Hydrochar Generation from Hydrothermal Carbonization of Organic Wastes

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Abstract. Organic wastes from leftover food contributes to a large fraction of municipal solid waste. Because of its high moisture content, it is not suitable to be processed in a conventional way of burning. This study is interested in the possibility to apply hydrothermal carbonization (HTC) process to organic wastes. The objective was to study characteristics of HTC products as a function of temperature and residence time (180-250°C and 1-6 h). Samples of organic waste from discarded foods were processed in a HTC reactor. From the result of hydrochar analysis, it was shown that highest heating value and energy densification were 30 MJ/kg and 1.80 respectively, at 250°C and 3 h. The aqueous solution was found to contain minor concentration of fertiliser nutrients. These products may be used as fuel and chemicals as well as applications in agriculture. It was confirmed that valuable products can be generated from organic waste using hydrothermal carbonization.

1. Introduction
Organic wastes from leftover food is one of the most challenging issues society is encountering globally. Large percentages of the food intentionally prepared for consumption is wasted, with significant environmental and socio-economic implications. Food waste represents a significant fraction of municipal solid waste which is largely underutilized. There are more than 200 kg/day of food wastes from Chiang Mai University canteens. It is not only cooked foods but also fruit juices, seasoning or vegetables from cooking and fruits peels. These wastes contain high moisture and become bad with rancid smell quickly. Sustainable food waste management is urgently needed. In this work, processing of these organic wastes by hydrothermal carbonization (HTC) is chosen.

HTC is a thermochemical conversion process, reacting wet organic substrates in hydrothermal conditions or in hot pressurized liquid water [1]. HTC process conditions are usually in mild temperatures range (180-260°C) at 15-25 bar. Typical residence times range between a few to several hours. Hot pressurized water exhibits a higher ion product than at ambient conditions, behaving as an acid/base catalyst precursor and acting as a solvent and a reactant [2]. The main product of HTC process after conversion is hydrochar, a carbonaceous solid organic material. Its chemical composition is similar to low rank coals such as peat or lignite [3]. The interest in HTC is motivated by its suitability to handle high moisture materials and application of hydrochar as solid fuel [4]-[7].
In this work, application of HTC to food waste was carried out. The process has potential to lower the overall cost for waste disposal. The characteristics of the obtained hydrochar and the liquid filtrate product were investigated.

2. Materials and Methods

2.1. Raw materials
Organic wastes were obtained from a local fresh food market in Chiang Mai University campus, Thailand. They were then sorted to remove solid impurities such as bones, small pieces of wood, seeds and stones. The waste sample was subsequently dried at 105°C for 24 h to achieve constant weight and then comminuted and sieved into uniform size. It was ground to particle diameter of less than 2.36 mm and stored in a desiccator for later use. All chemicals used were of analytical grade from Thailand Institute of Scientific and Technological Research in Bangkok, Thailand.

2.2. HTC experiments
The experiments were carried out in a 10 L cylindrical pressure reactor equipped with 14 kW heaters and internal sensors for temperature control, shown in Figure 1. The reactor was designed and constructed by Febix International Co., Ltd (Chiang Mai, Thailand). Dried organic waste (260 g) was dispersed in 5.7 L of distilled water contained in a round-bottomed flask. The mixture was stirred until a homogeneous suspension was created. It was then loaded to the HTC reactor. The heater was switched on. The temperatures set were 180, 215 and 250°C. It was kept at this condition for 1, 3 and 6 h. After which the heater was turned off. When the reactor was cooled down to room temperature and pressure decreased to ambient level, the products (hydrochar and liquid product) were discharged through drain pipe to a temporary container.

![Figure 1. HTC experimental setup.](image-url)

The solid hydrochar and liquid product were subsequently separated by filtration and all liquid product were collected in a container. The hydrochar was immediately dried in an oven for 24 h at 105°C, then reduced the size and collected in an airtight container for subsequent analyses. The hydrochar samples obtained were denoted according to carbonization conditions as H180-1, H180-3, H180-6, H215-1, H215-3, H215-6, H250-1, H250-3 and H250-6, respectively.

2.3. Characterization of products
The raw organic wastes and hydrochars were analysed for their chemical compositions. Ultimate and proximate analyses were conducted by the Thailand Institute of Scientific and Technological Research (Bangkok, Thailand), according to ASTM D 7582, D 5373, D 4239 and D 5865 standards. Liquid product was analysed by Central Laboratory Co., Ltd (Chiang Mai, Thailand).

3. Results and discussion

3.1. Hydrochars
Characteristics of the food wastes and their hydrochars were evaluated to study the changes of the raw material with respect to physical and chemical components. Figure 2 shows physical appearances for the raw food waste, and its hydrochars at various conditions. It was observed that at more severe carbonization conditions (higher temperature and longer time), hydrochars tended to become darker in colour.

![Hydrochars at different conditions](image)

**Figure 2.** Physical appearances of hydrochars at (a) 180°C 1h, (b) 180°C 3h, (c) 180°C 6h, (d) 215°C 1h, (e) 180°C 3h, (f) 180°C 6h, (g) 250°C 1h, (h) 250°C 3h and (i) 250°C 6h.

Table 1 shows solid yields, ultimate analysis, proximate analysis, and heating values of the hydrochars. The hydrochar yields obtained from the HTC were in the 23-46% range on a dry basis. The values here were lower than the reported by Basso et al. [1] and Li et al. [8], However, regarding energy densification which was defined as a ratio of HHV between the hydrochar and the starting material, this study showed higher values than those reported. It should be noted that treatment conditions were not exactly similar. However, the trend was clear that solid products decreased with increasing residence time. As shown in Figure 3, increasing the carbonization time and temperature led to reduction in yield due to larger overall decomposition of biomass material, or carbon, existing in organic waste as volatile matter, progressively reacted and diffused out. Increase in fixed carbon and decrease in volatile matter between the raw materials and hydrochars confirmed that carbonization took place. For the first 1 h, only volatile matter at the surface was removed. At longer reaction times, volatile matter in the interior of the particle was also removed, but with more difficulty than at the surface. Figure 4 shows that increasing HTC temperature and time tended to increase fixed carbon and decrease volatile content of the hydrochar. This was in line with change in elemental composition as a result of carbonization. HTC of the organic waste led to an increase in the carbon content from 45% (organic waste) to 58-64% in the hydrochar samples. The
high fraction of carbon was retained in the hydrochar products, while the rest mainly remained in the organic compounds that dissolved in the aqueous, similar to those reported in the literature [9, 10]. Transformation of organic material to carbon rich material or coalification process may be visualised using a van Krevelen diagram [11]. Plot of atomic H/C and O/C ratios for hydrochars in Figure 5 allows understanding of the evolution of the solid composition. HTC acts as a process for concentrating the carbon content of biomass, hence H/C and O/C atomic ratios are expected to decrease due to the reaction. The results confirmed such trend. Notably, the raw organic waste had a very high O/C atomic ratio. Increase in severity of HTC conditions (higher temperatures or longer times), the H/C and O/C ratios of hydrochars were expected to approach the values similar to those associated with peat and lignite. Further carbonization was possible to increase the extent of coalification. Reaction temperature selected was 180-250°C in which HTC at this condition was reported to be able to sufficiently generate solid product that was similar to coal quality [9].

Table 1. Chemical characteristics and properties of dried organic waste and hydrochars.

|                  | H180-1 | H180-3 | H180-6 | H215-1 | H215-3 | H215-6 | H250-1 | H250-3 | H250-6 |
|------------------|--------|--------|--------|--------|--------|--------|--------|--------|--------|
| Yield (% w/w)    | 46.2   | 30.8   | 26.9   | 36.5   | 30.8   | 25.0   | 34.6   | 26.9   | 23.1   |
| Ultimate analysis (%) |        |        |        |        |        |        |        |        |        |
| C                | 58.6   | 61.9   | 60.3   | 60.1   | 62.4   |        |        |        |        |
| H                | 1   | 1  | 1  | 2  | 2  | 2  | 2  | 2  | 2  |
| N                | 4.32  | 3.75  | 3.75  | 5.54  | 3.08  | 4.38  | 3.12  | 3.21  |        |
| O                | 27.4   | 22.4   | 24.6   | 23.5   | 20.8   |        |        |        |        |
| Proximate analysis (%) |        |        |        |        |        |        |        |        |        |
| Ash              | 23.32  | 23.32  | 24.96  | 20.98  | 2  | 4  | 21.27 | 3  |        |
| Volatile matter  | 3.79   | 1.78   | 3.06   | 2.86   | 3.43  | 3.05  | 3.08  | 2.36  | 4.85   |
| Fixed carbon     | 86.93  | 84.9   | 85.53  | 85.63  | 84.9  | 85.4  | 84.96 | 82.1  |        |
| HHV (MJ/kg)      | 5      | 3      | 7      | 1      | 6      |        |        |        |        |
| Energy densification | 1.69  | 1.60   | 1.71   | 1.63   | 1.74  | 1.68  | 1.67  | 1.80  | 1.71   |

Figure 3. Solid yields of hydrochar.
3.2. Liquid by-product
It is generally known that water plays a significant role as a solvent and reactant in the HTC process. The liquid phase is expected to contain a high loading of organics and inorganics. It may be recycled as a nutrient solution to agricultural lands. The liquid filtrate obtained was completely sterile after the HTC at 180-250°C. A slight drop in pH of the aqueous phase was observed after HTC reaction, becoming slightly acidic. It is noted here that original pH of deionized water was neutral. The decreasing pH may have some effect to the colour of liquid products. The colours tended to be darker (shown in Figure 6) when the pH was decreased. The liquid phase was also found to contain some nutrient content.
Figure 6. Colour of liquid products of each HTC process conditions.

4. Conclusion
In this work, HTC of food waste was performed at several process conditions. Solid and liquid products were collected and characterized. It was suggested that the hydrochar produced was suitable for energy purposes as its heating value as high as 30 MJ/kg can be achieved. Moreover, its elemental composition was becoming closer to that of peat and lignite, thus the hydrochar may be used in co-combustion with other coals. It was demonstrated that the HTC process offered alternative technique for conversion of organic waste to value-added products. Further works may be performed to gain better understanding of the underlying process, to characterize related properties, and to identify applications for these products.

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