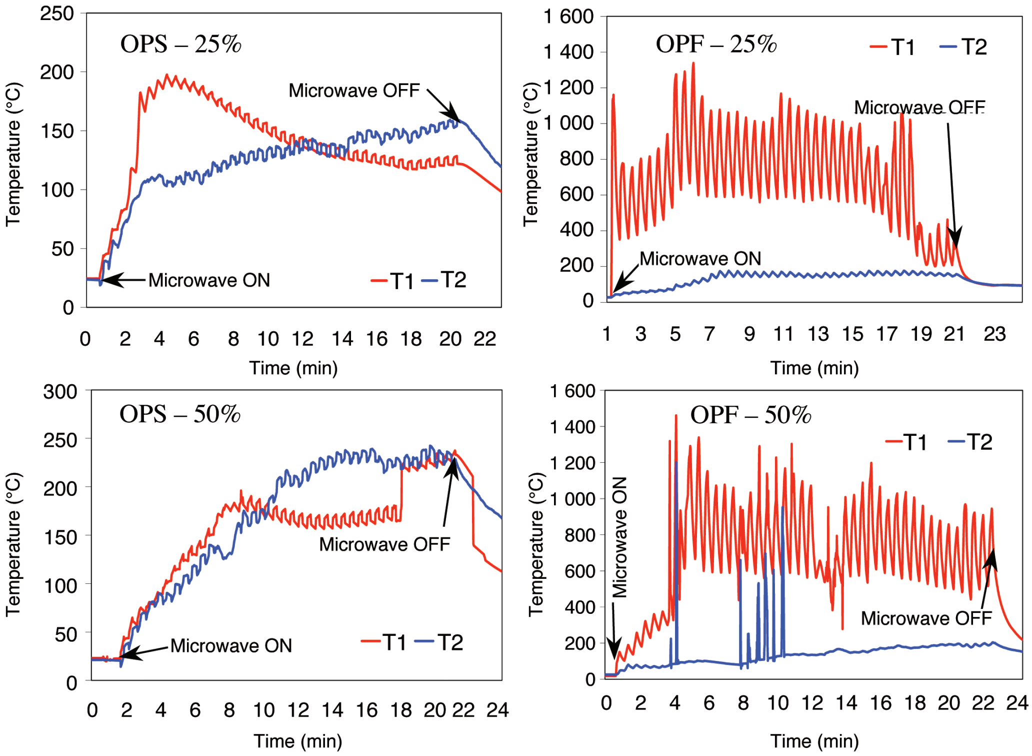


Figure 7. Real-time temperature profiles of (i) oil palm shell (OPS) and (ii) oil palm fibre (OPF) biomass without PSC-MA. T1: inside bed temperature, T2: bed surface temperature [microwaves (MW) power: 450 W].



Note: OPS – 25% : oil palm shell was mixed with 25 wt % PSC-MA.
OPF – 50% : oil palm fiber was mixed with 50 wt % PSC-MA.

Figure 8. Effect of palm shell char-microwave absorber (PSC-MA) percentage on real-time pyrolysis temperature profiles of oil palm shell (OPS) and oil palm fibre (OPF); T1: inside bed temperature, T2: bed surface temperature [microwaves (MW) power: 450 W].

thermo-chemical conversion, which significantly exposed the pores through which MW could be absorbed easily.

The addition of PSC-MA not only increased the temperature as illustrated in *Figure 8* but also initiated the pyrolysis process by generating vapours. The commencement of MW and generation of vapours were instantaneous. It appears that PSC-MA played a significant role by rapidly transferring the heat to the biomass materials via conduction. Once the raw biomass materials had converted into char, this fresh char was able to readily absorb MW directly via irradiation. Hence, the conduction mode of heat transfer is expected to dominate at the initial stage, with a gradual shifting towards the irradiation mode of heating. The bed temperature, T1, recorded for OPS at 25 wt% and 50 wt% PSC-MA was about 200°C and 237°C, respectively. Even though this temperature was below that reported by Islam and Ani (2000) to initiate pyrolysis (*i.e.* around 450°C), this was possibly because of the method of measuring temperature. The results also provided some interesting facts about low temperature pyrolysis which had otherwise been believed to take place rarely at such temperatures. Several possible reasons can be surmised at this stage. First, the method of temperature measurement during MW heating plays a role. This is because the core or centre of the biomass particles is at a higher temperature compared with the surface due to the penetrating nature of MW into the materials. In MW heating, the internal temperature of the sample is 10ºC to 100ºC higher than that of the surface temperature (Guo and Lua, 2000). Second, the hot spots in multimode domestic MW ovens can also mislead the actual temperature profile. Another reason may be the occurrence of low temperature pyrolysis of biomass in MW ovens as reported by Budarin *et al.* (2009). In their research, bio-oil was produced from wheat straw at a low pyrolysis temperature of about 120°C in a MW oven and within a very short time. They have reported that the release of volatiles at low temperature depends on the type of biomass and the additives used. This clearly shows that certain biomasses can be devolatilised even at a lower temperature under MW irradiation. However, in case of OPF, the temperature profile showed a much higher temperature compared with OPS. This could be due to the differences in the physio-chemical characteristics of the OPF biomass. Moreover, OPF is much lighter and smaller in diameter than OPS which is hard and thick.

The pyrolysis of oil palm biomass was carried out at 450 W of MW power. At less than this power neither did pyrolysis take place nor was any generation of vapour observed. The rationale behind this can be reconciled with the PSC-MA heating characteristics as shown in *Figure 6*, in that a temperature above 1000°C was achieved with a MW power of 450 W. It can also be observed from *Figure 6* that 180 and 300 W were not enough to achieve the desired pyrolysis temperature. A more comprehensive study on MW pyrolysis of OPS and OPF and their temperature profiles is reported and discussed in a recent article (Salema and Ani, 2011).

Finally, conventional pyrolysis requires proper preparation of the feedstock such as grinding, removal of moisture, *etc*., in order to enhance the heat and mass transfer to achieve a high bio-oil yield. Additional energy is needed to grind the particles to much smaller size, usually measured in microns. Furthermore, to remove moisture, the biomass has to be dried in an electric oven or similar equipment which also consumes energy. A unique finding from our present research was that the OPS biomass could be used as received without grinding, or removal of any moisture, or imposing other pretreatments. Such biomass can be handled by conventional pyrolysis but at the expense of heating rate, reaction mechanism as well as yield and quality of the bio-oil. Nevertheless, MW pyrolysis works better with large particle size and moisture because water is a very good MW absorber. Recently, a study by Zhao *et al.* (2010) also confirms the technical feasibility of considering large sized particles of biomass when using MW technology. Thus, according to our knowledge, the cost of grinding and removal of moisture can be avoided by employing a high heating rate, and a better product yield may be expected in MW-assisted pyrolysis. A similar conclusion was arrived at by Krieger-Brockett (1994). Rapid heating and instantaneous pyrolysis of biomass under MW irradiation contribute significant reductions in process energy and time.

Effect of the Microwave Absorber on the Pyrolysis Product Yield

Just as PSC-MA showed its effect on the temperature profiles of the oil palm biomass, it also induced a similar kind of effect on the yield of MW pyrolysis products, such as bio-oil, char and gas, at different ratios of biomass to PSC-MA as depicted in *Figure 9*. Maximum bio-oil yield for both types of oil palm biomass was obtained at 50 wt% PSC-MA. It should be noted that this bio-oil yield included the water content. Correspondingly, the lowest char yield was obtained at the same ratio. Most of the biomass was not pyrolysed maybe because of the small amount of PSC-MA; this consequently led to a lack of supply of heat to the whole biomass materials. Conversely, a higher amount of PSC-MA might have led to localised heating of the PSC material alone. The exact reason for this has to be investigated further and understood because the heating characteristics of MW were very fast. Uniform temperature measurement is also a difficult task in MW systems. In the present research, the maximum temperature attained by OPS at 50 wt% PSC-MA was 237°C, which is considered to be the initial degradation temperature for the release of volatile matters. Therefore, at this temperature low boiling volatile components might have condensed into the bio-oil, either leaving behind volatile matters in the char or entrained with flue gas because of the short residence time in the condensers. For OPF, such high temperature pyrolysis caused the yield of bio-oil to drop and increased the amount of gas. As a result, it can also be noted from *Figure 9* that the yield of bio-oil dropped much lower for OPF at 100 wt% PSC-MA compared with that of OPS. In addition, the catalytic cracking nature of the char plays a role in cracking the volatile matter released from the biomass materials (Lee *et al.,* 2005) into

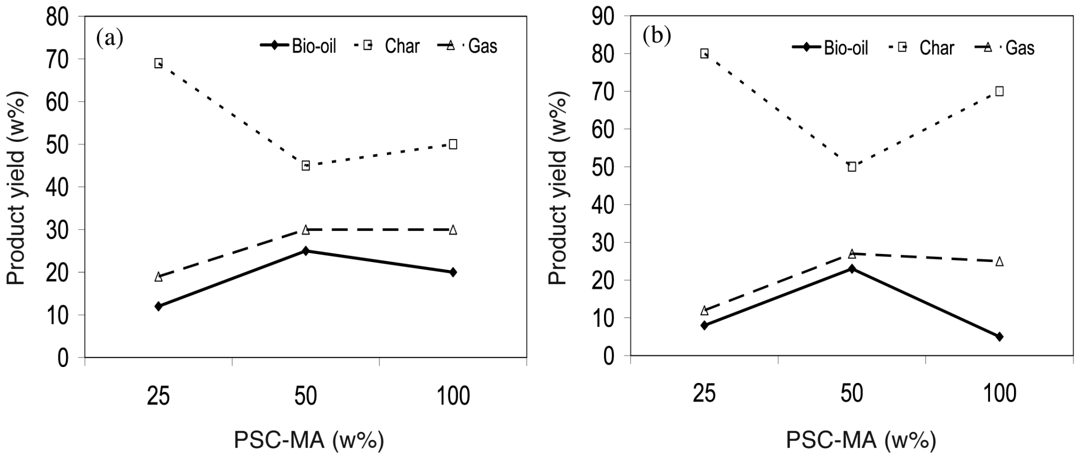


Figure 9. *Effect of palm shell char-microwave absorber (PSC-MA) on the yield of (a) oil palm shell (OPS) and (b) oil palm fibre (OPF) pyrolysis products [microwaves (MW) power: 450 W and time: 20 min].*

gaseous products. Hence, PSC-MA used during MW pyrolysis may also have been responsible for cracking down the volatiles released due to secondary reactions which led to the production of gas rather than condensing into bio-oil. However, this may also depend on the cracking time and on the intimate contact between the volatiles and the solid char materials (Fagbemi *et al.,* 2001). Fagbemi *et al.* also found that the metallic content in the ash is responsible for the catalytic cracking of organic volatile matters in the vapour. The effect of catalytic cracking of the char becomes even more prominent at a low temperature than the actual vapour residence time (Wang *et al.,* 2005).

Thus, the addition of MA (Guo *et al.,* 2006) or additives (Kreiger-Brockett, 1994; Budarin *et al.,* 2009) significantly affects the yield of bio-oil. For instance, a study by Guo *et al.* (2006) shows that the optimal ratio at which maximum bio-oil yield was obtained was 3:1 for glycerol to biomass, and 2:1 for ionic liquid to biomass, respectively, under MW irradiation. However, they used liquid as a MA medium rather than biomass char like in our case. Nonetheless, detailed understanding of the role of MA on the yield of bio-oil is still at its infancy. Lastly, it is apparent from the present study that MA or a catalyst does affect the yield of pyrolysis liquids and other products.

CONCLUSION

The heating characteristics of PSC-MA in terms of temperature profile show encouraging results for the use of oil palm biomass char as MW receptors for poor MW-absorbing materials. An MW power of 450 W and above was found to be suitable for the effective heating of PSC-MA in the present experimental work. Continuous temperature measurements of PSC-MA depicted sinusoidal temperature profiles while batch temperature measurements showed linear profiles in a domestic microwave system. It is recommended that the temperature be recorded continuously during the MW operation in order to avoid misleading temperature measurements. OPS biomass revealed low temperature MW pyrolysis compared with high temperature pyrolysis for OPF. A minimum MW power of 450 W was required to carry out the pyrolysis process. Moreover, PSC-MA caused a significant change in the pyrolysis process as well as in the yield of products (bio-oil, char and gas). High temperature can be achieved within a few seconds, and thus can save considerable time and energy. This was achieved by using eco-friendly PSC-MA that showed efficient heating characteristics, and assisted in carrying out the pyrolysis at low MW power. In other words, it is also feasible to pyrolyse biomass materials with large size and different physio-chemical characteristics with less power consumption under MW irradiation. However, future work on energy distribution and calculation may lead to more confidence in the MW pyrolysis process for biomass materials.

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