This paper presents a technology to utilize bio-char and bio-tar from the pyrolysis of oil palm empty fruit bunch, EFB. In this study, tar vapor from pyrolysis of EFB was infiltrated within porous bio-char and carbon deposition occurred on the pore surface by chemical vapor infiltration process. For preparation, EFB particles were made into pellets. In the first part of experiments, porous bio-char pellets were produced by slowly heating the EFB pellets in a tube furnace in argon atmosphere to terminal temperatures of 500–800°C. In the second part, the porous bio-char pellets were used as precursor for tar decomposition process to deposit carbon within the bio-char pores. Tar vapor was obtained from the pyrolysis of EFB at 400–500°C at a fast heating rate for tar decomposition to occur. The purpose of this research is to investigate the amount of carbon deposited within bio-char by this tar carbonization process as compared to carbon contents of metallurgical coke. We showed how EFB bio-char was used as the tar filter and in the process to produce carbon-infiltrated bio-char, a useful renewable energy source for ironmaking process.

KEY WORDS: bio-char; bio-tar; carbon deposition; chemical vapor infiltration; renewable energy.

1. Introduction

At present, fossil fuels have been the main energy source worldwide. Observing the increasing trend of world energy consumption, utilization of efficient alternative energies is highly demanded. These alternatives include renewable energy sources and one of the aims is to reduce the extensive utilization of the non-renewable energy sources which is now facing depletion and causing environmental pollutions. Biomass is one of the most attractive renewable energy sources, which is being produced approximately 146 billion metric tons per year worldwide. The conversion of biomass to energy includes thermo-chemical and biochemical process.1)

Biomass being a renewable energy source exists abundantly in Malaysia, particularly in the form of palm agricultural residues considering the fact that Malaysia is one of the largest palm oil producers in the world. However, the waste management from this industry has yet to be carried out effectively. For palm solid wastes, technologies have been implemented to utilize them as fuels for electricity generation.2) However, due to the abundance of palm oil production, there are still lots of these palm wastes being underutilized and/or being discarded in improper ways which leads to environmental deterioration.3)

Therefore, it is important to find alternative or potential applications to utilize and benefit from these palm wastes. One of the most prominent methods to use biomass is by pyrolysis, a thermo-chemical process. Pyrolysis produces useful fuel gases, bio-char and bio-tar. Fuel gases from this process can be used directly as an energy source. Bio-char is a highly carbonaceous material produced in pyrolysis, and the material is normally used in agricultural industry in soil amendment because of its porous characteristic which makes it able to trap impurities excellently.4–8) Bio-tar from biomass pyrolysis has been a problem in pyrolysis process because it clogs fuel lines, filters, and engines, thus reducing the efficiency of biomass utilization.9) Even so, tar contains a mixture of naturally occurring compounds, including carbon, which makes it attractive to be collected and used as a fuel source. Therefore, many studies have been conducted to decompose tar into fuel gas. Researchers are using various minerals as catalysts in this decomposition process such as olivine,10–13) clay minerals14,15) and iron ores.16–18)

Scrutinizing the properties of each biomass pyrolysis product, it is highly likely that bio-char can be used as a catalyst for decomposition of bio-tar, and which will increase the efficiency of biomass utilization. Studies on bio-char production19–25) and bio-tar catalytic decomposition,26–32) have been conducted separately. The combination of bio-char production and catalytic bio-tar decomposition to produce a material containing fixed carbon similar to that of coke has yet to be studied and explained. One study33) focuses on bio-tar decomposition process within porous steel-making slag using the chemical vapor infiltration, CVI
method to partially substitute coke breeze in sintering machines in steelworks. Employing the same CVI method, another study focused on the reduction process of iron ore by tar decomposition within low-grade iron ore. Low-grade iron ore is made porous by dehydration process where combined water content within it is removed, causing cracking to initiate and propagate.\textsuperscript{35-37} Production of carbon-infiltrated carbonaceous materials especially by using CVI method has been done to densify graphitic carbon to produce C/C composites.\textsuperscript{38,39} This paper is focusing on a study to produce high carbon-content material using only empty fruit bunch as the raw material to produce bio-char as the precursor, and the deposited carbon.

Materials containing high amount of lignin and low hemicellulose are good candidates to be used in pyrolysis to produce a higher bio-char yield.\textsuperscript{40} Besides a higher bio-char yield, the amount of carbon content is also a crucial factor that needs to be observed. Important parameters to be considered in such studies include pyrolysis temperature, pyrolysis time, starting materials, and heating rate of the pyrolysis process. Studies have also been carried out to understand the effects of these parameters on the amount of carbon content in the bio-char produced.

The same starting biomass yields different pyrolysis products if the conditions for pyrolysis are different. For slow pyrolysis of biomass, the main product is bio-char, and the amount of carbon content is larger in bio-char than in bio-tar vapor and other gases. On the other hand, the main product for fast pyrolysis process on biomass is bio-tar containing high amount of carbon, and small amount of bio-char and gases.\textsuperscript{44} Therefore, in order to obtain bio-char containing high amount of carbon, combination of these slow and fast pyrolysis processes have to be well studied.

Figure 1 presents the general concept of this study. In the first step, slow pyrolysis conditions of oil palm EFB was conducted to obtain bio-char containing high carbon content. The porous carbonaceous bio-char was characterized for fixed carbon content in order to consider and evaluate the suitability of the bio-char to be efficiently utilized as an energy source. In the next step, fast pyrolysis of biomass was performed to obtain bio-tar containing high amount of carbon. In this step, the porous bio-char produced in the first step was used as the precursor for bio-tar decomposition. This step was important to further increase the carbon content of the bio-char by using the highly potential carbon resource, bio-tar. CVI technology was implemented in this catalytic bio-tar decomposition process where bio-tar vapor infiltrated within the porous bio-char, and decomposed into carbon and gases. Carbon got deposited on the pore surface and this resulted in the increase of the fixed carbon content to a level comparable with that of metallurgical coke. The chemical reaction during bio-tar decomposition is described below:

\[
\text{Tar(C}_{n-1}\text{H}_{m}) + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{C}_{n-1}\text{H}_m + \text{C} + \text{H}_2 + \text{CO} + \text{CH}_4 + \text{C}_2\text{H}_6 + \text{other hydrocarbons}
\]

The product of this research is expected to be used as an energy source which can significantly reduce the utilization of coal, a non-renewable fossil fuel.

2. Experimental

2.1. Production of Bio-char

Oil palm EFB was used as the biomass in this study. The elemental composition of EFB was C, 45.64 mass%; H, 6.19 mass%; N, 0.35 mass% and O, 47.82 mass% by difference. Biomass was defibrized and sieved with particle sizes ranging from 300–600 μm. These particles were then compacted into 3 g-pellets having 20 mm diameter and 10±1 mm height.

Pyrolysis of EFB pellets was carried out in a tube furnace with continuous flow of argon gas. Pellets placed in an opened SUS316L-400 mesh bag were heated to 500°C at a heating rate of 10°C/min and 30°C/min, and held for 10 minutes. Experiments were repeated by increasing the terminal pyrolysis temperatures to 600, 700 and 800°C. Carbon content of bio-char and pyrolysis product distribution were analysed, calculated and compared. Carbon content was examined using elemental analysis by combustion.

2.2. Tar Carbonization Within Porous Bio-char

Pellets of porous bio-char produced from the pyrolysis of EFB pellets were used as precursors in this tar carbonization process. Figure 2 shows the schematic diagram of the experimental apparatus. EFB, in the form of particles was used as the starting material to produce bio-tar. Thermal analysis of EFB indicated that the complete decomposition occurs after 380°C (Fig. 3). Tar carbonization process was conducted in the furnace with an argon atmosphere. Temperature was increased to 400°C at a heating rate of 60°C/min, and held for 5 minutes. Pyrolysis and tar decomposition processes were both performed at this experimental condition. Experiments were repeated by changing the experimental temperatures to 450 and 500°C, and the experimental time to 35 and 65 minutes.

The pyrolysis of biomass produced bio-tar vapor which infiltrated within the porous bio-char pellets. By CVI process, bio-tar vapor came in contact with the pores’ surface; where the tar decomposition occurred, leaving solid carbon within the pores. The residual gases were collected in a gas bag.
After tar carbonization process, the resultant carbon-infiltrated bio-char pellets were analyzed for carbon content by a carbon analyzer. The relative crushing strength of carbon-infiltrated bio-char produced at different temperatures was determined through a quasi-static crushing load that was applied using a Universal Testing Machine, Shimadzu Autograph (AG-X) Series with TRAPEZIUMX software for control and data logging. The micrographs of bio-char before and after carbonization were also captured by Field Emission Scanning Electron Microscopy (FE-SEM) to clearly observe the carbon deposition within the pores.

3. Results and Discussion

Production of bio-char experiments were conducted in a tube furnace with flowing argon to a terminal pyrolysis temperature of 500°C at 10°C/min and 30°C/min heating rates. Experiments were repeated for terminal temperatures of 600, 700 and 800°C. Figure 4 shows the carbon contents of bio-char after slow pyrolysis of empty fruit bunch as first step at different constant heating rates of 10°C/min and 30°C/min, which were examined using elemental analysis by combustion.

Fig. 2. (a) Schematic diagram of the experimental apparatus where samples were put inside a 100 mm-diameter Alumina tube inside a tube furnace with flowing argon before being heated to experimental temperatures from 500 to 800°C for bio-char production; and 400–500°C for tar carbonization process. (b) For step one, the sample was a 3 g-EFB pellet put in an opened SUS316L-400 mesh bag (3 cm φ × 4 cm); and for step two, the sample was the bio-char pellet (mass = 0.8±0.2 g) produced from step one and 3 g of EFB particles put in two separate opened SUS mesh bags (3 cm φ × 4 cm).

Fig. 3. Thermal analysis of empty fruit bunches performed on a dry basis. Decomposition completed after 500°C.

Fig. 4. Carbon contents of bio-char after slow pyrolysis of empty fruit bunch as first step at different constant heating rates of 10°C/min and 30°C/min, which were examined using elemental analysis by combustion.

In the second step, tar-carbonization was carried out at 400°C with a holding time of 5 minutes using bio-char pellet as the precursor material. In this process, EFB particles were used as the bio-tar source. Fast constant heating rate of 60°C/min was applied to ensure bio-tar containing higher carbon could be produced from the EFB particles. Bio-tar produced was expected to infiltrate within the porous bio-char pellet and carbonized on the pore surface, increasing the carbon content of the bio-char pellet. Figure 6 showed the increase of carbon content in bio-char pellet after tar car-
bonization process. Tar carbonization conducted using bio-
char pellet produced at 500°C and 800°C gave the largest
carbon increase, with smallest carbon content, and largest
carbon content with smallest carbon increase, respectively.
These results suggest that the pores created at lower pyroly-
sis temperatures are smaller than those created at higher tem-
peratures, which is a better condition for tar to carbonize.

Bio-char samples produced at 500°C and 800°C were
selected to be used in tar carbonization process carried out
at 450°C and 500°C (Fig. 6). Figure 7 indicated the in-
crease of carbon content after tar carbonization process
performed at 400, 450 and 500°C. Carbonization temperature of 450°C was found
to be the most optimum temperature for tar decomposi-
tion within the bio-char pellet. Carbon contents within bio-char pellet produced at 500°C and 800°C increased to 83.2
mass% and 88.5 mass% respectively, at 450°C carboniza-
tion temperature. The increases of carbon for both samples
were 6.7 mass% and 2.0 mass%, respectively (Fig. 7). Tar
carbonization at 500°C resulted in a decrease in the carbon
content because bio-char has started to devolatilize.

Tar carbonization experiments were repeated at 450°C for
35 and 65 minutes holding time to evaluate the effect of car-
bonization time on carbon deposition. Figure 8 indicated
that the carbon content within carbon-infiltrated bio-char
pellet decreased as the holding time of tar carbonization
increased. This suggests that at the initial stage of tar car-
bonization process with bio-char pellet being the precursor,
the pores within the bio-char provided large amount of active sites which assisted carbon, tar decomposition and carbon deposition within the pores. As time increased, more
tar decomposition occurred, generating more gases and
more carbon deposits as presented in Eq. (1). However,
simultaneously, carbon from the reactive bio-char (precur-
sor) was gasified by steam produced by pyrolysis of EFB,
hence the small amount of carbon content within the result-

Fig. 5. Product distribution after slow pyrolysis of EFB as first step
which was performed at different holding temperatures for 10
minutes after being heated at the constant rate of 10°C/min,
showing char ratio decreased with temperature drastically.

Fig. 6. Carbon contents of bio-char before and after tar car-
bonization at 400°C as second step. Bar chart indicates the
increase of carbon content after tar carbonization process
by Chemical Vapor Infiltration (CVI).

Fig. 7. Carbon contents of bio-char after tar carbonization at 400, 450
and 500°C as second step; the precursors for tar carbonization
were bio-char produced at 500 and 800°C as first step.

Fig. 8. Carbon contents of bio-char after tar carbonization at 450°C
as second step with holding time of 5, 35 and 65 minutes
(left, center, right respectively); the precursor for tar car-
bonization was bio-char produced at 500°C as first step.

Fig. 9. Morphology of bio-char pellets before and after carbon
infiltration; showing carbon infiltration within pores as sec-
ond step.
ing carbon-infiltrated bio-char.

Figure 9 presents the morphologies of bio-char pellets before and after carbon infiltration within the pores. Figure 10 portrayed the schematic diagram of optimization process of infiltration conditions within bio-char pores from this study. Tar vapor infiltrated within the bio-char pores, where decomposition occurred and left carbon deposit on the pore surface gradually, increasing the carbon content within the bio-char pellets.

4. Conclusions

Slow pyrolysis was employed to produce bio-char pellet from EFB pellet. The amount of carbon content within bio-char was analyzed from each experiment. In the next step, porous bio-char pellet was utilized as the precursor material for tar carbonization to occur, and EFB particles were used as the source of bio-tar. CVI technology was employed in this study where bio-tar vapor from EFB particles infiltrated within the porous bio-char pellet, and decomposed into carbon and gases. Carbon was deposited on the pore surface, resulting in increased carbon content of the bio-char pellet. From the preliminary results, conclusions drawn were as below:

1) Carbonization at 450°C within bio-char pellet produced at 500°C with a holding time of 5 minutes had the largest carbon deposit.

2) Crushing strength increased with increasing carbon deposit after carbonization which suggests the strengthening of bio-char pellet by the infiltration.

3) Tar vapor infiltrated and carbonized within pores in the bio-char.

Overall, this research suggests the usability of bio-char, by increasing the amount of carbon content after tar carbonization process, to enhance the efficiency of biomass utilization. The product, carbon-infiltrated bio-char, which is renewable and environmentally friendly is expected to be utilized as an energy source to partially substitute coke especially in steel making industry.

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