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Characteristics of hydrochar and liquid fraction from hydrothermal carbonization of cassava rhizome

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ABSTRACT

Hydrothermal carbonization (HTC) of cassava rhizome (CR) was performed to investigate the effect of process parameters including temperature, time, and biomass to water ratio (BTW) on characteristics of hydrochar and liquid fraction products. The effect of temperature was two-fold. First, an increase in reaction temperature from 160 to 180 °C decreased hydrochar yield from 54 to 51%, however, a further increase of temperature from 180 to 200 °C saw an increase in the hydrochar yield to 58%. This was associated to degradation, polymerization, and condensation reactions during HTC. The hydrogen/carbon and oxygen/carbon atomic ratios decreased from 1.4 and 0.6 at 160 °C to 1.2 and 0.4 at 200 °C, respectively. The liquid fraction contained various valuable chemical species including, glucose, furan compounds, (furfural, furfuryl alcohol, hydroxymethylfurfural), volatile fatty acid (succinic acid, lactic acid, formic acid, acetic acid, levulinic acid, and propionic acid) with their highest yields (wt.% dry raw material) of 4.5, 18.5, and 24.3, respectively.

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1. Introduction

In Thailand, cassava is one of the major economic crops with its increasing production to as much as 32 million tons in 2015 [11]. Cassava rhizome (CR), being the joint between cassava root and stalk, is the agricultural residue obtained from cassava plantation. The residue product ratio of CR is 0.2 [14], and the amount of CR in 2015 was estimated to be about 6.4 million tons. Although CR is typically disposed of as waste, its major compositions are hemicellulose and cellulose [36] that can be used to produce various valuable bio-based products.

Hydrothermal carbonization (HTC) is regarded as an effective thermochemical conversion technology for biomass. Currently, HTC receives great attention due to its several advantages. For instance, it could be operated at mild temperature (160–270 °C) [15] when compared with other thermochemical conversion technologies such as pyrolysis and gasification. HTC was also considered as a pathogen removal process [32]. Water is typically used as a reaction medium for HTC, and water could also act as a solvent or catalyst for the conversion lignocellulosic biomass. Therefore, wet biomass could be employed and a pre-drying process of feedstock could be avoided [7]. A series of reactions occurred during biomass decomposition in HTC including hydrolysis, dehydration, decarboxylation, condensation polymerization, and aromatization [16]. Products from HTC of lignocellulosic biomass are hydrochar (solid), liquid fraction, and gaseous product. Normally, hydrochar is the major product with higher hydrophobic properties and carbon content than the feedstock. The applications of hydrochar include fuel source [34], soil amendment [45], carbon-based catalyst [26], adsorbent [30], or energy storage [22]. Simultaneously, the liquid fraction product is composed of various valuable organic chemicals generated from decomposition of

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lignocellulosic components. Examples of these chemicals are furfural, hydroxymethyl-furfural (HMF), succinic acid, lactic acid, formic acid, acetic acid, levulinic acid, propionic acid, and furfuryl alcohol, etc., all these can be used as valuable bio-intermediate chemicals [24,47,50].

The characteristics of HTC products depend mainly on types of lignocellulosic biomass and process parameters such as reaction temperature, time, and biomass to water ratio (BTW). Recently, most studies revealed the effect of reaction temperature and time on characteristics of hydrochar from HTC of various feedstocks such as coniferous [41], corncob residues [49], olive mill, canned artichoke, orange waste [8], eucalyptus bark [17], and sewage sludge [37]. They found that higher heating value (HHV), fixed carbon content, and carbon content of hydrochar increased with reaction temperature and time, except hydrochar yield. The BTW was reported to have a slight impact on the hydrochar yield [3,40]. In addition, HHV of hydrochar increased significantly with cellulose content [27]. The liquid fraction obtained from HTC typically contained reducing sugar, furan compounds, volatile fatty acid, and phenolic compounds where, as mentioned above, the yields depended on the biomass characteristics and hydrothermal conditions [24,47,50]. These compounds are regarded as vital versatile intermediates for a wide variety of high performance fuels and high value-added chemicals which demonstrates the potential of biomass refinery options such as HTC.

There is therefore a clear need to further investigate the behavior of HTC process for the various types of biomass particularly the unwanted fractions obtained after the harvest such as CR. The purposes of this study are, hence, to: (1) investigate the potential of hydrochar, furan compounds, and VFA production by HTC of CR; (2) explore the characteristics of hydrochar and chemical composition in liquid fraction from HTC of CR; (3) identify the effect of reaction parameters such as reaction temperature, reaction time, and the biomass to water ratio on both hydrochar and liquid fraction products. Reaction mechanisms during HTC were proposed and the characteristics of liquid fraction was analyzed to quantify potential valuable chemical species and to examine their potential applications.

2. Methods

2.1. Biomass preparation

Cassava rhizome (CR) from Rayong province in Thailand was used as feedstock in this study. Its average moisture content was around 51%. This was chopped and washed to remove contaminants then dried at 70 °C for 24 h. After that, CR was pulverized to obtain powder with particle size smaller than 0.1 mm. It was then dried at 105 °C for 24 h and stored in a sealed plastic bag for further experiments.

2.2. HTC experiment

HTC of CR was conducted in a batch bomb type stainless steel reactor (500 mL, NK Laboratory Co., Ltd, Thailand) with fitting glass liners. The schematic diagram of apparatus is shown in Fig. 1. In each batch experiment, 70, 38, and 25 g of CR powders were mixed with 345, 377, and 390 mL of deionized water, respectively, in order to obtain the desired BTW (1:5, 1:10, and 1:15) at a working volume of 400 mL. The ratio of 1:5 was to ensure that all biomass was completely submerged underneath the water level. After that, the reactor was tightly closed and placed in the laboratory oven. The temperature mixture was measured with a pipe-fitting thermocouple probe (Type K). The reactor was heated up to the target mixture temperature (160, 180 and 200 °C) with the heating rate about 1 °C/min and maintained for various reaction times (1, 2 and 3 h). Upon the completion of the reaction, the reactor was submerged immediately in a cold-water bath to quench the reaction. Fig. 2 illustrates the temperature profile of the system where the heating from room temperature to the desired reaction temperature required approximately 170 min and the cooling period to 100 °C was about 30 min. Product mixtures were separated by vacuum filtration. Solid hydrochar was washed with deionized water until the pH of washed water was neutral after which it was dried at 105 °C overnight. Dried hydrochar was stored in a sealed plastic bag for further analysis. The liquid fraction and washed-water were stored in the dark at 4 °C for further analysis which was carried out within

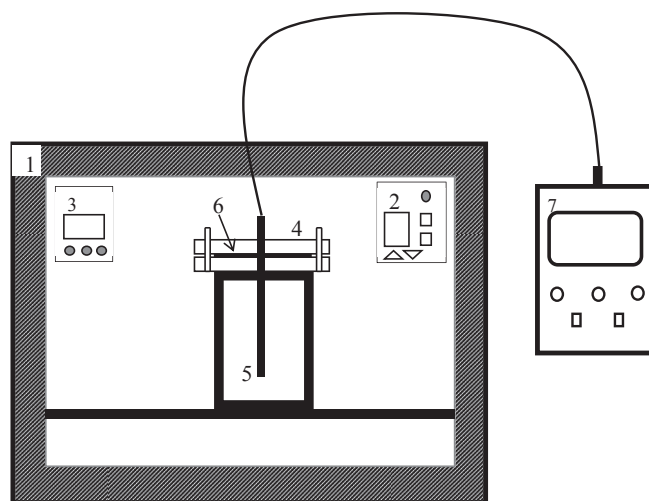


Fig. 1. Schematic diagram of HTC apparatus: 1. laboratory oven, 2. oven temperature controller, 3. stopwatch, 4. a batch bomb type stainless steel reactor, 5. a pipe-fitting thermocouple probe (Type K), 6. O-ring, 7. temperature display.

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