

Sludge stabilization and energy recovery by hydrothermal carbonization process



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ABSTRACT

Hydrothermal carbonization (HTC) is a thermal conversion process that converts high-moisture biomass into hydrochar. HTC was applied to stabilize and process sludge collected from septic tanks into hydrochar for practical energy recovery. Experiments were conducted with a 1-L high-pressure reactor operating at different temperatures and reaction times in which the sludge was mixed with catalysts and biomass at different ratios. The effects of catalysts (i.e., acetic acid, lithium chloride, borax, and zeolite) and biomass (i.e., cassava pulp, dried leaves, pig manure, and rice husks) mixing with sludge for hydrochar production were investigated. The experimental data showed acetic acid and cassava pulp to be the most effective catalyst and biomass, respectively, increasing energy contents to the maximum value of 28.5 MJ/kg. The optimum HTC conditions were as follows: sludge/acetic acid/cassava pulp mixing ratio of 1/0.4/1 (by weight), at a temperature of 220 °C, and reaction time of 0.5 h. The relatively high energy contents of the produced hydrochar suggest its applicability as a solid fuel.

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1. Introduction

Most developing countries in South and Southeast Asia, still lack sewer systems with centralized wastewater treatment facilities. An estimated 2.7 billion people worldwide are served by on-site sanitation systems such as septic tanks and cesspools [1] which are normally employed to treat toilet and grey wastewaters. The septic tank sludge, which is still highly polluted, needs to be periodically removed. Due to insufficient management, most septic tank sludge and faecal sludge (FS) is not properly treated; instead, it is discharged untreated (or partially treated) into nearby canals or agricultural fields, causing water and soil pollution and increasing health risks [2].

Hydrothermal carbonization (HTC) is a thermal conversion process that can be used to treat faecal sludge (FS) and convert it into a valuable solid product called “Hydrochar”. The process requires short reaction times (1–12 h) at a relatively low temperature range (180–250 °C), with corresponding pressures up to 30 bar [3,4]. HTC is applied to stabilize and process FS collected from septic

tanks into hydrochar so that pathogens are destroyed and energy recovery is possible. Advantages of HTC for treating FS over other thermal conversion processes such as pyrolysis and gasification are the relatively high hydrochar yield and higher energy efficiency [4,5]. Moreover, hydrochar produced from HTC has already been used for many applications such as solid fuel, energy storage, soil amendment, absorbent in water purification, catalyst, and CO₂ sequestration [4,6].

Applications of HTC on human wastes (untreated faeces and FS) and sewage sludge have been previously reported by Danso-Boateng et al. [7], Fakkaew et al. [3,5], and He et al. [8], most of whom obtained relatively low energy contents of the produced hydrochar (in range of 15–23 MJ/kg). Lynam et al. [9,10] reported about a 30% increase in energy contents of the produced hydrochar from HTC of lignocellulosic biomass with the addition of acetic acid and salt catalysts (i.e., calcium lactate, lithium chloride, and calcium chloride), which accelerated the hydrolysis reactions. Similarly, using zeolites [11–14] and borax [15] as catalysts in dehydration reaction of glucose or fructose produced hydroxymethylfurfural (HMF), an intermediate product, at a yield greater than 70%. In addition, the study of Oliveira et al. [16] found that adding easily-hydrolyzed carbohydrate biomass such as corn silage and dough residues into the HTC feedstock resulted in about 15% increase in

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energy content of the produced hydrochar. However, blending biomass with catalysts to increase the energy content of the produced hydrochar has not been investigated.

This study investigated the effects of adding catalysts and biomass on the energy content of hydrochar produced from HTC, using FS as feedstock. Optimum operating conditions, including mixing ratios between FS and the catalyst or biomass, temperature and reaction time, were determined.

2. Materials and methods

2.1. FS samples

FS samples were collected from a municipal emptying truck (vacuum truck) which serviced residential areas of Pathumthani, located near Bangkok, Thailand. The total solids concentration of these collected FS samples, initially measuring approximately 50 g/L, was adjusted to approximately 200 g/L using water bath evaporation before mixing with catalysts and/or biomass and feeding into the HTC reactor. Energy content and proximate analysis of FS samples and biomass are shown in Table 1.

2.2. Catalysts

Catalysts used in this study included acetic acid (RCI labscan, 99.7% min) and lithium chloride (Ajax Finechem, 98% min), which acted as hydrolysis catalysts; and borax (Ajax Finechem, 99.5% min), and zeolite (Gatt intertrade Co. Ltd., natural, powder form, $\text{SiO}_2/\text{Al}_2\text{O}_3 < 5$), which acted as dehydration catalysts. These catalysts were mixed with FS at the mixing ratios suggested by previous researchers, as shown in Table 2.

2.3. Biomass

Selected biomass used in this study were agricultural residues: cassava pulp, dried leaves, pig manure, and rice husks. These biomass samples were shaped into a homogeneous size of about 2 mm by a grinding machine before mixing with FS samples according to ratios given in Table 2. Energy content and proximate analysis of the selected biomass samples are shown in Table 1.

2.4. HTC experiments

Experiments were conducted with a 1-L high-pressure reactor made of stainless steel and equipped with pressure gauge, thermocouple and gas collecting ports, as illustrated in Fig. 1. An electric heater equipped with a control panel (Fig. 1a) was used to adjust reactor temperature and reaction time. Each HTC experiment was performed in triplicate with 350 mL of FS mixed with select additives such as catalysts and biomasses (Table 2). The operating conditions of the HTC process were controlled at a heating rate of 6 °C/min, temperature of 220 °C and reaction time of 5 h. Under these operating conditions, the generated pressure inside the HTC

Table 2

Mixtures of FS, catalyst and biomass, and mixing ratios.

Mixtures	Mixing ratio (by weight)
<i>FS: Catalyst</i>	
FS: acetic acid ^a	1:0.2, 1:0.4, and 1:0.8
FS: lithium chloride ^a	1:0.25, 1:0.5, and 1:1
FS: borax ^b	1:0.06, 1:0.12, and 1:0.25
FS: zeolite ^c	1:0.02, 1:0.05, and 1:0.10
<i>FS: Biomass</i>	
FS: cassava pulp	3:1, 1:1, and 1:2
FS: dried leaves	3:1, 1:1, and 1:2
FS: pig manure	3:1, 1:1, and 1:2
FS: rice husks	3:1, 1:1, and 1:2

^a Adapted from Lynam et al. [9].

^b Adapted from Titirici [15].

^c Adapted from Shimizu et al. [14].

reactor, 30 bar, was maintained. At the end of each experiment, the reactor was rapidly cooled to ambient temperature using water in a cooling jacket (Fig. 1b) at the cooling rate of about 45 °C/min to quench the reaction. After collecting the gas sample, the carbonized FS remaining in the reactor was separated into solid (hydrochar) and liquid products using vacuum filtration (Whatman filter paper, 1.2 μm). The produced hydrochar was subsequently dried in an oven at 105 °C for at least 12 h to remove the remaining moisture. The produced hydrochar was analyzed for its characteristics as described in the following sections.

The mixtures of FS and the selected catalyst or biomass were further tested in the HTC reactor operating at various temperatures and reaction times (Table 3). Each experiment was undertaken according to the HTC process explained above. Effects of process parameters, such as temperature and reaction time, and optimum conditions of the HTC process were determined.

2.5. Analytical methods

Since this study emphasizes energy recovery of the produced hydrochar and changes in physical properties of the treated biomass, only energy content and proximate analysis of these materials were analyzed. Energy content was determined by a bomb calorimeter (AC500, Leco, USA). The proximate analysis (moisture, volatile matter, fixed carbon and ash content) was measured using a thermogravimetric analyzer (TGA701, Leco, USA).

Liquid samples were analyzed for: Total Organic Carbon (TOC), Chemical Oxygen Demand (COD), Total Nitrogen (TN), Total Phosphorus (TP) and organic and volatile acids concentrations using the high temperature combustion method (TOC-V CPH, Shimadzu, Japan), closed dichromate reflux method, persulfate method, colorimetric method, and distillation method [17], respectively. Gas samples were analyzed for CO₂, CH₄, O₂, and N₂ using a gas chromatograph instrument (GC 7890A, Agilent, USA) equipped with flame ionization detector.

Table 1

Characteristics of FS and selected biomass.

Samples	Energy content (MJ/kg)	Proximate analysis (% dry weight)			
		Moisture	Volatile matter	Ash	Fixed carbon
FS	16.3	3.4	56.0	30.8	9.7
Cassava pulp	17.1	6.1	82.0	1.5	10.3
Dried leaves	20.7	3.6	71.3	9.8	15.2
Pig manure	15.5	5.7	64.3	24.8	5.1
Rice husks	20.0	5.1	64.7	16.2	14.0

Note: all in average values.

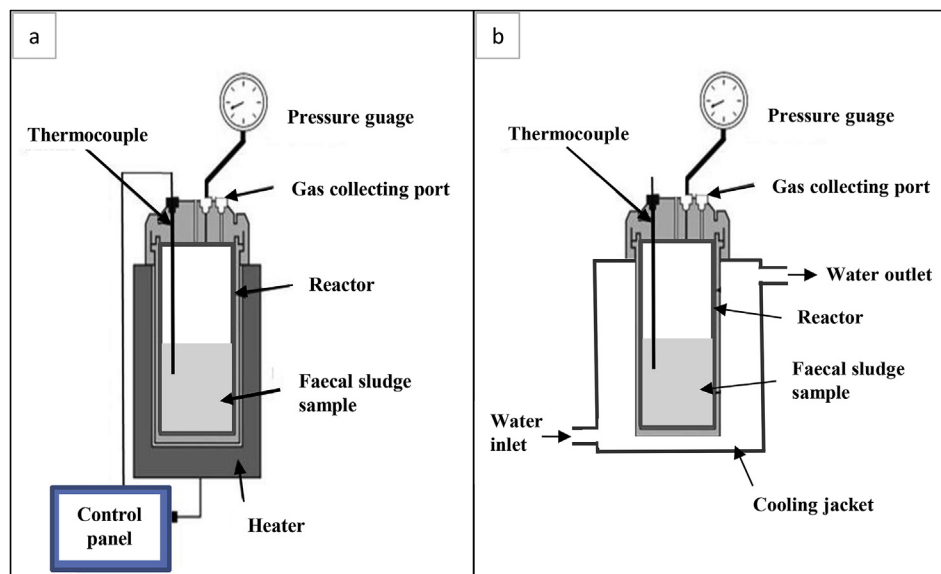


Fig. 1. Schematic of HTC reactor (a) heating system, and (b) cooling jacket.

Table 3
Experimental design of HTC operating conditions.

Experiment no.	HTC operating conditions	
	Temperature (°C)	Reaction time (h)
1	180	0.5
2	180	1
3	180	3
4	180	5
5	180	10
6	200	0.5
7	200	1
8	200	3
9	200	5
10	200	10
11	220	0.5
12	220	1
13	220	3
14	220	5
15	220	10
16	250	0.5
17	250	1
18	250	3
19	250	5
20	250	10

3. Results and discussion

3.1. Effects of catalyst addition

The effects of catalysts mixed with FS, at various mixing ratios, on the energy content of hydrochar produced by HTC at 220 °C and 5 h is shown in Fig. 2a. Using acetic acid as a catalyst, energy contents of the produced hydrochar were found to be 19.7, 21.4, and 19.5 MJ/kg at the FS to acetic acid mixing ratios of 1:0.2, 1:0.4 and

reaction rates [18] and, consequently, increased the energy content of the dried FS and the produced hydrochar (without catalyst) from 16.3 to 18.8 MJ/kg, respectively, to 20.2 MJ/kg in average.

When using borax as a catalyst, the energy contents of the produced hydrochar were found to be 18.5, 17.1 and 16.1 MJ/kg at the FS to borax mixing ratios of 1:0.06, 1:0.12 and 1:0.25, respectively (Fig. 2a). Borax increased the pH of the FS samples to a range of 8.3–8.7, higher than the optimum pH range of 3.0–7.0 recommended by Funke and Ziegler [18] and Liang et al. [19], resulting in low energy contents of the produced hydrochar.

When using zeolite as a catalyst, the energy contents of the produced hydrochar were found to be 18.6, 18.0 and 16.5 MJ/kg at the FS to zeolite mixing ratios of 1:0.02, 1:0.05 and 1:0.10, respectively (Fig. 2a). Similar results were obtained from HTC experiments using lithium chloride as a catalyst. At the FS to lithium chloride mixing ratios of 1:0.25, 1:0.5 and 1:1, the produced hydrochar contained energy contents of 18.6, 19.4, and 17.7 MJ/kg, respectively (Fig. 2a). There were no significant changes in pH of the samples mixed with these 2 catalysts, hence the zeolite and lithium chloride catalysts had little effect on the energy content of the produced hydrochar.

Hydrochar yield is widely known as the mass ratio of dried hydrochar to dried feedstock [8]. The HTC of FS mixed with catalysts such as borax, zeolite and lithium chloride generated higher hydrochar yields (about 73, 76 and 77%, respectively) than that using acetic acid as a catalyst which was about 70%. This higher yield could be due to the fact that small amounts of the inorganic catalysts remained in the produced hydrochar after the HTC process.

In order to identify the most effective catalyst for hydrochar production, the normalized energy yield, defined as the energy of the produced hydrochar per mass of dry initial feedstock [20], was calculated as shown in Equation (1).

$$\text{Normalized energy yield} = \frac{\text{energy content of hydrochar} \times \text{mass of hydrochar}}{\text{mass of dry initial feedstock}} \quad (1)$$

1:0.8, respectively (Fig. 2a). Adding acetic acid into FS samples resulted in the decrease of pH to 3.6–4.5, which increased the HTC

Given the data in Fig. 2b, the highest normalized energy yield of 14.5 MJ/kg-FS was found when using acetic acid at the mixing ratio

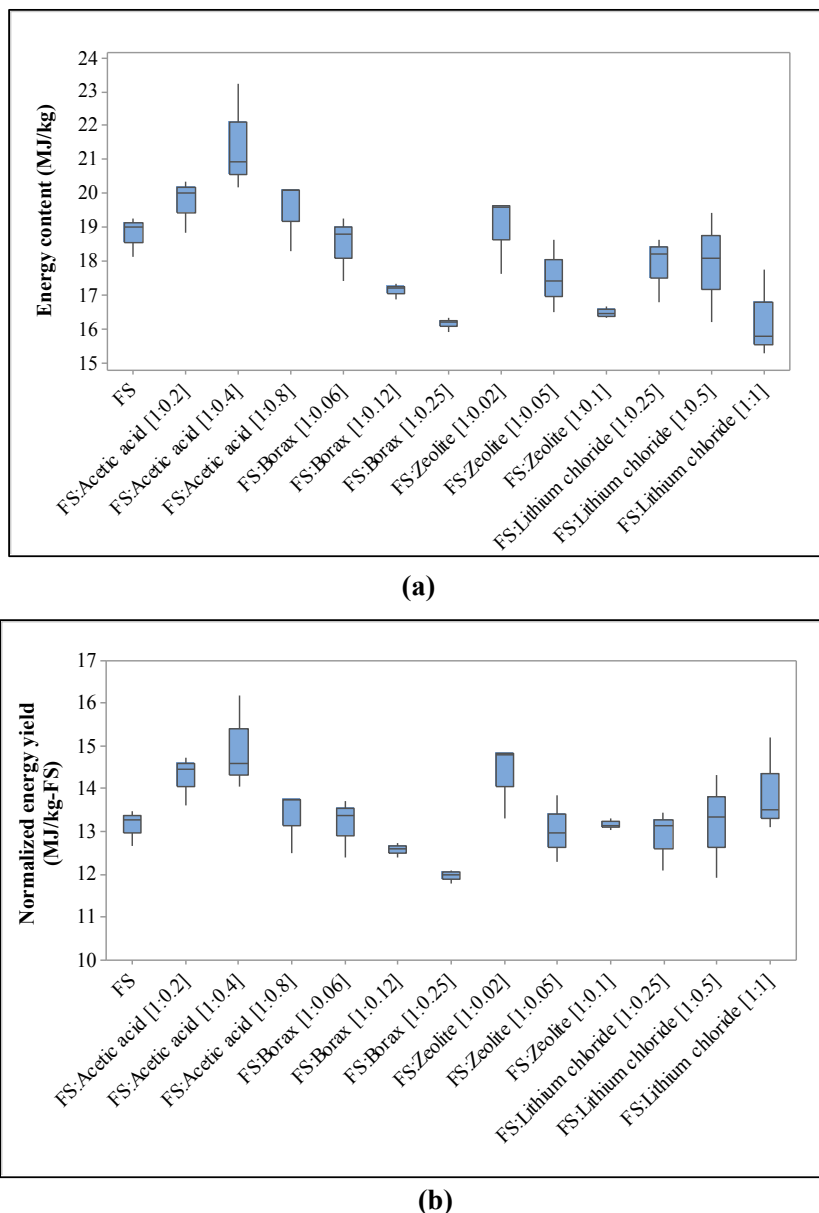


Fig. 2. (a) Energy contents of produced hydrochar and (b) Normalized energy yields of HTC of FS with catalysts at various mixing ratios operating at temperature of 220 °C and reaction time of 5 h.

of 1:0.4. Acetic acid was further chosen as an effective catalyst for the study on the effects of HTC process parameters such as temperature and reaction time on the energy contents and hydrochar yields. However, other catalysts operating at different conditions may also produce hydrochar with high energy contents. Further investigations on this aspect are recommended.

Fig. 3a shows the effects of temperature and reaction time on energy content of the produced hydrochar. At the reaction time of 1 h, the maximum energy contents of 23.0, 22.9 and 25.3 MJ/kg were achieved at temperatures of 180, 200 and 220 °C, respectively. Acetic acid may accelerate the hydrolysis process in a relatively short reaction time. In contrast, after 3 h of reaction, energy contents of the produced hydrochar dropped to a range of 16–19 MJ/kg. The lowest energy contents of the produced hydrochar were observed at the temperature of 250 °C for all reaction times (Fig. 3a), probably due to decomposition of HMF, as intermediate product, at the high temperatures and long reaction times [21].

In order to determine the optimum HTC conditions, the normalized energy yields were determined as shown in Fig. 3a. The optimum temperature and reaction time of the HTC of FS with acetic acid were 220 °C and 1 h, respectively, giving a normalized energy yield of 19.8 MJ/kg-FS. At these conditions, the energy contents and yields of the produced hydrochar were 25.3 MJ/kg and 73%, respectively, higher than those obtained from other operating conditions.

3.2. Effects of biomass addition

Experimental results of the HTC using FS mixed with different biomass as feedstocks are shown in Fig. 4. At the FS to biomass mixing ratio of 3:1, energy contents of the produced hydrochar of 20.0–21.5 MJ/kg were obtained due mainly to the large proportion of FS with low energy content (Table 1) in the feedstock. Likewise, relatively high energy contents of the produced hydrochar of

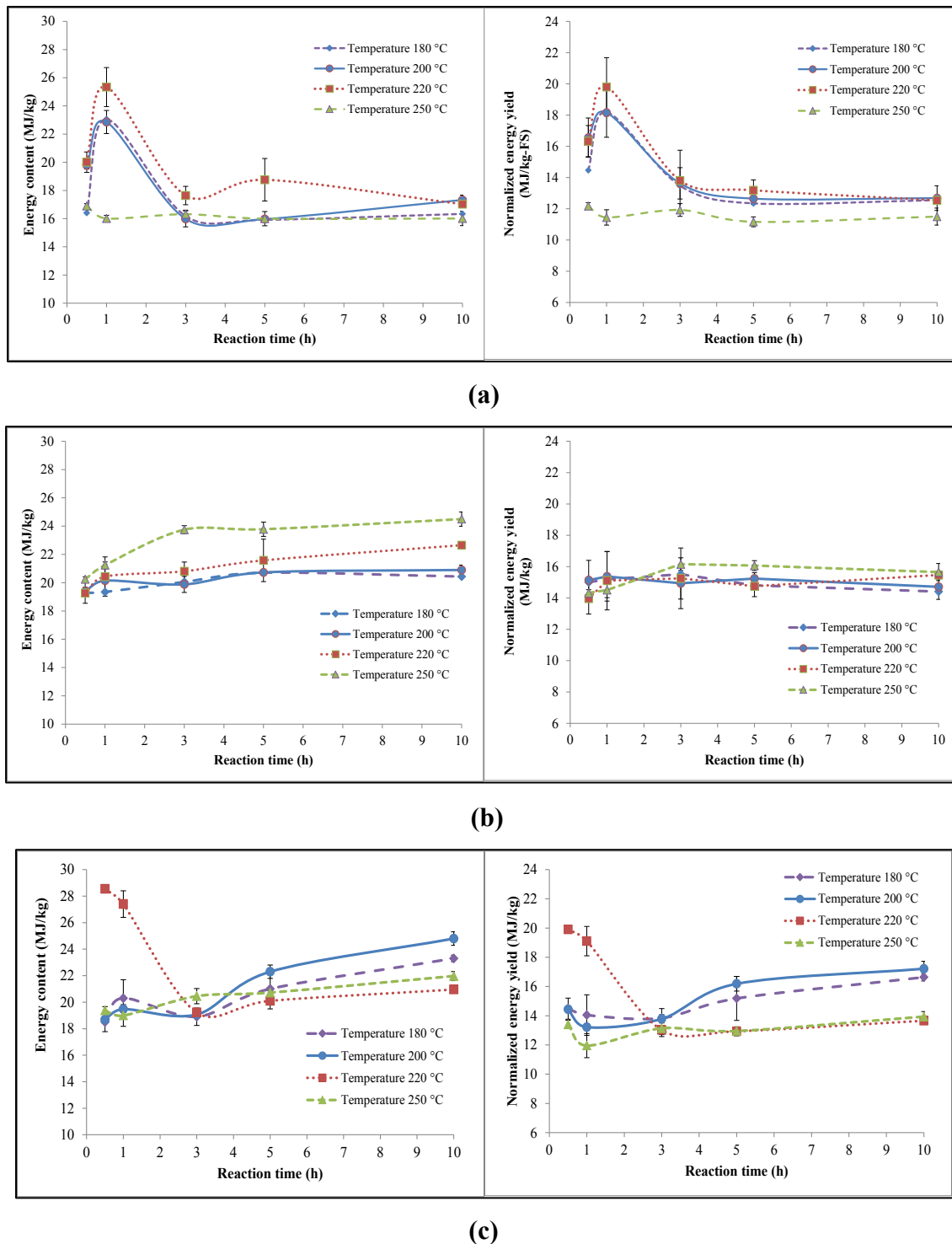


Fig. 3. Energy contents of produced hydrochar and normalized energy yields of HTC of (a) FS: acetic acid mixture (1:0.4), (b) FS: cassava pulp mixture (1:1), (c) FS: acetic acid:cassava pulp mixture (1:0.4:1), at various temperatures and reaction times.

23.5–23.7 MJ/kg were obtained with the FS to biomass mixing ratio of 1:2 due to the larger proportion of biomass with high energy content (Table 1) in the feedstock.

At the mixing ratio of 1:1, energy contents of the produced hydrochar were found to be about 21.0–22.7 MJ/kg, while the highest energy content of 22.7 MJ/kg was obtained with the cassava pulp mixture. Cassava pulp could be easily hydrolyzed in the HTC

process; therefore, the rate of carbonization stage was increased, resulting in the increased energy contents. This could be shown by the fixed carbon content in the produced hydrochar, which was about 22.6%, higher than those of the hydrochar produced from FS alone (12.0%). The fixed carbon contents of the raw FS and cassava pulp were 9.7 and 10.3%, respectively.

Hydrochar yields for the FS and any biomass mixtures ranging

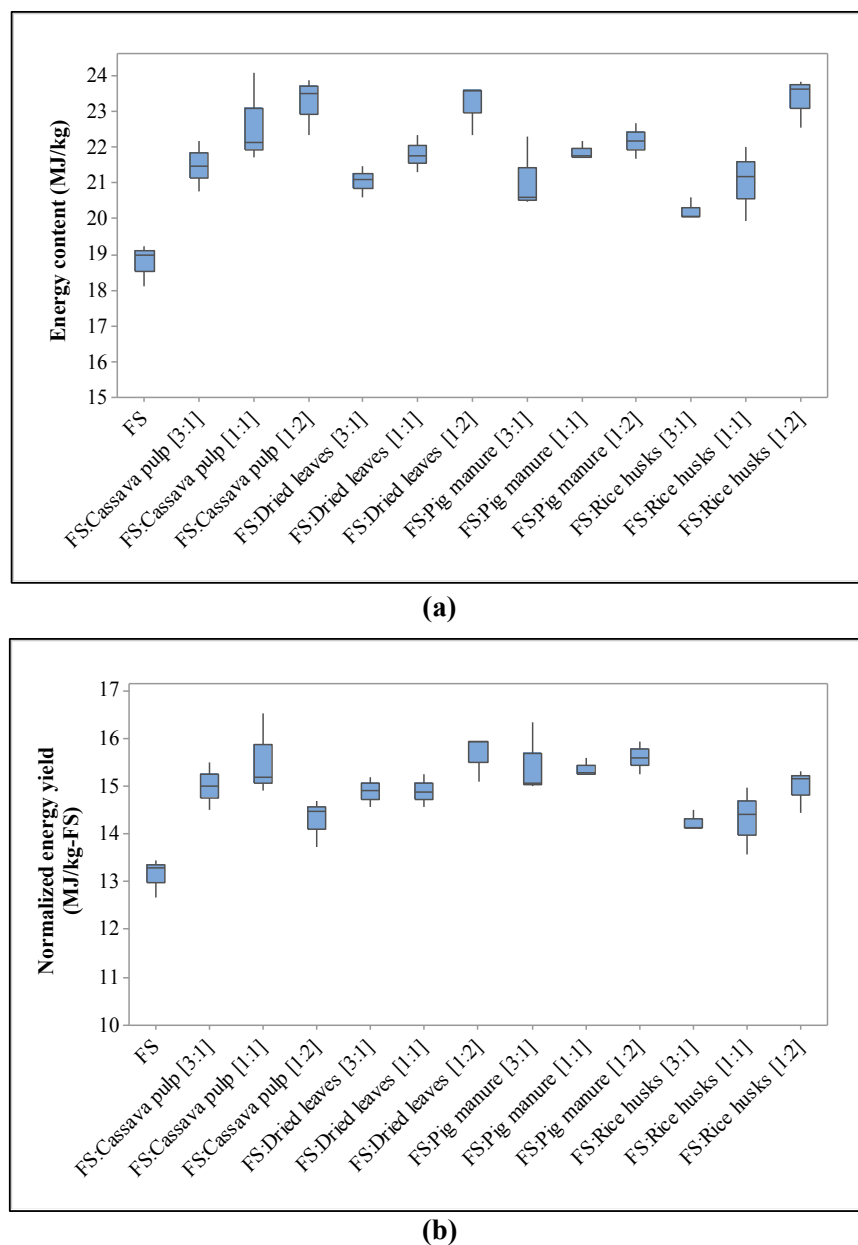


Fig. 4. (a) Energy contents of produced hydrochar and (b) Normalized energy yields of HTC of FS with biomasses at various mixing ratios operating at temperature of 220 °C and reaction time of 5 h.

from 60 to 70% depending on characteristics of the feedstocks were lower than those of the FS and catalyst mixtures (70–80%) probably because hydrolysis of the biomass resulted in lower hydrochar yields.

According to Fig. 4b, the FS to cassava pulp mixing ratio of 1:1 gave the highest normalized energy yield; therefore, it was selected for further study, as shown in Fig. 3b. Energy contents of the produced hydrochar ranged from 19.3 to 22.6 MJ/kg at the temperatures of 180, 200 and 220 °C and reaction times of 0.5–10 h. Higher energy contents of the produced hydrochar of 23.7, 23.8 and 24.5 MJ/kg were obtained at the reaction times of 3, 5 and 10 h, respectively, at the temperature of 250 °C. These results were the opposite of those with acetic acid most likely because there were no effects of the catalyst on HMF decomposition.

At the normalized energy yield of 16.1 MJ/kg-FS (Fig. 3b), the HTC temperature of 250 °C and reaction time of 3 h were found to

be optimum for treating the FS and cassava pulp mixture at a ratio of 1:1. These optimum conditions resulted in the energy content and yield of the produced hydrochar of 23.7 MJ/kg and 68%, respectively.

3.3. Combination of catalyst and biomass

Based on the experimental results obtained from previous sections, a mixture of FS, acetic acid and cassava pulp, at a ratio of 1:0.4:1, was selected as an example to determine energy contents of the produced hydrochar at various temperatures and reaction times. Results shown in Fig. 3c indicate that at a temperature of 220 °C, energy contents of the produced hydrochar of 28.5 and 27.4 MJ/kg were obtained at the reaction times of 0.5 and 1 h, respectively. These values are higher than previous data of the mixtures of FS and acetic acid (Fig. 3a) or cassava pulp (Fig. 3b). The

role of acetic acid acting as a catalyst in accelerating the thermochemical reactions in the HTC process was evident. Lower energy contents of the produced hydrochar were obtained at reaction times of 3–10 h and at temperatures of 180, 200 and 250 °C.

Based on the data in Fig. 3c, the temperature of 220 °C and reaction time of 0.5 h were found to be optimum for HTC treatment of the mixture of FS, acetic acid and cassava pulp at 1:0.4:1 ratio, giving the normalized energy yield of 19.9 MJ/kg-FS. These optimum conditions resulted in energy content and yield of the produced hydrochar of 28.5 MJ/kg and 70%, respectively.

It is apparent that the energy content of the hydrochar produced from the HTC of FS could be increased by adding either acetic acid or cassava pulp. Moreover, the energy content could be further increased when using the mixture of FS, acetic acid and cassava pulp as a feedstock. The produced hydrochar obtained from these experiments had the energy contents of 27.4–28.5 MJ/kg, higher than those of natural coals such as lignite and sub-bituminous which are 15.0 and 18.2 MJ/kg, respectively [22]. However, pilot or full-scale experiments on HTC treatment of these mixtures should be conducted to validate the laboratory-scale results.

3.4. Mass balance and HTC product characteristics

Mass balances of the HTC process were carried out at 3 optimum HTC conditions, as shown in Table 4. Results indicated that a significant proportion of organic matter in the feedstock (68–73%) was hydrothermally carbonized into hydrochar. About 17–21% and 10–11% of the remaining mass were processed into liquid and gas by-products, respectively.

Characteristics of the HTC products from the mixtures of FS, acetic acid and cassava pulp (at the optimum conditions) are shown in Table 5. As a result of carbonization in the HTC process, there were increases in the fixed carbon contents in the produced hydrochars, compared to those in raw materials such as FS and cassava pulp (Table 1). On the other hand, the volatile matter contents in raw materials were hydrolyzed, dehydrated and converted into hydrochar, liquid and gas by-products. The increase of fixed carbon and decrease of volatile matter in the produced hydrochar probably resulted in increased energy contents of the produced hydrochar. High values of ash content in the produced hydrochars were observed (Table 5), most likely due to accumulation of inorganic matters and destruction of organic matters after

Table 4
Mass balances of HTC process.

Feedstock		HTC products		
Mixtures	Dry weight (g)	Products	Dry weight (g)	Yield ^a (%)
FS: acetic acid	72.1 ^b	Hydrochar	52.3	72.5
		Liquid	12.0 ^b	16.6
		Gas	7.8	10.8
FS: cassava pulp	70.6	Hydrochar	48.1	68.1
		Liquid	14.8	21.0
		Gas	7.7	10.9
FS: acetic acid: cassava pulp	67.3 ^b	Hydrochar	47.0	69.8
		Liquid	13.3 ^b	19.8
		Gas	7.0	10.4

Note; all in average values.

^a Yield (%) = mass of product (g-dry weight) × 100/mass of feedstock (g-dry weight).

^b Excluding mass of acetic acid.

Table 5
Characteristics of products from HTC of mixtures of FS, acetic acid and cassava pulp.

Products	Characteristics	Unit	Mixtures		
			FS: acetic acid	FS: cassava pulp	FS: acetic acid: cassava pulp
Hydrochar	Proximate analysis				
	Moisture	%wt	1.2	0.1	0.8
	Volatile matter	%wt	44.8	44.1	39.8
	Fixed carbon	%wt	12.6	22.6	24.6
	Ash	%wt	41.4	33.2	34.8
	Ultimate analysis				
	Carbon	%wt	37.0	48.3	48.5
	Hydrogen	%wt	4.2	4.6	4.6
	Nitrogen	%wt	1.8	2.2	2.0
	Sulfur	%wt	1.8	1.4	1.5
Liquid	Oxygen	%wt	13.8	10.3	8.6
	Energy content	MJ/kg	25.3	23.7	28.5
	TOC	g/L	47.2	18.2	48.8
	COD	g/L	132.3	47.8	134.9
	TN	g/L	5.5	9.8	6
	TP	mg/L	88	90	120
	Organic and volatile acids	g/L	96.1	5.2	97.8
Gas	pH		3–4	5	3–4
	CO ₂	%V	61.0	63.0	64.1
	CH ₄	%V	2.5	0.5	0.7
	O ₂	%V	2.2	2.7	1.8
	N ₂	%V	21.4	21.3	20.1
	Other	%V	12.6	12.5	13.3

Note; all in average values.

carbonization in the HTC process. Because raw materials used in the HTC process originated from domestic and agricultural sources, the produced hydrochar should not contain heavy metals and other hazardous materials.

The liquid by-product still contained high concentrations of organic matters (such as TOC and COD), TN and TP (Table 5). It is apparent that, to minimize environmental pollution and producing valuable products, these liquid by-products need to be further treated, e.g. by anaerobic digestion [13,23]. These liquid by-products containing the recovered acetic acid of about 96–98 g/L (or about 72.8% recovery) could be directly reused as a catalyst in the HTC process to increase the energy content of the hydrochar and reduce operation costs of the HTC and wastewater treatment.

Analysis of the gas by-products showed CO₂ to be the main component; however, there were trace amounts of CH₄, O₂, N₂, and other gases, as shown in Table 5. To eliminate the greenhouse gas emissions, the produced gases can be further treated, possibly by activated carbon adsorption or a wet scrubber [24,25].

In this study, the technical feasibility of applying an HTC process to treat and convert FS to the high-energy content hydrochar was demonstrated. Application of the produced hydrochar as a solid fuel, including its combustion behavior, marketability and social acceptance, should be investigated. Further studies on the scale-up effects and cost-benefit analysis of the HTC process are strongly recommended prior to implementation of a full-scale HTC reactor for treating FS. Other benefits from HTC treatment of FS, such as pollution control and health risk reduction, should also be considered.

4. Conclusions

Given the results of this study, the following conclusions can be made:

1. Acetic acid and cassava pulp were found to be the most effective catalyst and biomass, respectively, in increasing energy content of the hydrochar produced from the HTC of FS.
2. Energy content of the produced hydrochar could be further increased by using a mixture of FS, acetic acid and cassava pulp as a feedstock in HTC process.
3. At optimum conditions, energy contents of the hydrochar produced from the HTC of the mixtures of FS: acetic acid, FS: cassava pulp and FS: acetic acid: cassava pulp were found to be 25.3, 23.7, and 28.5 MJ/kg, respectively.
4. Energy contents of the produced hydrochar were comparable to natural coals, which could be a significant substitute for fossil fuels in combustion processes.

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References

- [1] L. Strande, *Faecal Sludge Management, Systems Approach for Implementation and Operation*, IWA Publishing, United Kingdom, 2014 chapter 1.
- [2] United States Agency for International Development, *A Rapid Assessment of Septage Management in Asia*, 2010.
- [3] K. Fakkaew, T. Koottatep, T. Pussayanavin, C. Polprasert, Hydrochar production by hydrothermal carbonization of faecal sludge, *J. Water Sanit. Hyg. Dev.* 5 (3) (2015) 439–447.
- [4] J.A. Libra, K.S. Ro, C. Kammann, A. Funke, N.D. Berge, Y. Neubauer, M.M. Titirici, C. Fuhner, O. Bens, J. Kern, K.H. Emmerich, Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, processes and applications of wet and dry pyrolysis, *Biofuels* 2 (1) (2011) 89–124.
- [5] K. Fakkaew, T. Koottatep, C. Polprasert, Effects of hydrolysis and carbonization reactions on hydrochar production, *Bioresour. Technol.* 192 (2015) 328–334.
- [6] M.M. Titirici, M. Antonietti, Chemistry and materials options of sustainable carbon materials made by hydrothermal carbonization, *Chem. Soc. Rev.* 39 (2010) 103–116.
- [7] E. Danso-Boateng, R.G. Holdich, G. Shama, A.D. Wheatley, M. Sohail, S.J. Martin, Kinetics of faecal biomass hydrothermal carbonization for hydrochar production, *Appl. Energy* 111 (2013) 351–357.
- [8] C. He, A. Giannis, J.Y. Wanga, Conversion of sewage sludge to clean solid fuel using hydrothermal carbonization: hydrochar fuel characteristics and combustion behavior, *Appl. Energy* 111 (2013) 257–266.
- [9] J.G. Lynam, C.J. Coronella, W. Yan, M.T. Reza, V.R. Vasquez, Acetic acid and lithium chloride effects on hydrothermal carbonization of lignocellulosic biomass, *Bioresour. Technol.* 102 (2011) 6192–6199.
- [10] J.G. Lynam, M.T. Reza, V.R. Vasquez, C.J. Coronella, Effect of salt addition on hydrothermal carbonization of lignocellulosic biomass, *Fuel* 99 (2012) 271–273.
- [11] H. Jadhav, E. Taarning, C.M. Pedersen, M. Bols, Conversion of D-glucose into 5-hydroxymethylfurfural (HMF) using zeolite in [Bmim]Cl or tetrabutylammonium chloride (TBAC)/CrCl₂, *Tetrahedron Lett.* 53 (2012) 983–985.
- [12] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros, G. Avignon, Dehydration of fructose to 5-hydroxymethylfurfural over H-mordenites, *Appl. Catal. A Gen.* 145 (1996) 211–224.
- [13] I. Oliveira, D. Blöhse, H.G. Ramke, Hydrothermal carbonization of agricultural residues, *Bioresour. Technol.* 142 (2013) 138–146.
- [14] K. Shimizu, R. Uozumi, A. Satsuma, Enhanced production of hydroxymethylfurfural from fructose with solid acid catalysts by simple water removal methods, *Catal. Commun.* 10 (2009) 1849–1853.
- [15] M.M. Titirici, *Sustainable Carbon Materials from Hydrothermal Processes*, John Wiley & Son, United Kingdom, 2013.
- [16] V.V. Ordonsky, J.V.D. Schaaf, J.C. Schouten, T.A. Nijhuis, The effect of solvent addition on fructose dehydration to 5-hydroxymethylfurfural in biphasic system over zeolites, *J. Catal.* 287 (2012) 68–75.
- [17] American Public Health Association/American Water Works Association/Water Environment Federation, *Standard Methods for the Examination of Water and Wastewater*, twenty-first ed., 2005. Washington, DC.
- [18] A. Funke, F. Ziegler, Hydrothermal carbonization of biomass: a summary and discussion of chemical mechanisms for process engineering, *Biofuels Bioprod. Biorefining* 4 (2010) 160–177.
- [19] J. Liang, Y. Liu, J. Zhang, Effect of solution pH on the carbon microspheres synthesized by hydrothermal carbonization, *Procedia Environ. Sci.* 11 (2011) 1322–1327.
- [20] L. Li, R. Diederick, J.R.V. Flora, N.D. Berge, Hydrothermal carbonization of food waste and associated packaging materials for energy source generation, *Waste Manag.* 33 (2013) 2478–2492.
- [21] Y. Li, X. Lu, L. Yuan, X. Liu, Fructose decomposition kinetics in organic acids-enriched high temperature liquid water, *Biomass Bioenergy* 33 (9) (2009) 1182–1187.
- [22] United States Environmental Protection Agency, *Climate Leaders Greenhouse Gas Inventory Protocol Core Module Guidance: Direct Emissions from Stationary Combustion Sources*, May 2008. EPA430-K-08–003.
- [23] J. Poerschmann, B. Weiner, H. Wedwitschka, I. Baskyr, R. Koehler, F.D. Kopinke, Characterization of biocoals and dissolved organic matter phases obtained upon hydrothermal carbonization of brewer's spent grain, *Bioresour. Technol.* 164 (2014) 162–169.
- [24] C. Polprasert, *Organic Waste Recycling: Technology and Management*, third ed., IWA Publishing, UK, 2007.
- [25] S.A. Rackley, *Carbon Capture and Storage*, Butterworth-Heinemann, USA, 2010.