The effect of heat storage to properties and energy recovery of pyrolysis products from agricultural waste

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Abstract. The pyrolysis process is the conversion of a biomass into biofuel but the process requires a high amount of external heat in order to increase the temperature of raw material which affects the production costs and energy efficiency. The effect of heat storage to control a temperature on the shell of pyrolysis reactor for the properties and energy recovery of pyrolysis products were considered in this study. Agricultural waste drop tube pyrolysis reactor that was designed into double layer shell wall to contain ceramic bead for heat storage. The parametric test of this study as temperature (350 °C – 550 °C), and biomass type (corncob, coffee grounds and coffee husk) were investigated. This result showed that, the heating rate of the reactor when starting to the setting temperature of the comparison testing (CT) was lower than that of the heat storage testing (HT). It indicated that the energy input for the reactor in case of HT was lower than that from CT. The yield of bio-oil and bio-char of the HT were lower than that of the CT in the same pyrolytic temperature. When increasing temperature for 350 °C to 550 °C effected to decreasing the yield of bio-char while the maximum yield of bio-oil found in the temperature of 450 °C. The heating value of pyrolysis products were increased in the higher temperature. The bio-fuel products from corncob had the higher heating value (HHV) and the energy recovery higher than that from another biomass.

Keywords: Heat Storage, Energy Recovery, Agricultural Waste, Pyrolysis, Drop Tube Reactor.

1. Introduction

Bioenergy from agricultural wastes could use in term of renewable energy and the environmental solving. Displacement of agricultural residue waste after the harvest as direct burning in field which have effect to air pollution and season smog crisis. Thermochemical process is the biofuel conversion by degradation of the biomass such as pyrolysis, gasification torrefaction and carbonization. The main product from thermochemical process are biochar, syngas and bio-oil that could use for supply and present energy crisis solution. Pyrolysis is one of the thermochemical degradations of organic material under the oxygen and air-limited environmental at a moderated temperature of 400 – 700 °C, the pyrolysis product is considered to biofuel that has a high energy content and renewable combustion
properties. Biomass pyrolysis is usually for bioenergy production under the reason of relative simplicity, flexibility in the quality and type of raw material and inexpensiveness. The products of pyrolysis have the difference properties and selecting for used in term of the energy replacement. A liquid product as bio-oil is the mixture of chemical compounds from the decomposition of biomass. Hundreds of organic compounds such as organic acids, sugars, aldehydes, alcohols, ketones, esters, phenols, ethers, nitrogen and sulfur that represent to the fuel characteristic of bio-oil [1]. Different pyrolysis processes, biomass source and conditions have effect to physicochemical characteristics of bio-oil and the formation of pyrolytic biomass at different lengths of the polymeric chain are randomly broken relevant to specific perform to the chemical characterization of bio-oils [2]. In term of the bio-oil advantage for energy that could substitute for some of liquid fossil fuel but most cases it not be suitable for directly to using and requirement to improve the quality closed to crude oil in petroleum refineries. However, for the modified pyrolysis processes could produce and upgrade bio-oil from biomass and waste to the commercial grade fuels and high value of precursors in the chemical industry [1]. The solid product from pyrolysis process is biochar, which is a carbon-rich solid and porous residue product and it has an energy density close to lignite, the obvious synergistic interactions were observed between biochar and lignite during co-combustions, resulting in increased thermal efficiency and environmental benefits [3]. Biochar production not show in term of energy section, but that have functions well for soil improvement and soil amendment to improve crop production. Returning biochar to soil could change some physical behaviors and structures of soil, fertilizer utilization rate and crop yield. Furthermore, biochar could perform an important role in helping to sequester carbon from the atmosphere, the stable form of carbon that could contain in biochar product more than 50% from the biomass. This mean that we could keeping and sequestration of CO₂ return to the nature [4]. During bio-fuel production, energy for pyrolysis reactions is required. The previous research analyzed the energy balance of biofuel production from palm oil empty fruit bunches (EFB) and found that the total energy demand was 2.75 MJ kg⁻¹ EFB, and the energy input from diesel fuel and electricity consumption were 2.31 and 0.39 MJ kg⁻¹ EFB, respectively. The net energy output in the form of biochar was 5.72 MJ kg⁻¹ EFB. The net energy yield was 11.47 MJ kg⁻¹ EFB and the energy output/input ratio of the bio-char production was positive [5]. On the other hand, another work investigated the bio-char production from dried human manure and found that the feedstock moisture content affected a net energy output and it should be lower than 57% for the benefit of the pyrolytic system [6].

The effect of heat storage to the pyrolysis production via drop tube reactor was considered in this study. Ceramic beads were selected for the heat storages material that was put around a shell of the reactor, the comparison between the production under heat storage (Heat storage testing – HT) and comparison testing (CT) were shown in that result of yield and properties for pyrolysis products. The energy recovery calculations indicated that the suitability of the biofuel production process for that utilization.

2. Experimental Apparatus and Procedure

2.1. Biomass Feedstock.

The biomass of corncob, coffee grounds and coffee husk were selected for used in this pyrolyzed testing. Raw material preparing by sizing and it was dried at room temperature for one week and at 60 °C for 24 h before testing.

2.2. Porous Fixed Bed Reactor Pyrolysis System and Procedure.

The schematic diagram of the pyrolysis production was shown in Figure 1. The stainless-steel drop tube reactor was designed in a double layer of the cylinder. Each sample (200 g) was fed into inner pipe after the reactor heat into the temperature set and the ceramic beads were put in a shell of the reactor. Nitrogen gas was fed through a layer of ceramic beads before coming to the inner reactor for around 30 minutes at a flow rate of 1 l min⁻¹ to remove air inside the reactor before testing. The test
was initiated by heating up the reactor to a set temperature (350 – 550 °C). The gas leaving the reactor was condensed in two water-cooled glass condensers and the liquid product was stored in two collecting flasks while the solid residue (biochar) remained in the reactor. The effect of the pyrolysis temperature on the bio-product yield and properties were evaluated. Furthermore, the comparison in the case of not using ceramic beads was considered.

![A schematic sketch of the pyrolysis experiment setup.](image)

**Figure 1.** A schematic sketch of the pyrolysis experiment setup.

### 2.3. Analysis of biofuel product.
The properties and the chemical composition of agricultural waste and bio-energy products were determined for proximate analysis. The ultimate analysis was estimated by CHNS which determined the elemental composition of the raw material and bio-energy products. The total of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) was used for calculating H/C and O/C ratio by the mole ratio on a dry basis. Higher heating value (HHV, MJ kg⁻¹) was calculated from the equation below [7].

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HHV = 0.3491C + 1.1783H + 0.1005S - 0.1040O - 0.0151N - 0.0211Ash
\]

Scanning electron microscopy (SEM) was applied to characterize the porous surface of bio-char products.

### 2.4. Energy Recovery
The energy recovery of the bio-oil and biochar product could be calculated by the ratio of the energy carried by bio-oil and biochar to the energy contained in the biomass (corn cob, coffee ground and coffee husk) from the equation below.

Energy recovery (%) = 100 x \[(\text{HHVbio-oil} \times \text{amount of bio-oil produced}) + (\text{HHVbio-char} \times \text{amount of bio-char produced})]/(\text{HHVbiomass} \times \text{amount of biomass}) \] [8].

### 3. Results and Discussion.

#### 3.1. Thermal profiling in the reactor.
The thermal temperatures in a reactor from the testing with CT and HT that used in calculation and comparing with the heating rate when heating up inside the reactor. The result was shown in Figure 2.
which was presented that the HT had more of the heating rate than that of the CT around 46.3 – 48.5% in a difference measurements position, this mean that the time for heating before testing and energy input of the HT was lower than that from CT.

3.2. The effect of pyrolysis temperature.
The yields and the composition of biofuel product from pyrolysis process under the CT and the HT in the difference temperature testing was shown int Figure 3. It was found that, the biochar yield was decreased when increasing the temperature setting while the maximum yield of bio-oil found in the temperature of 450 °C and the gas yield show in the opposite result of biochar. The secondary decomposition of the bio-char could produce non-condensable gases at higher temperatures contributing to an increase in gaseous product and decrease in bio-char product [9]. The highest yield of bio-oil from corncob was found at all pyrolyted temperature when comparing with bio-oil from the agricultural waste of a coffee production. Biomass constituent affect to the bio-oil and biochar yield, lignin and cellulose are the composition of biomass that is considered in the biomass enhance the formation of biofuel. The biomass which has more lignin show in higher biochar yield as compare to cellulose [4].

3.3. Properties of biofuel in the difference pyrolytic condition.
The properties of biochar from difference pyrolytic temperature of corncob material was shown in Table 1. that was indicated to the composition of biofuel specific in biochar have more fixed carbon when the temperature in the reactor decreasing, the HT have effect to increasing the heating value and decreasing the Oxygen component when comparing with the CT. The physical properties of biochar from coffee husk was presented in Figure 4., the result from SEM micrographs indicated to more of porosity of bio-char that found when use heat storage as ceramic bead in the reactor at the same pyrolysis temperature of 550 °C, that could explicitly display when comparing with the CT testing.

3.4. The energy recovery from biooil and biochar product.
The energy recovery demonstrates for the ratio between the energy carried by biooil and biochar and the energy contain in the biomass. The parametric study has an effect to the energy recovery of the product as shown in Figure 5. It could be found that, the energy recovery of the HT more than the CT around 3 – 13 %, in the biofuel production from coffee ground and coffee husk at the pyrolysis temperature of 450 °C had higher than that from another temperature setting while in case of corncob at
the temperature of 550 °C the energy recovery shown in more than the lower pyrolytic temperature. The biofuel from corncob have the energy recovery more than coffee ground and coffee husk of 77.62, 56.11 and 32.65, respectively at 550 °C and in the HT process.

![Graph showing biofuel yield of difference pyrolysis temperature.](image)

**Figure 3.** Biofuel yield of the difference pyrolysis temperature.

![SEM micrograph of bio-char product at HT and CT testing.](image)

**Figure 4.** SEM micrograph of bio-char product at the HT and CT testing.
Table 1. Chemical composition and properties of biochar from corncob in different conditions.

| Property                | Corncob |               |               |               |               |               |
|-------------------------|---------|---------------|---------------|---------------|---------------|---------------|
|                         | HT      | 350           | 450           | 550           | CT            | 350           | 450           | 550           |
| Proximate analysis (wt% dry basis) |         |               |               |               |               |               |               |               |
| Moisture                | 2.72    | 1.97          | 1.35          | 2.83          | 2.79          | 1.22          |               |               |
| Volatile Matter         | 56.22   | 48.99         | 39.61         | 43.93         | 29.98         | 27.12         |               |               |
| Ash                     | 3.38    | 4.53          | 4.79          | 1.93          | 2.67          | 3.33          |               |               |
| Fixed Carbon            | 38.05   | 44.51         | 54.25         | 51.31         | 64.56         | 68.33         |               |               |
| Ultimate analysis (wt% dry basis) |         |               |               |               |               |               |               |               |
| Carbon                  | 66.89   | 74.4          | 77.14         | 68.18         | 73.44         | 81.94         |               |               |
| Hydrogen                | 4.94    | 4             | 4.41          | 4.84          | 4.12          | 3.78          |               |               |
| Oxygen (diff.)          | 27.58   | 20.99         | 17.83         | 26.44         | 21.82         | 13.67         |               |               |
| Nitrogen                | 0.58    | 0.6           | 0.61          | 0.54          | 0.62          | 0.61          |               |               |
| H/C                     | 0.89    | 0.65          | 0.69          | 0.85          | 0.67          | 0.55          |               |               |
| O/C                     | 0.31    | 0.21          | 0.17          | 0.29          | 0.22          | 0.13          |               |               |
| HHV (MJ kg\(^{-1}\))   | 26.08   | 28.04         | 29.92         | 26.72         | 28.17         | 31.56         |               |               |
4. Conclusion.
The effect of heat storage to the pyrolysis production via drop tube reactor was investigated in this work. It was found that, increasing of pyrolysis temperature had an effect to decreasing the bio-char and bio-oil yield in but gas yield is increasing. Heating rate of the reactor in case of using heat storage have more than the comparison case around 46.3 – 48.5 %. The yield product from the pyrolysis process are lower when we use the heat storage in the reactor in the same pyrolytic temperature. The energy recovery from biofuel of corncob was higher than from coffee grounds and coffee husk. The production with the heat storage had the energy recovery higher than that from the comparing testing around 3 – 13 % in the highest pyrolysis temperature.

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