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Article

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Characterization of hydrochar from hydrothermal carbonization of maize residues

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Abstract

Utilization of agro-residues from maize production as biorenewable energy source is considered to be a very good and sustainable waste management method. Hydrothermal carbonization (HTC) is a thermochemical conversion process for solid organic materials at elevated temperature and pressure in the presence of water. Through hydrolysis, dehydration and decarboxylation, a solid hydrochar as well as gaseous and aqueous products are generated. The energy density and the macromolecular structure of the solid product are improved, giving rise to a carbonized product that is simpler to convert to heat, power or fuel than the starting materials. This study was about applying HTC to upgrade maize residues. The residues used were cobs derived from a maize processing factory. The HTC experiments were carried out in a batch 10-dm³ pressure reactor equipped with 14 kW heaters and internal temperature control. About 0.5 kg of biomass was loaded with 5 dm³ of deionized water into the reactor. The effects of temperature (180–250 °C) and time (60–360 min) were examined. The hydrochar was recovered by filtration and dried for subsequent analyses. With increasing temperature and time, the amount of hydrochar was found to decrease, while the gaseous and aqueous products increased. Hydrochar yields were in the range of about 35%–72%. From the analysis result, hydrochar produced was found to have improved fuel qualities. Its elemental composition was coalified with H/C and O/C atomic ratios moving towards that of lignite.

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Keywords: Agricultural waste; Biomass conversion; Hot compressed water; Renewable energy; Wet pyrolysis

1. Introduction

Maize is a major economic crop in Thailand. During the harvesting and processing, a large amount of maize residues is generated and usually left as waste. These residues are not normally utilized, but burned openly in the field, hence, a large amount of air pollutants is emitted to the environment, partially contributing to haze problem in

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northern region [1]. Attempts have been made to utilize maize residues as energy via densification [2–4], pyrolysis [5–7], gasification [8,9] and combustion [10]. However, fresh residues tend to have high moisture content, hence, energy conversion efficiency may be very low. To handle fresh biomass, hydrothermal carbonization (HTC) may be adopted. The technique has been shown to convert wet biomass into valuable carbon materials [11]. HTC is thermal treatment process of biomass that is submerged in water at elevated pressures. The energy density of the solid product is improved. The macromolecular structure of the original biomass is also modified, giving rise to a porous carbonized product that is simpler to convert to heat, power or fuel than the starting materials [12–14].

In this work, experimental investigation of maize biomass upgrading into hydrochar via HTC method was carried out. The method can potentially offer alternative means and lower the overall cost for management of agricultural residues. The characteristics of the obtained hydrochar were examined.

2. Materials and methods

2.1. Raw materials

Maize residues were obtained locally from highland farms in Chiang Mai, Thailand. They were cleaned, reduced in sized, sorted, dried and kept in tight storage. Samples of the biomass materials were sent for analysis.

2.2. Experimental setup

HTC experiments were performed in a laboratory 10-dm³ pressure reactor equipped with 14 kW heaters and internal temperature control (as shown in Fig. 1). About 0.5 kg of dried maize residues was suspended in deionized distilled water at fixed biomass to water ratio of 1:10. A number of tests were conducted at varying temperature and residence time of 180–250 °C and 60–360 min, respectively. Solid and liquid by-products were collected by filtration and subsequently dried for further analyses. The hydrochar samples obtained were denoted according to carbonization conditions (temperature in °C – reaction time in min) as 180–200, 190–120, 190–300, 215–60, 215–210, 215–360, 240–120, 240–300 and 250–210, respectively. In this work, experiments were repeated at least three times for each condition.

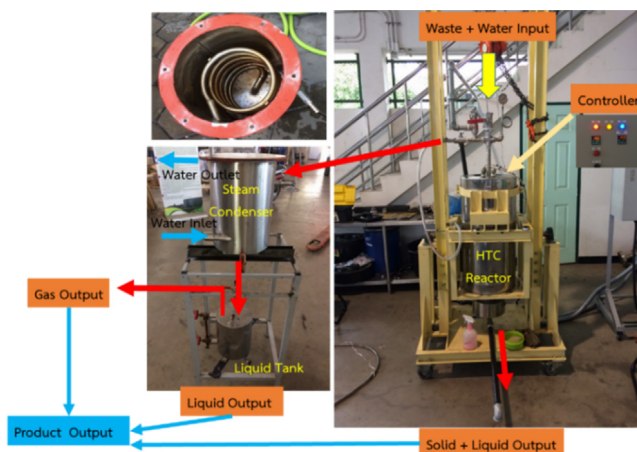


Fig. 1. Experimental setup of the HTC reactor system.

2.3. Characterization of products

Yields were determined on mass basis. Characteristics of maize residues and their hydrochars were investigated to study the changes with regards to physical and chemical components. Ultimate and proximate analyses were conducted by the Thailand Institute of Scientific and Technological Research (Bangkok, Thailand), according to

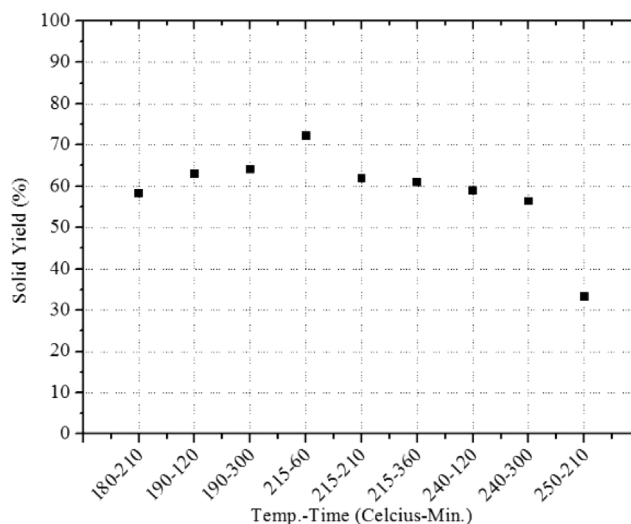
Table 1. Chemical characteristics and properties of maize residue and hydrochars.

Samples	Raw	180–210	190–120	190–300	215–60	215–210	215–360	240–120	240–300	250–210
C (%)	45.81	47.36	46.72	46.14	49.45	46.36	49.82	46.95	48.59	47.2
H (%)	5.6	5.65	5.84	5.8	5.97	5.84	6.24	5.78	5.8	5.13
N (%)	0.94	0.14	0.1	0.15	0	0.09	0	0.11	0.14	0.11
O (%)	39.89	41.84	42.62	42.25	43.54	40.36	42.76	40.92	40.87	41.3
S (%)	0.08	0.06	0.05	0.05	0.02	0.05	0.03	0.05	0.06	0.05
Ash (%)	7.68	4.95	4.76	5.61	1.02	7.30	1.15	6.19	4.54	6.21
Volatile matter (%)	73.56	77.59	77.9	76.39	81.06	74.17	80.61	75.16	75.59	75.31
Fixed carbon (%)	18.76	17.46	17.34	18	17.92	18.53	18.24	18.65	19.87	18.48
HHV (MJ/kg)	16.37	15.90	16.53	16.34	18.13	16.61	16.81	16.83	17.42	17.47
Energy densification (–)	–	0.98	1.01	1.00	1.11	1.01	1.03	1.03	1.06	1.07
Energy recovery (–)	–	0.58	0.65	0.65	0.80	0.63	0.64	0.61	0.62	0.38

ASTM D 7582, D 5373, D 4239 and D 5865 standards. Energy densification defined as an HHV ratio between the hydrochar and the starting material, as well as energy recovery defined as a ratio between energy content in the hydrochar divided by that in the maize residues were also calculated.

3. Results and discussion

Table 1 shows ultimate and proximate analysis results, as well as higher heating values (HHV) of the hydrochars, energy densification and energy recovery. Fig. 2 shows solid yields on a dry basis for each HTC condition. The hydrochar yields obtained were found to be in the range of 35–72%. The values here were in similar range to those reported by Machado et al. [15] and Zhang et al. [16], but higher than that by Zhang et al. [17] for maize residues. It should be noted that HTC conditions used in the reported literature were slightly different from our work. Higher treatment temperature and residence time were expected to decrease the hydrochar yields [13,14], but from the findings, change in the mass yields did not vary much with the HTC conditions considered in this work.

**Fig. 2.** Hydrochar yields as a function of the HTC conditions.

From Table 1, significant changes in fixed carbon and volatile matter content between the raw materials and hydrochars as a result of carbonization were not observed. It was expected that the volatile matter of the agro-residues would be reduced and the fixed carbon content of the hydrochars would be increased. Nonetheless, change in elemental composition of the solid materials was observed. HTC of the maize residues led to a slight increase in the carbon content of the solid products from about 45 to almost 50%. Conversion of organic material to carbon rich product or coalification may be viewed using a van Krevelen diagram.

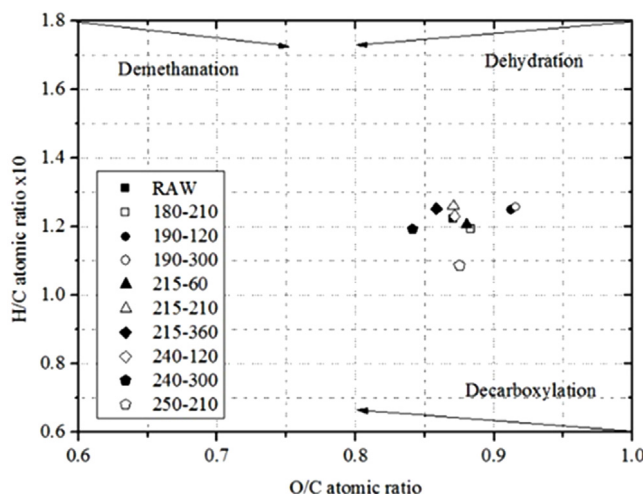


Fig. 3. Van Krevelen diagram of the hydrochars.

Fig. 3 depicts relationship between atomic H/C and O/C ratios for the maize residue and its hydrochars. Pathways for demethanation, dehydration, and decarboxylation were also shown in the plot. From Fig. 3, it can be seen that the H/C and O/C ratios tended to decrease due mainly to dehydration and decarboxylation. This trend was in agreement with that reported by Kantakanit et al. [18] for similar HTC conditions. Higher degree of carbonization was anticipated to enhance the extent of coalification. At higher degree of HTC severity conditions (higher temperatures or longer times), the corresponding atomic ratios of the solid products were expected to move closer to those of lignite.

Also shown in Table 1 are analysis results of the hydrochar energetic content in terms of HHV, energy densification and energy recovery. The HHV was found to slightly increase from 16.37 to 18.13 MJ/kg. This was lower than those reported for maize residue hydrochars in the literature [15–17]. Improvement in the energy densification was rather small, in a range of 0–11%. Nonetheless, this observation appeared to be in accord with the rise in carbon content of the hydrochars. With regards to the energy recovery, the values obtained varied considerably, ranging from 38 to about 80%.

It was quite clear that, for the current setup, the HTC conditions considered in this work did not significantly affect chemical composition of the hydrochars. The solid products showed only slight change in compositions for all conditions considered. Further investigation may be needed to improve understanding of the fundamental process and the product characteristics.

4. Conclusion

In this work, HTC of maize residues was conducted at several operating conditions. It was evident that HTC could be used to quickly treat maize residues and convert 35%–72% of the dry matter into hydrochar. Hydrochars obtained had HHV of about 18.1 MJ/kg. Their H/C and O/C atomic ratios were approaching those of peat and lignite, thus possibly suitable for co-combustion with other coals. HTC process appeared to offer alternative conversion route for maize residues to value-added products.

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