Title: A study on experimental characteristics of microwave-assisted pyrolysis of palm kernel shell

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Abstract:

Pyrolysis of palm kernel shells was successfully done via microwave-assisted carbonization system with different microwave power levels at a fixed reaction time, nitrogen flow rate and sample mass of 30 minutes, 150 mL/min and 40 g, respectively. Temperature profiles, temperature rising rate and the char properties were analyzed in order to determine optimum conditions of the pyrolysis process using thermogravimetric, elemental and FTIR analysis. Increasing microwave power levels resulted in increasing of maximum reaction temperature as well as the temperature rising rate, with lower char production. The chars obtained at power 300, 600 and 1000 Watt have comparable properties in terms of fixed carbon, volatile matter contents and the calorific values with an average values of 60 wt%, 35 wt % and 30 MJ/kg, respectively. Evidently, low microwave power of 300 Watt was sufficient enough for a complete pyrolysis of palm kernel shells, thus proving that 300 Watt is the best power to obtain high quality chars for further applications in the industry.

Keywords: microwave-assisted pyrolysis, palm kernel shell, char

Introduction

The world is currently relying on fossil fuels for power generation. However, continuous depletion of the sources, instability market prices, and massive CO_2 emissions leading to global warming are among the drawbacks of utilizing the non-renewable energy sources (Mohamed and Lee, 2006). World energy crisis that reached the boiling point in 2008 triggered pandemic of global insecurity, questioning the stability and sustainability of fossil fuels to meet the demands for the primary energy sources worldwide (Kijärstad and Johnsson, 2009).

Lavish attentions are being paid on biomass to be developed as among the most potential alternative energy due to the continuous availability, extremely low cost in comparison to other sources as well as the environmental-friendly factors since it produces zero emission of CO_2 and other polluting by-products (Demirbas et al., 2009). Biomass-to-energy field has grown tremendously and researches to exploit and fully utilize them for replacing natural energy sources are of paramount important. Thus, it is imperative to explore all opportunities and widen the scopes of biomass-to-energy conversion field to harness its true potential as well as reducing the global dependency on the fossil fuels.

Malaysia has become the largest producer and exporter of palm oil products, namely crude palm oil (CPO) and crude palm kernel oil (CPKO), thus it is not surprising that the industry contributes massive amounts of the wastes such as empty fruit bunches, palm mesocarp fibres, palm kernel shells and etc. These wastes are normally used as fuel sources to generate energy required for the operation of the mills, however the methods are inefficient as they contribute to the environmental issues such as pollutions (Yusoff, 2006). Studies had been done to convert these wastes to more useful, value-added products through thermochemical conversion processes such as bio oil and bio char (Kim et al., 2010). Among the thermochemical conversion processes, pyrolysis was found to be the best, viable method in upgrading lignocellulosic materials such as palm oil wastes. It is a thermal destruction process in the absence of oxygen, cracking the polymeric structure of lignocellulosic materials and converting it into gasses, tar/liquid and carbon rich, solid residue known as char (Goyal et al., 2008). The solid fraction draws major attention since it can be widely used as an activated carbon or potential clean solid fuel for combustion due to its higher fixed carbon contents and calorific value compared to the raw waste (Yanik et al., 2007).

For the past few decades, microwave has been widely used as an energy conversion tool of biomass samples, including sawdust (Wang et al. 2009), coffee hulls (Dominguez et al., 2007), rice hulls (Hu et al., 2008) and sewage sludge (Menendez et al, 2005). Rapid reaction time, uniform sample heating due to its volumetric heating properties, and cost saving overcome the drawbacks of conventional heating methods using furnace, fluidized bed reaction etc (Thostenthon and Chou, 1999). Evidently, biomass can successfully be converted into solid (char), liquid (bio-oil) and gas fractions using microwave system. The char produced has upgraded properties in comparison to the raw biomass including higher fixed carbon and calorific value content, and lower ash and volatile matters content, making them useful for various applications such as activated carbon, feeding materials for boilers and carbon nanotubes (Goyal et al., 2008).

Pyrolysis of PKS was investigated using microwave-assisted pyrolysis system to study the effect of microwave power on the product distribution yields and the quality of the char produced. As far as the authors are aware, there are very few discussions on the microwave assisted pyrolysis of PKS (Selema & Ani, 2011), and effects of microwave power on pyrolysis performance including the maximum reaction temperature, temperature rising rate, product distribution yield as well as the quality of the char produced are even less explained. Thus it is imperative to understand the trends before the potential energy values of PKS could be fully harnessed. The aims of this study are to obtain high quality char from PKS at low microwave power level for the purpose of energy saving as well as to reduce the cost of char production. Low microwave power levels that produce high quality char; with high fixed carbon and calorific values from the pyrolysis process was found to be necessity in this study before any further application of utilization in the industry could be explored.

Materials and Methods

Materials

Palm Kernel Shell (PKS) was kindly supplied by a local palm oil mill in Kedah, Malaysia. The sample was cleaned and dried overnight at oven temperature of 80°C. Then the sample was pulverized and sieved through a progressively finer screen to obtain a particle size of < 212 μm. Proximate, ultimate analysis and calorific values of raw PKS sample were shown in Table 1.

Table 1: Sample assays of palm kernel shell (PKS).

Analyses	**PKS**
Proximate analysis (db) [wt%]	
Volatile matter	77.5
Fixed carbon	20.3
Ash	2.2
Ultimate analysis (daf) [wt%]	
Carbon	47.5
Hydrogen	7.9
Nitrogen	1.6
Sulphur	0.6
Oxygen[a]	42.4
Calorific value [MJ/kg]	16.3

[a]calculated by difference

Experimental set up

Pyrolysis of PKS was carried out in a fabricated microwave, model Panasonic NNJ-993 with a maximum power of 1000 Watt at frequency of 2450 MHz. Schematic diagram of the microwave-assisted pyrolysis system was shown in Figure 1. PKS is one of biomass samples that have very poor absorbance properties towards microwave irradiation. Thus, the system was improved with carbon bed surrounding the sample quartz reactor to overcome the problem. PKS sample was placed in the reactor and subjected to microwave irradiation with nitrogen gas used as inert carrier gas. Final temperature of the sample during pyrolysis process was measured using type-K thermocouple. The condensable volatile matters were collected using condenser with cooling water at a constant temperature of 0-5 °C. Solid and liquid fraction was determined from weight change before and after the reaction completed, while gas fraction was taken by differences. All experiments were replicated to ensure constant results and avoid error of uncertainties.

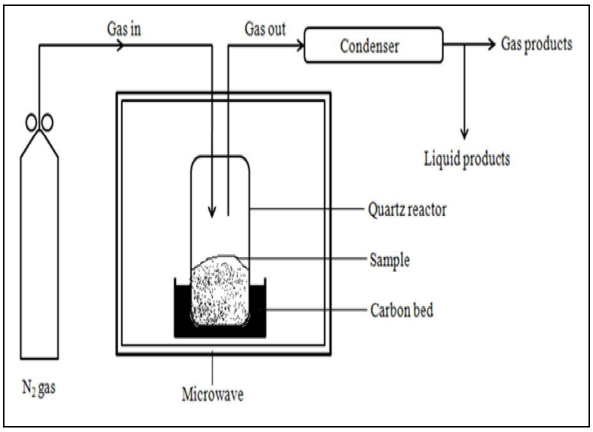

Figure 1: Schematic diagram of microwave-assisted pyrolysis system.

Sample Analyses

Proximate analysis was done to determine the percentage of moisture, volatile matters, fixed carbon and ash content in the sample using Thermogravimetric Analyzer, DTA/DSC TA Model SDT Q600 according to the ASTM D297 under nitrogen gas atmosphere. Ultimate analysis was done using Elemental Analyzer CHNS-932 series model with helium gas as carrier to determine the percentage of C, H, N and S. The percentage of oxygen was determined by difference. Calorific value of the sample was determined using Bomb calorimeter Leco AC-350 model according to ASTM D5468.

Results and discussions

Temperature profiles

Table 2 showed maximum temperatures achieved during pyrolysis of PKS sample at different power levels of microwave irradiation. It was clearly shown that the maximum temperature was directly proportional to the microwave power level used for the pyrolysis process. The stronger the power used, the higher the maximum temperature measured by the thermocouple. The main reason is that as the microwave penetrated the sample, rapid movement of the sample at molecular level resulted in heat generation. Higher microwave power used causes faster movement of the sample molecules, resulting in the sample being heated, from inside out, faster than using low microwave power (Thostenhon & Chou, 1999).

Table 2: Maximum temperature achieved with different microwave power levels.

Microwave power [Watt]	100	300	600	1000
MaximumTemperature[°C]	173	511	692	742

Figure 2 showed the temperature profiles of the pyrolysis process at different microwave power levels. Evidently, the temperature profiles increased significantly as the microwave power increased, and the three stages of pyrolysis curves were observed for each microwave power used except for the curve of 100 Watt. The first stage shown by the sharp temperature increase in the first minute of reaction for each curve may be due to the moisture removal step. Moisture which is highly receptive to microwave absorbed the energy rapidly, thus resulting in a sudden increase in the temperature profiles (Selema & Ani, 2011). The second stage indicated the devolatilization region, where volatile matters were removed from the sample and char formation occurred during this stage. When all volatile matters were removed, the char may reach equilibrium between heat loss and heat generated from the microwave, thus the temperature becomes relatively stable onwards (Du et al. 2012). On the other hands, the temperature profile for microwave power of 100 Watt showed a very slow increase until the 30th minute. It may be concluded that at low microwave power, the molecular movement of the sample occurred at a very slow rate and the stages of pyrolysis were hardly to be determined. In a nutshell, all temperature profiles for pyrolysis of PKS using different power level showed very distinctive curves with different temperature rising rates. Quantitative and qualitative analyses were done using the char produced in order to determine the optimum power for the pyrolysis process of the PKS sample.

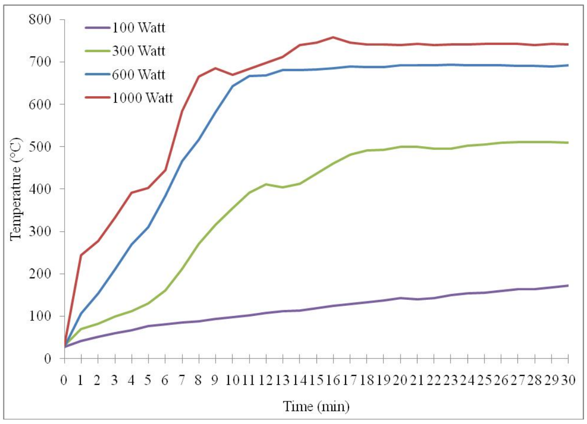

Figure 2: Temperature profiles for pyrolysis of PKS under different microwave power levels.

Product distribution yields

The weight percentages of the pyrolysis products under different microwave power levels are presented in Figure 3. Solid fraction (char) production decreased from 84 to 38 wt% for the microwave power of 100 and 300 Watt, respectively and then there were no significant changes of the char yield from 300 to 1000 Watt. The main reason for this trend to occur is because the pyrolysis of PKS was not adequately occurred at power below 300 Watt. Complete decomposition of the samples might only reach at power 300 Watt onwards with temperature ranging from 350 °C to 450 °C (Luangkiattikhun et al., 2008) , which can also be explained from the maximum temperature shown in Table 1. Lower microwave power level resulted in lower heating rates of the pyrolysis process, thus favoring in higher production of the char (William and Beslers, 1996). On the other hands, the yields of liquid and gas fractions respectively decreased and increased gradually over the range of microwave power level studied. Increasing the microwave power can increase the heating rate of the pyrolysis process, thus resulting in secondary cracking of the liquid fraction into incondensable gases (Hu et al., 2012). Therefore, as the power increased, the production of liquid fraction decreased and gas fraction increased.

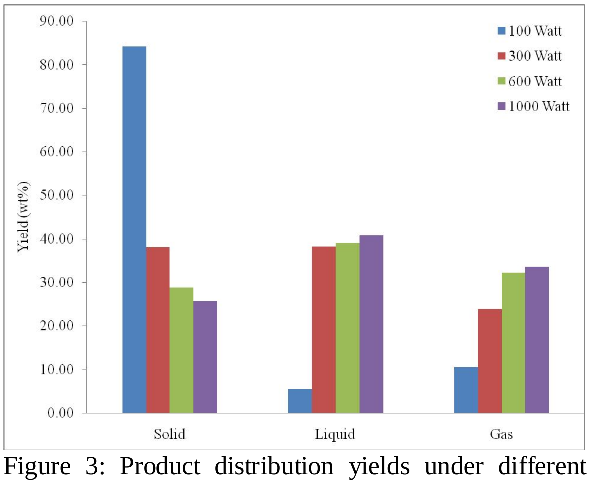

Figure 3: Product distribution yields under different microwave power levels.

Analysis of chars

Char characteristics

Proximate analyses together with the calorific values of char obtained from the pyrolysis reaction were shown in Figure 4. It is worth to notice that as the microwave power increased from 100 Watt to 300 Watt, the volatile matters of the chars decreased while fixed carbon content and the calorific values increased. From 300 Watt to 1000 Watt microwave power used, there were slight increases of the volatile matters, fixed carbon content and the calorific values of chars. The percentage of the ash content has no significant change over the range of microwave power used. The main reason for the change is that there was an incomplete devolatilization of PKS sample at low microwave power of 100 Watt, at low temperature. Complete removal of volatile matters might only occur starting at power 300 Watt onwards with minimum temperature of 500 °C and above. Volatile matter content of the sample was not adequately removed at temperature below 500 °C and thus resulted in its high content in the char.

The ultimate char analysis in Table 3 shows an increase in carbon contents and decrease in other elements as microwave power increased. This might be due to the increase of pyrolysis temperature shown in Table 2. Increasing microwave power caused an increase in pyrolysis temperature, which affected the removal of volatile matters and concentration of the carbon contents in the chars produced. At 100 Watt, the temperature of 173 °C was not sufficient to break the bonds of moisture and volatile matters in the sample, thus resulting in high amount of oxygen and hydrogen contents in the char. As the power increased, the temperature became high enough to release the moisture and volatile matter in the form of O-H, C-H and others gaseous products such as NO_x and SO_x, thus causing the carbon content to become more concentrated. The trends observed were comparable to the previous study of microwave pyrolysis of other biomass sample; however the values varied due to different constituents of the individual biomass sample used (Domínguez et al, 2007, Wang et al, 2009).

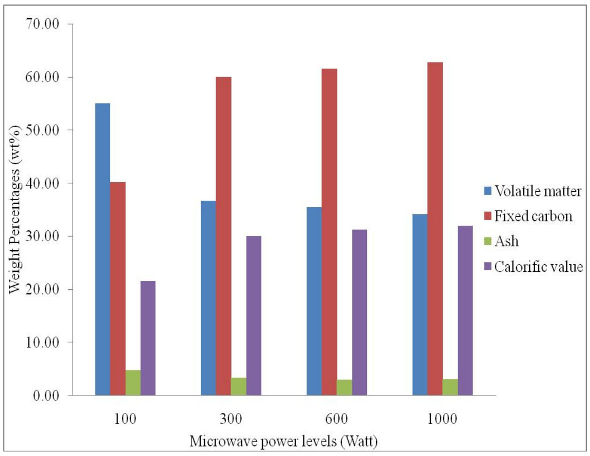

Figure 4: Proximate analysis and calorific values of chars at different microwave power levels.

FTIR analysis

Fig. 5 shows IR spectra for raw PKS sample as well as the chars obtained from microwave-assisted pyrolysis at different power levels. It was observed that raw PKS consisted of O-H (3600-3000 cm^{-1}), C-H_n (2970-2860 cm^{-1}), C=O (1730-1700 cm^{-1}, 1560-1510 cm^{-1}), and C=C (1632 cm^{-1}), which are the main components in most biomass samples. When the sample underwent pyrolysis at 100 Watt, the char characteristic was almost similar to the raw PKS sample. However, as the microwave power level increased from 300 to 1000 Watt, the content of hydroxyl group in the chars was removed, along with the reduction of others functional groups to different extend. It was observed that from power 300 to 1000 Watt, the characteristic of the char was very similar and comparable. Evidently, at low microwave power levels, the microwave energy absorption of PKS was lower and the movement of the sample molecules was less intense and thus generated less heat. On the other hands, as the power increased, the microwave density of cavity increased and the sample absorbed microwave energy more. This resulted in increasing heat from the intense movement of the sample at a molecular level, thus increasing the temperature as shown in Table 2. It was clearly shown that low microwave power level of 100 Watt was insufficient to generate heat to remove the hydroxyl group as well as other functional groups. Therefore, it can be concluded that the pyrolysis process of PKS sample can be accomplished at low power of 300 Watt, with a maximum temperature of 500 °C.

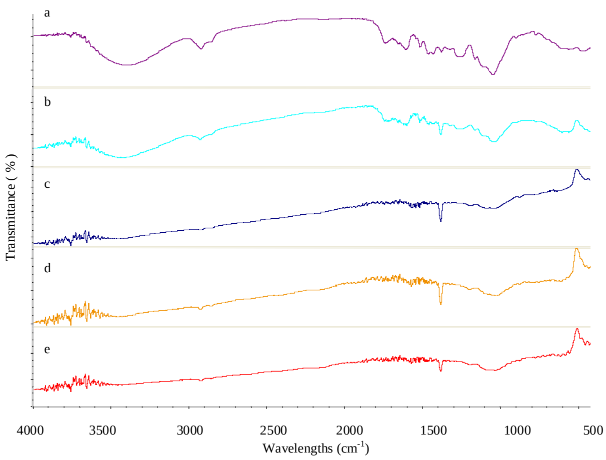

Figure 5: IR spectra of a) raw PKS, b) char at 100 Watt, c) char at 300 Watt, d) char at 600 Watt and d) char at 1000 Watt.

Conclusions

Study on effects of microwave power level to the pyrolysis performance of palm kernel shell was successfully done via microwave-assisted pyrolysis system. Increasing microwave power led to the increase of maximum reaction temperatures, fixed carbon and carbon contents of the char as well as their calorific values. Complete removal of moisture and volatile matters could be reached at a microwave power as low as 300 Watt, and the properties of char were comparable at a power range of 300 to 1000 Watt. Thus it may be concluded that low microwave power of 300 Watt is sufficient enough to convert the PKS sample into highly potential solid fuel via microwave-assisted pyrolysis system.

Acknowledgment

The work has been funded by Sime Darby Research Sdn Bhd and Universiti Teknologi MARA Perlis and all financial and continuous supports are greatly appreciated.

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