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Microwave-Assisted Co-Pyrolysis of Bamboo Biomass with Plastic Waste for Hydrogen-Rich Syngas Production

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Abstract: Concerns about diminishing fossil fuels and increasing greenhouse gas emissions are driving many countries to develop renewable energy sources. The knowledge of the dielectric property is essential to design and develop microwave technology for processing biomass materials. Bamboo biomass was subjected to microwave pyrolysis, to determine the influence of each process on the yield and composition of the derived gas, oil and char products. The influence of pyrolysis temperature and heating rate for the microwave pyrolysis was investigated. A microwave-enhanced co-pyrolysis of bamboo with plastic coupled with Ni/Al₂O₃ catalyst was studied to produce a high yield of hydrogen-rich syngas under mild operating conditions. Ni was applied as the catalyst loaded on Al₂O₃ supports. The co-pyrolysis with catalyst not only produced high hydrogen amounts but also improve the quality of the liquid bio-oil. The maximum H₂ content reached 54 vol% for the bamboo using activated carbon as the microwave absorbing agent with ratio of bamboo wood: Plastic at 80:20. The Ni/Al₂O₃ catalyst dramatically improved the gas yield as well as the hydrogen concentration.

Keywords: Bamboo Biomass, Plastic, Catalytic Reforming, Hydrogen, Microwave Pyrolysis, Microwave Absorber

Introduction

The high-dependence on fossil fuel by the power generation industry and transportation sector has given rise to adverse effects on the global environment including climate change. Solutions to develop sustainable energy sources and to mitigate or reduce CO₂ emissions are being intensely sought. As part of the growing interest in waste recycling, alternative treatments have been investigated with the aim of recovering the energy. New solutions are being pursued to develop a series of novel chemical processes based on renewable feed stocks, typically biomass. Theoretically, biomass resources are the world's largest sustainable energy source. Data from Food and Agriculture Organization of United Nation (FAO) indicates that Malaysia has an estimated forest area of about 22.16 million hectares, while the agriculture area is around 7.84 million hectares (FAO, 2014). Biomass combustion has the largest potential to contribute to global energy demands; however it is considered to be a carbon neutral solution and so it does not address the issue of increasing CO₂ emission adequately. Over the past few years, the development of products from biomass through the pyrolysis technique has been intensively researched.

Through pyrolysis rather than combustion, biomass can lead to carbon negative liquid, gaseous and solid fuels. Biomass pyrolysis is a thermo-chemical process conducted at 450-550°C in which biomass is rapidly heated in the absence of oxygen. Three products are always produced during pyrolysis (syngas, condensable liquid oil and char); however the proportions can be varied over a wide range by adjustment of the process parameters. A high temperature and high residence time promotes the production of gases; a high temperature and low residence time results in increased yield of condensable products and a low temperature and low heating rate leads to increased char production (Bridgwater, 2012). Pyrolysis as a means to convert waste materials to combustible gas or syngas is receiving a lot of attention. Syngas basically consists of hydrogen (H₂) and carbon monoxide (CO). It also contains small amount of carbon dioxide (CO₂), nitrogen (N₂), water, hydrocarbons such as CH₄, C₂H₄, or C₂H₆ depending on the feedstock (biomass) and pyrolysis condition. In addition, microwave technology when applied to fast or flash pyrolysis is suitable for producing higher gas yield with more syngas content (Dominguez *et al.*, 2008; Dufour *et al.*, 2009).

Carbon materials are, in general, very good absorbents of microwaves, i.e., they are easily heated by microwave radiation. This characteristic allows them to be transformed by microwave heating. The ability of a material to be heated in the presence of a microwave field is defined by its dielectric loss tangent: $\tan \delta = \frac{\epsilon''}{\epsilon'}$.

The dielectric constant (ϵ') determines how much of the incident energy is reflected and how much is absorbed, while the dielectric loss factor (ϵ'') measures the dissipation of electric energy in form of heat within the material (Herrero *et al.*, 2007). For optimum microwave energy effect, a moderate value of ϵ' should be combined with high values of ϵ'' (and so high values of $\tan \delta$ is obtained), to convert microwave energy into thermal energy. Inorganic oxides and most carbon materials, are excellent microwave absorbers. The loss tangents of most of the carbons, except for coal, are higher than the loss tangent of distilled water ($\tan \delta$ of distilled water = 0.118 at 2.45 GHz and 298 K). The microwave heating of a dielectric material, which occurs through the conversion of electromagnetic energy into heat within the irradiated material, offers a number of advantages over conventional heating such as: (i) Non-contact heating; (ii) energy transfer instead of heat transfer; (iii) rapid heating; (iv) volumetric heating; (v) quick start-up and stopping; and (vi) heating from the interior of the material body (Appleton *et al.*, 2005).

Application of microwave energy for pyrolysis is an efficient method for biomass pyrolysis, because the biomass particles undergo volumetric heating as a result of the dielectric heating effect (Yin, 2012; Ren *et al.*, 2014). Microwave pyrolysis utilizes the conversion of electromagnetic energy in microwave frequency spectrum into molecular kinetic energy and heat. The heat generated in bodies of biomass will reach most of parts of biomass, which increases the energy efficiency (Lam and Chase, 2012). It also produces less polycyclic Aromatic Hydrocarbon (PAHs)- one of a class of organic pollutants, requires less feed pre-treatment since uniform heating happens on biomass and reduces the secondary pyrolysis reaction since the biomass surface temperature is lower than the biomass core temperature thus reducing the contact between hot char and volatiles (Huang *et al.*, 2010; Kuan *et al.*, 2013; Aziz *et al.*, 2013; Wu *et al.*, 2014). The microwave-enhanced pyrolysis is a superior method for enhancing and accelerating pyrolysis reactions, in comparison with conventional heating methods (Motasemi and Afzal, 2013). In addition, microwave heating can also lead to the high yield of biogas with a greater proportion of syngas (CO+H₂) or high quality bio-oil compared with the conventional pyrolysis (Wu *et al.*, 2014).

Microwave pyrolysis has been applied to a range of materials; some of the materials than have been reported recently include: Sawdust pellets (Bridgwater, 2012;

Huang *et al.*, 2010), oil palm fibres (Salema and Ani, 2011), waste tyres and plastics (Ludlow-Palafox and Chase, 2006; Yatsun *et al.*, 2008; Zahid *et al.*, 2012) and sewage sludge (Zuo *et al.*, 2011). Not all materials absorb microwaves, hence, microwave absorber are normally added to facilitate heating in microwave-assisted pyrolysis process. In spite of the obvious advantages of microwave pyrolysis, the stochastic nature of the pyrolytic degradation usually results in the production of a wide range of molecular masses, which necessitates costly processing and separation of the desirable short-chain hydrocarbons. Catalytic pyrolysis has the potential to narrow the range of molecules produced. The use of catalysts and other additives (co-pyrolysis) to improve the yield or quality of pyrolysis gas or liquid fuels is still in its infancy (Bridgwater, 2012; Kuan *et al.*, 2013; Huang *et al.*, 2010). While there are numerous studies underway, more research is necessary to explore co-pyrolysis using biomass and hydrocarbon coupled with wide range of conventional and unconventional catalysts.

Therefore, this study will examine microwave enhanced pyrolysis of biomass with an additive (co-pyrolysis) coupled with reforming catalyst for a highly selective production of hydrogen rich syngas. In order to increase the amount of hydrogen in the gaseous stream, the addition of plastics High Density Polyethylene (HDPE) to the biomass is an interesting alternative, in that they contribute to increasing the content of hydrogen in the feed. Bamboo is the most notable among biomass resources because it is one of the fastest-growing plants on earth and is found in diverse climates from cold to tropical or subtropical regions. The abundant availability of bamboo biomass in Malaysia with the addition of another waste material, plastic, which is abundantly present in municipal solid waste, would be a good choice for microwave co-pyrolysis.

Methodology

Materials

The pyrolysis process was carried out in the single-mode (focused) microwave oven (Samsung CE2877N) with 2.45-GHz frequency. The maximal incident power of micro-wave generator was 850 W and minimum power was 100 W. The time setting provided by the device was from 0-30 min.

All other chemicals were obtained from Sigma-Aldrich Corp (St. Louis, MO). All materials were used as received.

Natural dry bamboo sticks were purchased from local retail store. The main constituents of bamboo are cellulose, hemi-cellulose and lignin, which amount to over 90% of the total mass. The minor constituents of bamboo are resins, tannins, waxes and inorganic salts.

Compared with wood, however, bamboo has higher alkaline extractives, ash and silica contents. The bamboo sticks were grinded to become powder like. The particle size of the grinded bamboo was between 0.4-1.0 mm. The sample was dried using conventional oven set at 105°C for 25 min. (moisture content below 10%) and then ground to obtained particle size of the powdered bamboo of between 0.4-0.8 mm.

Plastic High Density Polyethylene (HDPE) grocery bags were collected from local retailers (represent the typical ones used in grocery stores). HDPE is manufactured from ethylene, a by-product of gas or oil refining. The co-pyrolysis of biomass and plastics has been studied with the aim of exploring the synergetic effects between these two materials in order to increase hydrogen concentration and production in the gaseous fraction.

Another factor that may lead to higher gas production is the presence of catalyst. The influence of Ni catalyst (Ni/Al₂O₃ catalyst) on the yield and composition of the final products was investigated.

All pyrolysis experiments were carried out in a batch microwave reactor as shown in Fig. 1. Circular holes were cut at the top of the microwave oven chamber, through which tubes were connected to the sample crucible in the microwave reactor. The Perspex material was used as a microwave leak-proof agent, which was provided at the top of the cavity where the holes were drilled. The thermocouple wires were connected to a Pico data acquisition system. To ensure that no microwave leakages occur during the experiments, frequent monitoring of leakages was done using a MW leakage detector model TX90. Activated carbon of coconut was used as a microwave absorbing agent.

Catalyst Preparation

Nickle from Ni(NO₃)₂ was applied as the active components Al₂O₃, was used as catalysts supports. The Ni based catalysts were prepared by wet impregnation method. The Nickel (II) Nitrate [Ni(NO₃)₂.6H₂O] solution prepared by adding 20.8 g of nickel nitrate hex a hydrate in 20 mL of distilled water. Forty-gram of γ-Al₂O₃ was added to the nickel nitrate solution. The loading of Ni in the catalyst was 10 wt.%. The mixture was then heated to 90°C on a hotplate and continuously stirred for more than one hour (until all the water in the mixture has evaporated). The catalysts were then dried in an oven for 24 h, at temperature 110-115°C followed by calcination at 450°C for 4 h. These temperatures and duration are important to produce an even distribution of Ni on the surface and into the pores. The calcined catalyst was subjected to a reduction reaction using hydrogen (flow rate 100 mL min⁻¹) at 450°C for 3 h.

Microwave Pyrolysis of Bamboo with Microwave Absorber

Before the experiment started, the microwave absorbent, the activated carbon, was first added into the quartz reactor and then the crucible was placed on the carbon layer. The carbon was first heated for one hour at 450 W output power (as shown in Fig. 1). This would allow the temperature of the reactor to be stable. Subsequently, the carrier gas, N₂ (pure) was allowed to flow at rate of 100 mL min⁻¹, for 3-5 min to remove the air from the reactor.

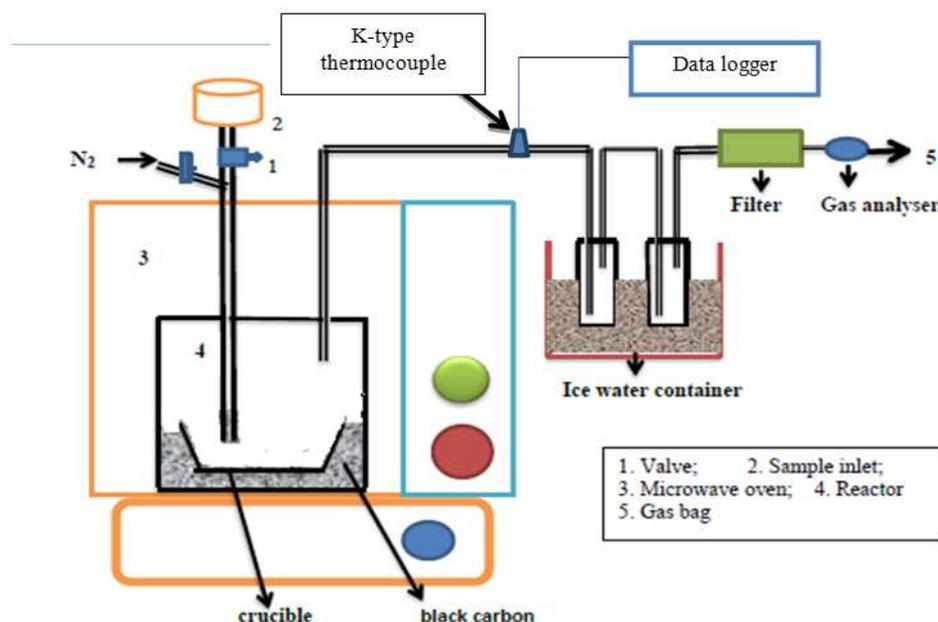


Fig. 1. Schematic diagram of the microwave assisted system for pyrolysis

The flow rate of the gas was reduced to 40 mL min⁻¹ and the feed valve near the sample inlet was open to allow the sample into the crucible. The sample consisted of 100 g of bamboo powder (constant mass), while the percentage of the microwave absorber activated carbon was varied at 0, 20 and 40% of the weight of the biomass. The prepared sample was then subject to pyrolysis in the reactor at three different values of microwave power, i.e., 300, 600, 850 Watt and two different values of microwave absorbent as shown in Table 1. A K-type thermocouple connected to a data logger was used to record the real time temperatures of pyrolysis product during microwave pyrolysis.

Product Yield

The liquid was collected from the condensation unit (an iced-cooled water system of around 7-10°C) was used to cool the condensable vapor to liquid (bio-oil) and subsequently weighed to obtain the mass of the liquid product. The residual non-condensable gas was collected by a gas bag. At the end of the experiment, the microwave was off and the carrier gas flow was increased to 100 mL min⁻¹. After 3-5 min, the crucible was taken out. The char was collected from inside the crucible and then weighed. To obtain the final percentages of the products (liquid and char), all of the yields were calculated using the following Equation 1:

$$Y_p = \frac{X_1}{x_2} \times 100\% \quad (1)$$

Where:

Y_p = The product yield

X_1 = The mass of the desired product

X_2 = The initial weight of the raw material.

The gas yield was determined by subtraction:

$$\text{Gas yield} = 100 - (\text{liquid yield} + \text{char yield})$$

The product gases of the pyrolysis were analysed by a Portable Multi-gas Analyser (Rapidox 5100-Sensotec UK).

Catalytic Co-Pyrolysis of Bamboo and Plastic with Catalyst

The co-pyrolysis of bamboo with plastics was carried out using the same method as described earlier varying the plastic content from zero to 20 wt.% in the final feedstock. Similar to the previous procedure, the microwave absorbent, the activated carbon, was first added into the quartz reactor and then the crucible was placed on the carbon layer. The carbon was first heated for one hour at 450 W output power. The carrier gas, N₂

(pure) was allowed to flow at rate of 100 mL min⁻¹, for 3-5 min to remove the air from the reactor. The flow rate of the gas was reduced to 40 mL min⁻¹ and the feed valve near the sample inlet was open to allow the sample into the crucible. The sample consisted of 100 g of bamboo powder (constant mass), while the percentage of the microwave absorber activated carbon was at 40% of the weight of the biomass. The mass of plastic (plastic HDPE grocery bags cut into small strips) was varied from zero to 20% of the bamboo mass. One gram of the prepared catalyst Ni/Al₂O₃ was placed on top of the bamboo/activated carbon mixture supported on quartz wool. When the experiment was carried out without catalyst, only quartz wool was placed on top of the sample. The prepared sample was then subject to pyrolysis in the reactor at the microwave power of 600 Watt for 5-7 min. Once the pyrolysis gas from the reactor reached 600°C, it was kept constant for 20 min.

Results and Discussion

Pyrolysis of Bamboo with Activated Carbon and Product Yield

The effects of different power ratings and amount of microwave absorbent were studied. Table 1 shows the operating conditions of microwave pyrolysis of bamboo with and without microwave absorber. The data (Table 1) shows that the pyrolysis temperature of bamboo with no absorber loading is always lower than 400°C for all the three different microwave power. This shows that the bamboo biomass is a poor microwave absorber. The higher the microwave power, the higher is the heating rate because the sample will experience a greater dielectric heating effect (Yin, 2012). Bamboo, like other types of biomass, has low $\tan \delta$ value; therefore, the microwave pyrolysis of biomass should be added with microwave absorber, such as charcoals, ionic or acid liquids, to enhance the ability of biomass in absorbing microwave energy. The increasing ability of hot activated carbon in absorbing the microwave energy will cause a significant increase in the heating rate.

Table 2 shows the effect of microwave power and activated carbon loading on the yields of char, bio-oil and syngas. To obtain the maximum yield of syngas, the combined effect of microwave power and activated carbon (microwave absorber) loading is important. Combination of high microwave power and high activated charcoal loading enhances yield of gas dramatically. Microwave power is a factor that determines the heating rate and pyrolysis temperature. Previous studies have identified the effects of microwave power on bio-oil yields and characteristics from various types of biomass, such as corn (Lei *et al.*, 2009), microalgae *Chlorella vulgaris* (Hu *et al.*, 2012) and sewage sludge (Tian *et al.*, 2011) among others.

Table 1. Pyrolysis of bamboo at different microwave power in the presence (or absence) of microwave absorber

Microwave power (Watt)	Microwave absorber loading (%)	Temperature of the product gas after 20 min. (°C)
300	0	340
3300	20	453
300	40	670
600	0	370
600	20	710
600	40	830
850	0	395
850	20	837
850	40	853

Table 2. Pyrolysis temperatures and pyrolysis products yields at different microwave pyrolysis operating conditions

Microwave power (Watt)	Microwave absorber loading (%)	Average temperature after 20 min (°C)	Bio-Char yield (%)	Bio-oil yield (%)	Syngas yield (%)
300	0	340	62.32±0.62	32.46±0.35	3.11±0.12
300	20	453	38.28±0.86	38.52±0.33	23.20±0.20
300	40	620	31.11±0.23	43.13±0.23	25.76±0.17
600	0	370	56.64±0.74	36.72±0.29	6.64±0.10
600	20	710	27.53±0.35	38.21±0.22	34.26±0.21
600	40	830	22.52±0.27	39.13±0.28	38.35±0.15
850	0	395	51.10±0.65	41.14±0.33	7.76±0.07
850	20	837	22.75±0.25	32.79±0.31	44.46±0.16
850	40	853	20.18±0.20	27.54±0.22	52.28±0.28

All studies including this one suggest that the heating rate and pyrolysis temperature increase with the increase of microwave power. It has been shown that the type of biomass also affects the microwave assisted pyrolysis process. It can be seen that with the increase of pyrolysis temperature, the solid char yields decreases continuously. This indicates that thermal decomposition of the biomass is favorable at higher temperature under microwave pyrolysis. This observation is also seen with the conventional heating systems (Demibas, 2004; Menendez *et al.*, 2007). Interestingly, it has been reported that the solid bio-char yield under microwave pyrolysis was lower than that of conventional pyrolysis (Menendez *et al.*, 2007). The reasons given for this is that the heating rate of microwave was higher and there is significant self-gasification reaction between the char and CO₂ during microwave pyrolysis; both of which would decrease the char yield (Menendez *et al.*, 2007). Farag *et al.* (2014), has stated that higher heating rates can be achieved when microwave assisted pyrolysis uses higher microwave power. The results from this work is in agreement and hence the role of heating rate in yielding higher fraction of gas using microwave pyrolysis is crucial. It is also important to note that, in general, the dielectric properties (constant and loss factor) will decrease in the early stage of the pyrolysis and increased rapidly in the later stage. This phenomenon could be attributed to the removal of free or surface water from the biomass material in the early stage (Hani and Salema, 2015). At the later stage the

biomass will usually have a sharp increase in both the dielectric constant and loss factor, owing to the honeycomb-like carbon structures with a high delocalised electron density of the carbon char (Beneroso *et al.*, 2016). Furthermore, the addition of microwave absorber proved to be an effective way to reduce the energy consumption of the pyrolysis process, because it provided the bulk with a high $\tan \delta$ at lower temperature (Beneroso *et al.*, 2016). Hence, the use of microwave absorber such as activated carbon is important as it will allow the usage of lower microwave power to produce higher heating rates. Another factor that may improve the heating rate is the diameter of the bamboo wood biomass. In this study the bamboo biomass was smaller than 1 mm, instead of several centimeters as in other reported work (Miura *et al.*, 2004; Dominguez *et al.*, 2007). In this way, the microwave pyrolysis rate was fast and the pyrolysis process was completed in less than 10 min. It is worth to notice that the char produced from the biomass would also absorb the microwave energy, thus accelerating the pyrolysis process.

From Table 2, it can be seen that the amount of bio-oil produced is affected by the microwave power and the amount of activated carbon. Feed stocks with high lignin content produce the highest bio-char yields when pyrolyzed at moderate temperatures (approx. 500°C). In general biomass with high volatile matter produces high quantities of bio-oil and syngas, whereas higher fixed carbon amount in the biomass will increase the bio-char production. The bio-oil or pyrolysis liquid obtained

appeared to be dark brown to dark red in colour. Minor quantities of very fine carbon particles originally present in the pyrolysis reactor were also detected. They are likely to escape from the reactor and co-migrate with the pyrolysis oil. These carbon particles can be easily removed by filtration. The highest bio-oil yield of 43 wt.% was obtained at 40% microwave absorber and 300 W microwave power. This can be explained if consideration is given to the maximum pyrolysis temperatures attained. The desired pyrolysis temperature (for bio-oil) of around 600°C obtained at 40% microwave absorber and 300 W microwave power. Also the data shows decrease in bio-char percentage accompanied by increase in gaseous products as the microwave absorber percentage was increased, although the bio-char percentage at 20 and 40% with microwave power at 850 W was about the same. Pyrolysis liquid is a blend of oxygenated organic compound and water formed by de-polymerization or breakdown of cellulose, hemicelluloses and lignin at high temperature (Vamvuka, 2011; Mohan *et al.*, 2006). The oxygenated organic compounds consist of alkenes, alcohols, ethers, sugars, aromatics, phenols, acids, ketones and aldehydes (Vamvuka, 2011). It has been reported that bio-oil produced by microwave pyrolysis may differ in terms of product composition when a microwave absorber is added to the sample mixture (Frag *et al.*, 2014). Pyrolysis with microwave absorber produces oxygenated compounds, aliphatic and cycloalkanes; with the latter two being between 35-45% of the bio-oil content (Beneroso *et al.*, 2014; Zuo *et al.*, 2011). Therefore, the addition of microwave absorber such as activated carbon contributes to the production of more aliphatic and cycloalkanes, which are more desirable compounds for further processing of the bio-oil into biofuel (Robinson *et al.*, 2015). It can be concluded that bio-oil yielded greatly influenced by the application of microwave absorber. Besides that, it was also reported that application of microwave absorber helps the microwave pyrolysis to work at low power input.

Moisture content in biomass has an influence in the heat transfer process with significant effects on product distribution (López *et al.*, 2002). It has been observed that an increase in moisture content results in increased liquid product yield while the solid and gas yields decrease (Minkova *et al.*, 2001). The non-condensable gases in all cases were short-chain aliphatic which could be used as fuels (e.g., natural gas, LPG) or as feedstock for a range of chemicals. The non-condensable gas usually includes H₂, CH₄, CO, CO₂, C₂H₄, C₂H₆, aromatics and cycloalkanes. There has been recent interest in microwave pyrolysis. The conversion of wood (Miura *et al.*, 2004); sewage sludge (Dominguez *et al.*, 2008); waste automotive oil (Lam *et al.*, 2012) are among some of the other studies reported in the fields of microwave pyrolysis and bioenergy. Among the

advantages reported about microwave processing of materials such as wood are increased process yield, environmental compatibility, savings in process time and low requirements for space and capital equipment. It has also been reported that oils from microwave pyrolysis of sewage sludge contain no harmful compounds such as heavy Polycyclic Aromatic Hydrocarbons (PAHs), which was the case for oils from conventional pyrolysis of the same feedstock (Dominguez *et al.*, 2008).

Statistics Division

Co-Pyrolysis of Bamboo and Plastic

The co-pyrolysis of bamboo biomass and polypropylene (plastic) was carried out with and without catalyst to determine the influence of the plastic content on hydrogen production and the contribution of the catalyst. This process involves two or more different materials as feedstock. The mechanisms of co-pyrolysis and normal pyrolysis are almost the same, whereby; the process is performed using moderate operating temperatures and the absence of oxygen. The mass balances and the product yields for different biomass/plastic ratios are shown in Table 3. The residue or char obtained after pyrolysis was calculated by difference between the initial and final weight of the sample placed in the sample holder. As can be seen in the Table 3, the decrease in char yield was obvious when the mass weight of bamboo was reduced in the feed sample. It has been reported that presence of lignin in the biomass favors the production of a high amount of char (Mohan *et al.*, 2006). The production of liquid bio-oil increases with the addition of plastic. The maximum oil yield of 53.5 wt% was obtained for the pyrolysis of bamboo biomass plus plastic (bamboo: Plastic ratio; 80:20). This liquid yield is higher than that obtained from for the pyrolysis of bamboo biomass alone (38.8 wt%). It has been reported that synthetic polymers such as polypropylene (plastic) is an excellent hydrogen source; hence, it could provide hydrogen during thermal co-processing with wood biomass, which can lead to an increase in liquid production (Brebú *et al.*, 2010). The presence of polystyrene could provide more hydrocarbons during co-pyrolysis with bamboo biomass and can lead to an increase of liquid production.

Currently, developments in the production of pyrolysis oil as a renewable liquid fuel from biomass are attracting more and more attention. One important reason for this interest is the abundant amount of biomass that is now available around the world. The addition of plastic plays an important role in the rise of bio-oil production. Usually, the bio-oil from lignocellulosic biomass contains large amount of oxygen (usually around 40-50 wt%). This can lead to low calorific values, corrosion problems and instability (Lu *et al.*, 2009).

Table 3. The main products yields for different biomass/plastic ratio

	Without Catalyst				With Catalyst (Ni/Al ₂ O ₃)			
	100	95	90	80	100	95	90	80
Bamboo wood (wt%)	100	95	90	80	100	95	90	80
Plastic (wt%)	0	5	10	20	0	5	10	20
Mass balance of product (wt. %)								
Gas	32.1±1.9	32.9±2.1	33.7±1.7	34.9±1.5	45.7±3.1	68.7±2.8	78.2±3.5	81.1±2.6
Liquid	38.8±2.1	40.8±2.3	47.8±2.3	53.5±3.2	34.5±2.9	22.0±1.8	12.9±1.1	10.3±0.7
Char	29.1±1.2	26.3±1.7	18.5±2.1	11.6±1.4	19.8±2.1	9.3±0.9	8.9±1.1	8.6±0.4

For quality improvement, the liquid needs to be upgraded. Catalytic cracking and hydro-deoxygenation are the most commonly used upgrading processes, which potentially can cost more than the oil itself. Thus, a novel approach is necessary to overcome this issue and make the oil from lignocellulosic biomass more competitive and reliable as a renewable fuel (Zhang *et al.*, 2013; Mortensen *et al.*, 2011). Co-pyrolysis is a technique which is simple and suitable for the production of high-grade pyrolysis oil. The Table 3, shows that in the un-catalyzed reaction, gas yield was between 32.1-34.9 wt% when HDPE plastic was used as the co-pyrolysis raw material (increased plastic loading from 0 to 20 wt.%). In addition, the char generated decreased with increasing plastic content. This suggests that there is suppression of secondary reactions, such as condensation and re-polymerization reactions. The hydrogen released by the poly-olefin polymer in the co-pyrolysis reaction is responsible for the inhibition of re-condensation reactions forming the char (Wu and Williams, 2010). It can be seen that the thermal pyrolysis (without catalyst) produced highest liquid fraction. The obtained bio-oil from microwave co-pyrolysis was dark brownish in color and the pH was found to be around 2.9-3.3 for both with and without catalyst. The presence of catalyst reduced the liquid fraction and increased the gaseous fraction. The catalyst can enhance the cracking reaction of the pyrolysis gas. Long chain hydrocarbons have been cracked into lighter hydrocarbon gases. The gas yield corresponding to the mass of biomass and plastic increases from 34.9 to 81.1 wt.% for a biomass/plastic ratio of 80/20, from 33.7 to 78.2 wt.% for a ratio of 90/10 and from 32.9 to 68.7 wt.% for a ratio of 95/5. Furthermore, an increase in gas yield in the catalytic process was much more pronounced than in the non-catalytic system. This indicates that the Ni catalyst plays a significant role when more plastic is present in the mixture. The effect of Ni catalysts in the pyrolysis/gasification processes has been extensively studied by several researchers for plastics and biomass separately (Wu and Williams, 2010; Efika *et al.*, 2012). The catalytic process for the mixture of biomass and polypropylene suggest the existence of synergetic effects on the product distribution when the Ni/Al₂O₃ is used. This synergy is probably related to secondary cracking

reactions involving tars and heavy gas compounds in the gasification step. The catalyst can be reused, however, some studies have suggested that there is a tendency for deactivation, which is mainly caused by carbon deposition on the catalyst during the pyrolysis process. The study by Guo *et al.* (2009), noted that the catalysts gradually deactivate upon repeated regenerations after the first three times. In this study it can be envisaged that the deactivation of the catalyst will be low because the carbon char production was reduced greatly.

The gaseous fraction was mainly composed of CO, CO₂ and hydrogen. Table 4 shows the composition of the gases present in the syngas, which was determined by the portable multi-gas analyzer (Rapidox-5100). When the experiments were carried out without catalyst, the highest hydrogen production was obtained for plastic with 20% loading. These results are consistent with those obtained in previous work by Wu and Williams (2010). Plastic (HDPE), as a poly-olefin polymer, represents a significant source of hydrogen. This increase may be due to the higher H/C molar ratio caused by the higher amount of plastic in the feed. When more H and OH radicals are released, they act as hydrogen donor species, promoting the cracking of the aromatic compounds in the biomass (Krerkkaiwan *et al.*, 2013).

As shown in Table 4, the catalyst plays a significant role in the increase of hydrogen production. The quantity of H₂ and CO₂ increases, whereas those of CO and light hydrocarbons decrease in the catalytic co-pyrolysis reaction with bamboo biomass and plastic. In the presence of Ni/Al₂O₃ catalyst, the highest hydrogen production was obtained with HDPE and bamboo (54 vol %). As explained by Wu and Williams (2010), this is due to more alkanes and alkenes derived during the co-pyrolysis of biomass with plastics; whereby these compounds are then easily reformed in the gasification stage in the presence of catalysts. Based on other previous studies, the permanent gas collected usually comprised of H₂, CO, CO₂ and gaseous hydrocarbons (mainly CH₄) (Dominguez *et al.*, 2007). Among the gases the CO and H₂ gas are the main ones; the percentage of both can reach up to 60%. The trends of the syngas components produced in this study were in agreement with the literature.

Table 4. Composition of Syngas for different bamboo biomass/plastic ratios

	Without catalyst				With catalyst (Ni/Al ₂ O ₃)			
	100	95	90	80	100	95	90	80
Bamboo wood (wt%)	100	95	90	80	100	95	90	80
Plastic (wt%)	0	5	10	20	0	5	10	20
Composition of gasses in the syngas (vol. %)								
CO	35±1.2	31±1.3	27±1.2	24±0.9	28±0.5	27±0.9	25±1.0	23±1.1
CO ₂	23±0.9	25±1.2	28±1.3	30±0.7	23±1.3	21±0.4	20±1.2	16±1.3
H ₂	27±1.3	31±0.8	34±0.9	36±0.6	39±1.1	42±0.6	46±1.1	54±1.0
CH ₄	15±0.6	13±0.4	12±0.2	10±0.3	10±0.6	10±0.5	9±0.4	7±0.3

Generally, temperature in co-pyrolysis can be adjusted within the range of 400-600°C to maximize liquid yield production (Du *et al.*, 2012; Maddi *et al.*, 2011). It is important to highlight the salient features of co-pyrolysis process being regarded as a promising, economic and environmental friendly technology for both the energy production and waste remediation (Lin *et al.*, 2014). Numerous studies on co-pyrolysis for producing pyrolysis oil have been carried out recent. The addition of plastic during the pyrolysis of lignocellulosic biomass can improve the quantity and quality of the oil product. Abnisa *et al.* (2014), studied the co-pyrolysis of palm shells and polystyrene to obtain high-grade pyrolysis oil. Their results showed that by adding the same weight ratio of polystyrene during the pyrolysis of palm shell, the oil yield increased to approximately 61.63-46.13 wt% (using palm shells biomass alone). The same authors reported that the High Heating Value (HHV) of the bio-oil product was approximately 11.94 MJ kg⁻¹ (pyrolysis of palm shells alone) but with co-pyrolysis of palm shells polystyrene, the value of HHV of bio-oil raise to 38.01 MJ kg⁻¹. Although fuels from biomass, especially wood-based biomass, typically have lower energy content than fossil fuels, the use of the co-pyrolysis technology can improve this condition. The improvement in the quality of the bio-oil is due to higher amounts of aromatic hydrocarbons produced from catalytic pyrolysis than non-catalytic pyrolysis (Mihalcik *et al.*, 2011). Studies have shown that lignocellulosic derived organics can be deoxygenated and cracked to produce aromatics when catalysts are used (Mihalcik *et al.*, 2011; Cheng *et al.*, 2012). It is important to note that the improvement using co-pyrolysis was achieved without any change in parameter settings. The oil produced from biomass pyrolysis has been well received as a more environment-friendly fuel because it contributes to reducing the amount of CO₂ in the atmosphere, which also has the effect of minimizing the emission of greenhouse gases.

Conclusion

Comparing with conventional pyrolysis, there has a lot of advantages for microwave pyrolysis, such as increased process yield, environmental compatibility, savings in

process time and low requirements for space and capital equipment; which will ultimately improve the energy efficiency for the process. The application of carbon based material as an absorbent in microwave pyrolysis process can increase the temperature of sample material. This situation contributes to low power microwave usage which indirectly leads to energy saving. Besides that, products such as pyrolytic liquid, solid and gas yield will also be influenced by the microwave absorber. The results of the co-pyrolysis study concluded that the addition of plastic in the pyrolysis of lignocellulosic biomass successfully improved the quantity and quality of pyrolysis oil and syngas. A reduction in CO₂ yield concentration was obtained when the amount of plastic was increased from 0 to 20 wt.% in the initial feedstock mixture. The Ni/Al₂O₃ catalyst seems to be suitable for high hydrogen yield due to its high activity for C-C bond rupture and a low char deposition. The addition of plastic and the catalyst markedly increased the yield of the gaseous fraction and the hydrogen content in the syngas.

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Author's Contributions

N. Saifuddin: Conceived in idea, designed the experiments, analyzed the data, wrote the paper, edited and finalized the manuscript.

P. Priatharsini: Performed the experiments, analyzed the data and contributed to the writing of the manuscript.

S.B. Hakim: Performed the experiments, analyzed the data, designed the research plan and organized the study.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of

the other authors have read and approved the manuscript and no ethical issues involved.

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