



Upgrading agricultural wastes using three different carbonization methods: Thermal, hydrothermal and vapothermal

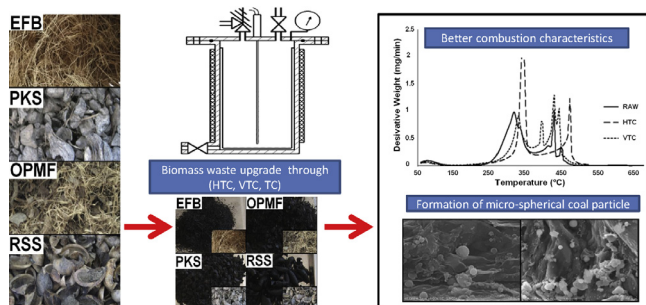


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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Hydrothermal carbonization
Vapothermal carbonization
Thermal carbonization
Hydrochar
Energy densification

ABSTRACT

In this study, three different methods for high quality solid fuel production were tested and compared experimentally. Oil palm empty fruit bunches, mesocarp fibers, palm kernel shells and rubber seeds shells were treated using thermal (TC), hydrothermal (HTC) and vapothermal (VTC) carbonization. All thermochemical methods were accomplished by using a custom made batch-type reactor. Utilization of novel single reactor equipped with suspended internal container provided efficient operation since both steam generator and raw materials were placed inside the same reactor. Highest energy densification was achieved by VTC process followed by TC and HTC processes. The heating value enhancement in VTC and TC was achieved by the increase in fixed carbon content and reduction in volatile matter. The formation of the spherical components in HTC hydrochar which gave a sharp peak at 340 °C in the DTG curves was suggested as the reason that led to the increment in energy content.

1. Introduction

In Malaysia, agricultural plantation is one of the main economic activities where the main crops are oil palm fruit, rubber, paddy, coconut and coco. Huge amounts of by-products and residues are produced annually with an estimated potential of about 55,000 GWh of electricity (Shafie et al., 2012). One of the most promising solutions for the high carbon footprint in the large-scale coal fueled power plants is

to co-fire coal with biomass. This could drastically reduce the greenhouse gas emission as biomass has no net CO₂ emission throughout the bio-cycle and also reduce harmful emission such as NO_x and SO_x (Acharya et al., 2015). However, low-grade biomass solid fuel suffer from the low energy density and high moisture that can affect combustion quality. Other than that, biomass feedstock can differ considerably in term of their physical, chemical and morphological characteristics due to their heterogeneous natural. They are usually bulky

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<https://doi.org/10.1016/j.biortech.2018.06.024>

Received 20 April 2018; Received in revised form 8 June 2018; Accepted 9 June 2018

Available online 15 June 2018

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and easily subjected to fungal attack or biodegradation as well. All these characteristics of biomass lead to a higher complexity and cost for feedstock preparation, handling, transportation and storage. Also, the higher ash content in the feedstock can cause fouling and deposits on the boiler tubes (Chen et al., 2015b; Chew and Doshi, 2011). To overcome these problems, biomass is usually converted into various forms of energy carriers such as ethanol, biodiesel, producer gas, biogas and solid biofuels which are higher in energy density and can be handled and stored with relative ease.

Biochemical and thermochemical conversions are two major routes for enhancing biomass properties. Compared to biochemical conversion methods, thermochemical treatment has shown several advantages such as shorter processing time, higher conversion efficiency, ability to convert a variety of biomass feedstock, ability to produce a diversity of oxygenated and hydrocarbon fuel, lower cost of catalysts, ability to recycle catalyst and does not require sterilization process (Brown, 2011; Chen et al., 2015a; Liu et al., 2013). All these characteristics of thermochemical conversion method make it more viable in treating large amount of low-grade feedstock. Biomass torrefaction and thermal carbonization (TC) are some of the conventional thermochemical methods to enhance its grindability and increase its heating value (Anuar et al., 2017).

Hydrothermal carbonization (HTC) is another thermochemical conversion process that has the advantage of treating wet or green biomass material directly without any pre-drying (Park et al., 2018). In HTC process, biomass materials are submerged in sufficient amount of water, so that the solid materials react with liquid water at elevated pressure and temperature (Liu et al., 2013; Kalderis et al., 2014; Kongpanya et al., 2014; Lu et al., 2011; Novianti et al., 2014; Román et al., 2012). HTC operates above normal water boiling temperature up to 220 °C, followed by HT liquefaction and HT gasification at the sub-critical and super-critical zones, respectively (Kruse and Dahmen, 2018; Hrnčič et al., 2016). HTC process can be carried out without the addition of other chemicals or catalysts that makes it more attainable for large-scale solid waste upgrading (Kambo and Dutta, 2015).

Another thermochemical process to upgrade wet biomass feedstock is the vapothermal carbonization (VTC). It is also called vapor hydrothermal carbonization (Minaret and Dutta, 2016) or vapor-wet torrefaction (Acharya et al., 2015). In this method, biomass materials are no longer submerged in water but subject to high pressure saturated steam (Novianti et al., 2014; Titirici et al., 2015; Yoshikawa, 2009). The main difference between HTC and VTC methods is the reaction medium. In HTC, hot compressed liquid water is the reaction medium, while in VTC, the reaction medium is saturated steam (Quicker, 2015). It is hard to predict whether liquid water or saturated steam are more effective in upgrading biomass feedstock since both methods have their own advantages. Higher density of water allows higher heat transfer to the biomass materials, while saturated steam which has a lower density is able to penetrate the porous structure of the biomass material at a faster rate (Minaret and Dutta, 2016).

As any other thermochemical treatment of biomass, HTC and VTC also produce liquid and gaseous by-products beside the solid fuel as its main products. Investigation from other researchers revealed that the amount of by-products produced is insignificant with process parameter. As with the case of HTC, analysis of its liquid by-product showed that total organic carbon is proportional with reaction severity (Funke et al., 2013; Danso-Boateng et al., 2013). Moreover, degradation of mineral content during HTC can also be measured from analysis of liquid by-product, but its trend was found out to be insignificant with reaction severity (Basso et al., 2015). Basso D et al. also had established presence of gaseous by-product from pressure profile of the reactor during HTC treatment throughout the reaction time of 500 min (Basso et al., 2015). It was claimed that pressure rise during HTC was due to formation of gaseous products which consists of carbon dioxide (90%) and carbon monoxide (8%), while hydrogen, methane, and traces of light hydrocarbon build up the remaining 2% (Basso et al., 2015;

Hwang et al., 2012). However the formation of gaseous by-product was very low, only 2–3 bar increment in pressure was recorded for the entire 500 min treatment duration. Due to the insignificant volume of by-products and its low relationship to reaction severity, current study gives more emphasis on solid fuel properties produced from HTC and VTC, and its comparison with TC. No consideration was given to their respective liquid and gaseous by-products.

Only few experimental studies have been conducted to compare between HTC and VTC processes (Funke et al., 2013; Minaret and Dutta, 2016; Shafie et al., 2018). Studies showed that there are significant differences between the two processes but it is difficult to observe a clear trend in comparing the effects of these two methods on the product formed. In this study, HTC and VTC, additional to the conventional TC processes where all experimentally compared. Wide range of the common agricultural wastes in Malaysia were investigated. The characteristics of the raw materials and carbonized produces were thoroughly analysed in terms of composition, microstructure and combustion performance.

2. Material and methods

2.1. Experimental setup

In previous study (Shafie et al., 2018), a dual-chamber test rig was developed to evaluate the VTC process of high-moisture low-grade biomass. The experimental set-up was modified to compare the three carbonization methods: HTC, VTC and TC using single-chamber reactor design. The new reactor consists of a cylindrical chamber of 150 mm inner diameter and 400 mm height. The chamber was equipped with a 2 kW electrical heater band connected to a Type-K thermocouple and a temperature controller for fast and accurate control of the temperature. For steam pressure measurement, a 30 bar pressure gauge was used with steam release and safety valves. Fig. 1 shows a schematic drawing of the experimental test rig setup for HTC, VTC and TC processes.

2.2. Materials

In this study, four of the most abundant agricultural waste biomass materials in Malaysia namely: oil palm empty fruit bunches (EFB), oil palm mesocarp fibers (OPMF), oil palm kernel shells (PKS) and rubber seeds shells (RSS) were investigated. The materials were dried at 110 °C before the carbonization treatment process in order to ensure the consistency of the quality of the feedstock throughout the experiments.

2.3. Hydrothermal carbonization (HTC)

The hydrothermal carbonization process was conducted by fully submerging biomass in water under high temperature and pressure inside the chamber as shown earlier in the experimental setup in Fig. 1. Apart from reaction temperature and residence time, another factor which influence HTC process is termed as water-to-biomass ratio (later mention as W/B). W/B ratio can be defined as ratio of mass of water for HTC process together with moisture inside raw materials, to the mass of dried raw materials (Shafie et al., 2018). However this definition is applicable if wet materials are used directly during HTC. Since current study utilized dried raw materials for HTC process, only the mass of water used during HTC was considered for W/B ratio determination. Regardless of any predetermined W/B ratio, it must be ensure that all of the materials were submerged inside the water to avoid the effect of VTC on the non-submerged materials.

Water and biomass sample were both placed inside the 140 mm diameter removable container before placing the container inside the chamber and sealing the cover plate. The heater band controller was then set to maintain the temperature inside the chamber at 220 °C for one hour reaction period. After that, the gate valve on the cover plate was opened to release the steam from the chamber and then it was left

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