Pyrolysis Heating Performance of Oil Palm Shell Waste Biomass with Carbon Surfaces

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Abstract

Bio-fuels from solid waste biomass have been projected to provide renewable energy for the future. The thermal conversion of waste biomass to bio-fuels requires the development of energy efficient and quick heating processes. For this reason, Microwave (MW) heating process has attracted great attention in achieving quick heating conditions. In this study, solid Oil Palm Shells (OPS) waste biomass was subjected to multimode MW pyrolysis system operated at 2.54 GHz frequency with coconut activated carbon (CAC) surfaces. The effects of increasing OPS loading were investigated at 300 W, 35 wt% CAC loading and 4 liter per minute (LPM) of N_2 on pyrolysis heating performance, bio-oil yield and composition. The results indicated that increase in OPS loading provide slow heating of biomass solids. However, the final temperature reached in biomass solids were found encouraging in initiating pyrolysis conditions. 150g of OPS loading demonstrated quick and nearly uniform process heating compared to 175g and 200g OPS loading. The highest bio-oil yield of 31.76 wt% was obtained with 200g OPS loading. The phenols in the bio-oil detected remained 58.02-66.67 %GC-MS area. The findings of this study reveals that the heat generated from carbon surfaces and carried with N_2 gas can improve pyrolysis heating conditions in OPS solids at fairly low MW power, which can save process energy. The high phenols in bio-oil suggest potential use as chemical feedstock in petrochemical industry.

Keywords: Microwave Pyrolysis; Carbon Surfaces; Loading; Heating Profile; Bio-Oil Yield; Bio-Oil Composition.

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INTRODUCTION

The conventional fossil fuel resources, crude oil and natural gas still remain the dominant source of energy to power our modern societies. These finite fuel resources are considered valuable source of natural energy. However, their increasing supply and production has shown great concerns over fuel source depletion (BP, 2016). In addition, rising levels of CO_2 emissions from fossil fuel combustion has augmented search for alternate and renewable liquid and gas fuels. These concerns motivated scientists and researchers to explore sustainable and environmental friendly fuels. For this, waste biomass resources are considered renewable and CO_2 neutral. Over the recent decades, attempts to produce targeted liquid and gas fuels from waste biomass have captured growing attentions.

Waste biomass can be converted to fuels by combustion and pyrolysis methods. Among these, fast pyrolysis offers the most attractive method of converting waste biomass to liquid fuels at shorter duration (Bridgwater, 1999). Despite various developments in fast pyrolysis processes, it still faces technical challenges in improving biomass conversion and energy efficiency (Huber and Brown, 2017). Microwave (MW) pyrolysis of waste biomass offers a distinct heating approach, where the MW energy interacts with the moisture and other inorganic species present in waste biomass at molecular level, thereby converting MW energy to heat energy resulting in volumetric heating of solids. On the contrary, fast pyrolysis method requires the presence of external heating source to reach pyrolysis conditions requiring addition heat input source.

The presence of inherent moisture and inorganic species in waste biomass shows some improved MW absorption capacity. However, after the removal of moisture, the heat generated by the inorganic species is not enough to bring pyrolysis conditions. Therefore, suitable material is required with waste biomass to support pyrolysis conditions. Menéndez et al. (2010) discussed various carbon materials capable of converting good amount of MW energy to thermal energy, which can then be transmitted to the surrounding solids to improve pyrolysis conditions. In addition, carbon materials have been reported to improve targeted fuels by in-situ upgrading of pyrolysis vapours (Bu et al., 2011). The two-fold functions of carbons during MW pyrolysis provided a challenging environment to treat waste biomass to recover liquid fuels. The major technical challenges faced of using carbons with waste biomass in MW pyrolysis environment have been addressed (Mushtaq et al., 2014d). One critical challenge is the formation of hotspots. Hotspots are the regions created mainly as a result of non-uniform distribution of carbons with pyrolysis solids and increased MW energy absorption of carbons resulting localized heating regions. These localized regions create non-uniform heating affecting solid conversion and deteriorating pyrolysis reaction mechanism. We proposed and tested novel method of controlling the hotspots by distributing carbon surfaces over pyrolysis solids (Mushtaq et al., 2015; Mushtaq et al., 2014a; Mushtaq et al., 2014b; Mushtaq et al., 2014c; Mushtaq et al., 2016). This method not only controlled the hotspots to confined carbon surfaces but also heated the supported pyrolysis solids to reach pyrolysis conditions.

The primary aim of this research was to investigate the pyrolysis heating performance of waste biomass with carbon surfaces at increasing solid load. This loading environment will be helpful in determining the optimum loading capacity and process scale-up. The online pyrolysis process temperature, product distribution and bio-oil composition were compared and reported.

MATERIALS AND METHODS

The Oil Palm Shell (OPS) waste biomass was obtained from oil plam mill operated near Johor state of Malaysia. The moisture content present in as-received OPS nuts was determined 8.5 wt%. The lignocellulose content of OPS was reported 31% of cellulose, 20% of hemicellulose and 49% of lignin (Mae et al., 2000). The as-received OPS nuts were grounded to uniform particles size of 300-600 µm and used directly in MW cavity environment. The commercial grade Coconut Activated Carbon (CAC) was obtained from Kekwa Indah Snd Bhd, Malaysia. The as-received CAC solids were dried in conventional heating furnace at 105 ^{o}C for a maximum duration of 24 hours and sieved to obtain uniform particle size of 0.2-0.3 cm. The main purpose of drying CAC prior to use is the formation of plasma during MW heating environment (Mushtaq et al., 2015) which resulted in thermocouple arm meltdown during preliminary studies. The selection of the significant process variable under MW irradiation environment was based on Mushtaq et al. (2014d).

The MW pyrolysis experiments were performed in modified multimode MW system operated at fixed MW power of 300W at a frequency of 2.54 GHz. The details of experimental setup can be seen in (Mushtaq et al., 2015).The pyrolysis experiment was carried out for a maximum duration of 40 minutes. The MW pyrolysis system consisted of glass quartz reactor with wire mesh screen support, N_2 supply system, glass condenser connected with water recirculation chiller, data acquisition system for continuous monitoring of process temperature. Initially, the MW heating performance of pure OPS of 150g was investigated with 300W and 4LPM N_2 flow rate. The heating profile of the pure OPS sample was monitored by two thermocouples. These thermocouples were placed into the sample bed (in the middle of pure sample) and near the sample surface denoted as T_B and T_S, respectively. Finally, three representative samples of 150g, 175g and 200g loading capacity were prepared and tested. The maximum weight of the sample was selected based on the reactor dimensions. The pyrolysis heating performance was carried out fixed loading of 35 wt% CAC. This CAC loading was selected since below this value CAC particles did not fully covered the OPS particles and lacked of performing as carbon surface. During sample loading and preparation method, three layers of OPS and CAC solids were uniformly distributed in the MW quartz reactor. Each of the two materials were distributed uniformly and alternately in the reactor system forming the pattern OPS-CAC-OPS-CAC-OPS-CAC (bottom to top). In 3-surface distribution method, thermocouples were labelled as T_{UBS}, T_{MBS} and T_{BBS} to measure the temperature of Upper Biomass Surface (UBS), Middle Biomass Surface (MBS) and Bottom Biomass Surface (BBS), respectively as shown in Figure 1. In this study, CAC surface temperature profiles are not reported. N_2 gas was supplied at flow rate of 10 Litres per Minutes (LPM) to achieve pyrolysis atmospheric. The pressure in the quartz reactor was maintained at 1 atm. The temperature of re-circulation water in condenser was maintained 2-4 ^{o}C with continuous supply of

N_2 gas at 4 LPM. The bio-oil, bio-char and gas yields were measured using material balance method.

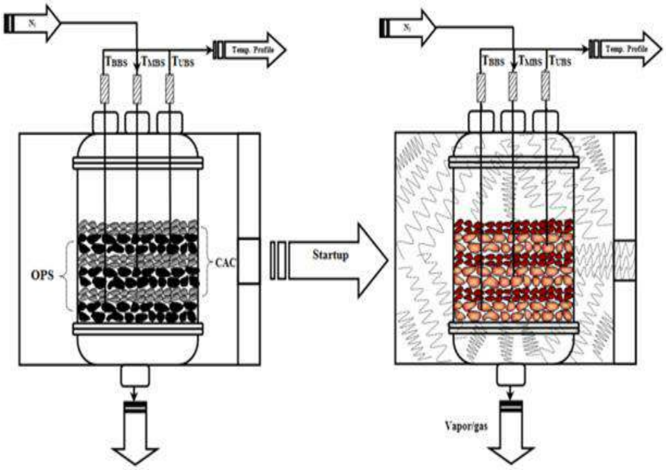

Figure 1: Distribution of OPS and CAC surfaces with thermocouple locations/labels (Mushtaq et al., 2016).

Temperature measurement

The pyrolysis process temperature was measured by carefully inserting three high temperature thermocouple probes (Coleparmer, model 0507979B-K) in the OPS solid surfaces and connected with data acquisition system (Picolog data logger and acquisition system model TC-08) for the online temperature measurement.

GC-MS analysis of the bio-oil

The bio-oil chemical composition were analyzed with Agilent Technologies 6890 GC-MS equipped with HP-5MS capillary column 30m length and 0.00025m diameter. The GC oven temperature was steady raised from initial temperature of 80-200°C at the rate of 10°C/min, and then to 300°C by maintaining 5°C/min. The final oven temperature of 300°C was held constant for about 10 min. Helium gas flow rate was maintained at 2 ml/min. The GC was connected to Agilent Technologies 5975 series Mass Spectroscopy (MS) equipped with inert Mass Selective Detector (MSD) operated at scanning acquisition mode. The MS conditions were: mode Electron Ionization (EI), ion source temperature 230°C, emission current 34.6 µA, ionization energy 70 eV, full scan range of 50-550 and quantification by Selected Ion Monitoring (SIM) mode. The Agilent Chemstation software was used to identify chemical compounds and peaks with the help of NIST library.

RESULTS AND DISCUSSION

Effects on process temperature

The MW heating behaviour of pure OPS solids (without any CAC surface) at 300 MW power and 4 LPM of N_2 flow rate is shown in Figure 2 (a). The heating profiles of pure OPS under MW operating conditions were found to control surface and bed heating rate, and maximum surface and bed temperature. During pure OPS experiment, essentially no pyrolysis took place. However, mild vapours were generated. These pyrolysis vapours were observed for extended duration with some vapours deposition inside the condenser and reactor wall, but essentially no pyrolysis oil was collected. Nonetheless, only water was collected during pure OPS pyrolysis experiment. Moreover, the final temperature was found much limited. The pyrolysis surface temperature profiles of OPS solids at 300W, 35wt% CAC loading at 4 LPM of N_2 gas is shown in Figure 2 (b)-(d). The heating profiles indicate that the biomass surfaces showed difference in heating rate and final pyrolysis temperature. With all three loading environments, the biomass surfaces demonstrated slow heating rate during drying phase. However, increased in heating rate was observed after drying stage.

The difference in heating rate can be associated to the difference is physiochemical properties of biomass solids. With 150g loading, the upper and middle biomass surfaces showed improved heating compared to bottom biomass surface (Figure 2, (b)). The quick heating of upper and middle biomass solids can be associated to quick heating of thin top CAC surface when incident with MW energy, this heat generated can then be used to heat inside biomass and CAC surfaces. However, the heating rate of bottom biomass solids can be referred to heat transfer limitation to supported CAC surface. With 150g loading, final temperature reached in biomass surfaces were observed T_{UBS}= 414°C, T_{MBS}= 403°C and T_{BBS}= 324°C, which sustained for longer pyrolysis duration. With increase in loading to 175g (Figure 2, (c)), upper, middle and bottom biomass surfaces showed slow heating rate compared to 150 g loading (Figure 2, (b)). The slow heating of biomass surfaces demonstrate that the incident MW energy is mainly used to heat thick top CAC surface resulting delayed heating of inside CAC and biomass surfaces. Further increase in loading to 200g demonstrated the similar effects (Figure21, (d)), however, the final temperature reached in middle and bottom biomass surfaces reached to higher pyrolysis temperature of T_{MBS}= 482°C and T_{BBS}= 446°C, compared to upper biomass surface of T_{UBS}= 313°C. The slow rise in T_{UBS} can be referred to the existence of thick CAC surface which might cause delayed simultaneous heat transfer to OPS solids. From the comparison of heating profiles of biomass surfaces (Figure 2, (b)-(d)), It can be clearly seen the 150g loading conditions favoured higher heating rate and sustained pyrolysis conditions for longer pyrolysis duration compared to 175g and 200g loading environment. At this stage, it can be suggested that higher loading of biomass and carbon solids when subjected to MW heating environment will affect biomass conversion. Therefore, optimum biomass and carbon solids loading shall be investigated for improved heating rate with sustained pyrolysis conditions for complete conversion of biomass solids. During optimization of solids loading in MW cavity environment, the difference in physiochemical properties of biomass and carbon solids and MW reactor dimensions shall be taken in to account.

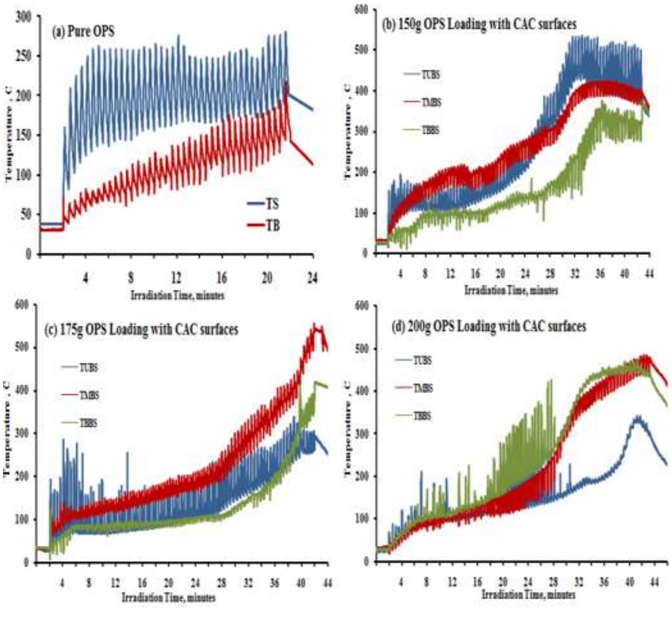

Figure 2: Biomass surface temperature profiles at various loading environment

Effects on product distribution

The effects of biomass loading on pyrolysis product distribution are shown in Figure 3, (a). The bio-oil yield remained fairly constant of 28.17-31.76 wt% with highest bio-oil production at 200g OPS loading. The increase in OPS loading demonstrated increased bio-oil production. However, char yield was found lowest of 45.71 wt% at 200g OPS loading compared to 150g and 175g OPS loading measured at 51.45 wt% and 52.31 wt%, respectively. The higher bio-oil yield with lowest detected char yield at 200g OPS loading indicated that higher temperature pyrolysis conditions could have improved biomass conversion. The slight increase in gas yield at 200g OPS loading suggest that cracking of pyrolysis vapors. Therefore, conditions favourable for higher bio-oil yield with minimum char and gas yield shall be investigated independently.

Effects on bio-oil composition

The chemical composition of the bio-oil obtained under various OPS loading environment are shown in Figure 3, (b).

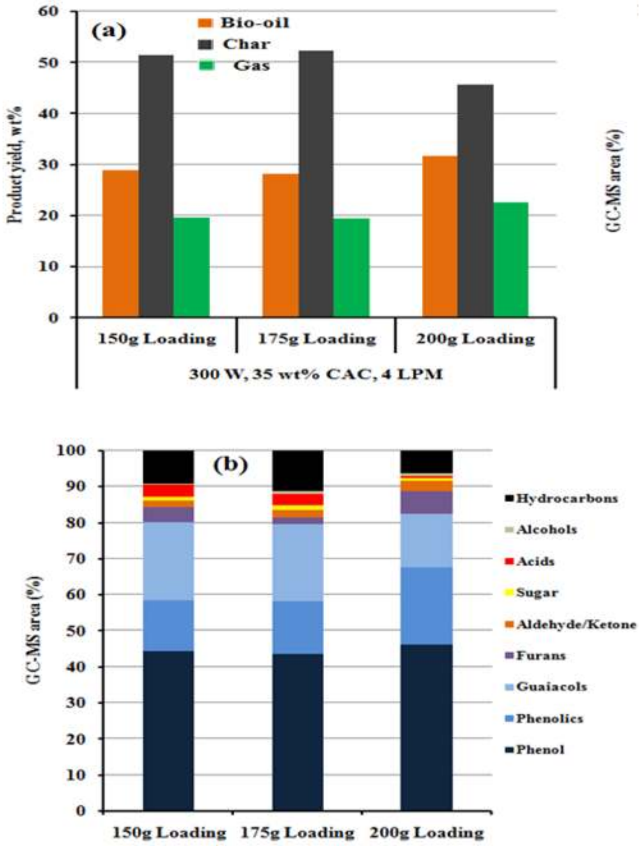

Figure 3: (a) Pyrolysis product distribution, (b) bio-oil composition.

The %GC-MS reported of the bio-oil are classified into pure chemical and chemical groups. The main pure chemical present in bio-oil include phenol of 44.29-46.13 %GC-MS area. The phenolics present was detected 14.07-21.54 %GC-MS with highest production at 200g OPS loading. The guaiacols were detected higher of 21.55-21.81 %GC-MS area at 150g and 175g OPS loading compared to 14.64 %GC-MS area with 200g OPS loading. The results indicated that the OPS loading environment did not affected the pure phenol content in bio-oil, however the formation of phenolics and guaiacols inter-changed to some proportion. The highest pure phenol and phenolics with lowest guaiacols formation at 200g OPS loading suggests that uniform process heating of OPS surface with optimum temperature to minimize secondary cracking and successive in-situ catalytic upgrading of pyrolysis vapors over carbon surfaces could result in improved phenol production.

CONCLUSIONS

The effects of OPS loading were investigated to compare the heating performances of biomass solid surfaces, pyrolysis product yield and bio-oil composition under MW cavity environment. The results of this study suggest that the heating performance of biomass surface depends on the OPS loading. At low biomass loading, the CAC surfaces are quickly heated by incident MW energy and simultaneous heat transfer to successive OPS and CAC surfaces resulting in sustained pyrolysis conditions with minimum final temperature difference. At high loading environment, OPS solids demonstrated slow heating rate with significant differences in final pyrolysis temperature. However, the major technical challenge is to achieve complete uniformity of process temperature, which requires heat balance between the incident MW energy, heat generated by carbon and OPS solids and heat carried away with inert gas. The uniform process heating of biomass solids in the presence of carbon surfaces at optimum temperature for sustained pyrolysis duration can improve biomass conversion, bio-oil yield and pure phenol content. The presence of higher phenol and phenolics in bio-oil suggests alternative fuel to petroleum based petrochemicals.

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