Effects of hydrolysis and carbonization reactions on hydrochar production

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HIGHLIGHTS

- Energy content of the hydrochar increased with increasing hydrolysis reaction time.
- Energy content of the hydrochar increased with increasing carbonization temperature.
- Energy input of the two-stage HTC was less than the conventional HTC.
- High energy efficiency could be found at the two-stage HTC.

ARTICLE INFO

ABSTRACT

Hydrothermal carbonization (HTC) is a thermal conversion process which converts wet biomass into hydrochar. In this study, a low-energy HTC process named "Two-stage HTC" comprising of hydrolysis and carbonization stages using faecal sludge as feedstock was developed and optimized. The experimental results indicated the optimum conditions of the two-stage HTC to be; hydrolysis temperature of 170 °C, hydrolysis reaction time of 155 min, carbonization temperature of 215 °C, and carbonization reaction time of 100 min. The hydrolysis reaction time and carbonization temperature had a statistically significant effect on energy content of the produced hydrochar. Energy input of the two-stage HTC was about 25% less than conventional HTC. Energy efficiency of the two-stage HTC for treating faecal sludge was higher than that of conventional HTC and other thermal conversion processes such as pyrolysis and gasification. The two-stage HTC could be considered as a potential technology for treating FS and producing hydrochar.

1. Introduction

Hydrothermal carbonization (HTC) is a thermal conversion process which was found to be effective in converting high moisture biomass into carbonaceous solids, commonly called hydrochar (Libra et al., 2011). According to previous reports (Falco et al., 2011; Funke and Ziegler, 2010; He et al., 2013; Sevilla and Fuertes, 2009), the hydrochar can be formed via two major conversion pathways: (1) direct solid–solid conversion of original biomass materials which undergoes devolatilization, intramolecular condensation, dehydration and decarboxylation, and (2) conversion of aqueous dispersion biomass materials which is dominated by reaction mechanisms including hydrolysis, dehydration, decarboxylation, fragmentation, polymerization and aromatization.

The advantage of HTC for treating faecal sludge (FS) is that it requires minimal FS drying. However, the challenges of HTC process are the high energy consumption and relatively low energy content of the produced hydrochar. Therefore, a low-energy HTC process named "Two-stage HTC" was explored in this research.

The concept of the two-stage HTC process is to separate reaction pathways into two stages, namely hydrolysis and carbonization stages which are different in the conversion reactions and operating temperatures (Fig. 1). In the hydrolysis stage, biomass materials are broken down to become low-molecular weight compounds such as oligosaccharides, glucose (or fructose), and amino acids (Funke and Ziegler, 2010; He et al., 2013) which can be occurred in the temperature range of 100–175 °C (Abelleira et al., 2012). The carbonization stage consists of the solid–solid conversion, dehydration and polymerization/aromatization reactions which require relatively high temperatures in the range of 160–280 °C (Falco et al., 2011). In this stage, the hydrolyzed products (i.e. glucose or fructose) are dehydrated to

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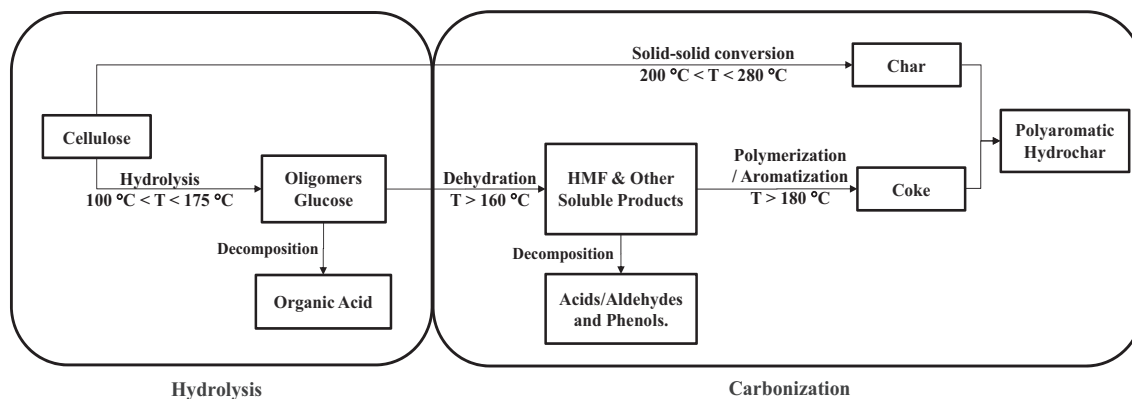 E-mail address: p-krai@hotmail.com (K. Fakkaew).

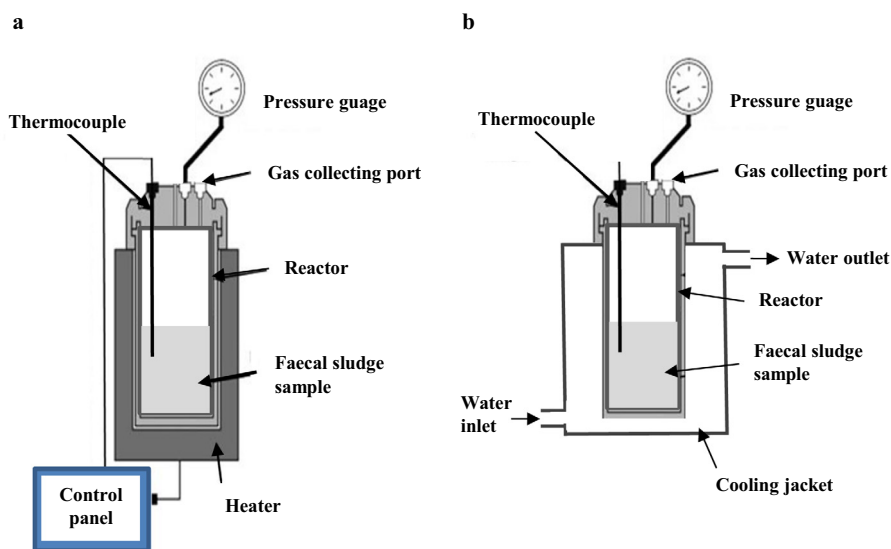**Fig. 1.** Two-stage HTC reaction pathways.

Fig. 2. Schematic of HTC reactor (a) heating system and (b) cooling jacket.

5-hydroxymethylfurfural (HMF) and subsequently polymerized and condensed to form the hydrochar (Sevilla and Fuertes, 2009). Simultaneously, the hydrochar is also formed via the solid–solid conversion of biomass materials (Falco et al., 2011). Based on this concept, the two-stage HTC should consume lower energy and result higher energy contents of the produced hydrochar than the conventional HTC.

In this study, the two-stage HTC using FS as feedstock was developed and optimized. The specific objectives of the research were to determine the effects of the process parameters such as temperature and reaction time of the hydrolysis and carbonization stages on the energy content of the produced hydrochar, to determine optimum conditions of the two-stage HTC that would result in low-energy input and high normalized energy yield and compared with the conventional HTC and other thermal conversion processes, and to analyze mass balance and carbon distribution of the two-stage HTC treating FS.

2. Methods

2.1. FS samples and HTC reactor

FS samples were collected from a municipal emptying truck which serviced residential areas in a city located near Bangkok, Thailand. Moisture contents of the collected FS samples, which were originally about 95%wt, were adjusted to be 80%wt using water bath before feeding to the HTC reactor. The 1-L high pressure reactor made of stainless steel and equipped with pressure gauge, thermocouple and gas collecting ports, as illustrated on Fig. 2, was used in this study. An electric heater equipped with a control panel (Fig. 2a) was used to adjust temperature and reaction time of the reactor.

2.2. HTC experiments

Two-stage HTC experiments were conducted by varying the hydrolysis temperature, hydrolysis reaction time, carbonization temperature, and carbonization reaction time, while energy content of the produced hydrochar was the responsive value. The design of the experiments showed in Table 1 was according to response surface methodology (RSM) with central composite design (Montgomery, 2005) using the Minitab-17 software. For comparison, the experiments of the conventional HTC of FS were also conducted with operating temperature of 250 °C and reaction time of 300 min obtained from an earlier research (Fakkaew, Unpublished results).

For each experiment, 350 mL of the FS sample was fed to the reactor which was operated at the designed temperature and

Table 1
Experimental design and results for two-stage HTC of FS.

Run order	Hydrolysis		Carbonization		Energy content (MJ/kg)
	Temperature (°C)	Reaction time (min)	Temperature (°C)	Reaction time (min)	
1	150	110	225	165	19.82
2	158	65	213	98	18.24
3	158	65	213	233	18.58
4	158	65	238	98	18.39
5	158	65	238	233	19.46
6	158	155	213	98	19.86
7	158	155	213	233	18.69
8	158	155	238	98	21.13
9	158	155	238	233	20.14
10	165	20	225	165	19.05
11	165	110	200	165	19.05
12	165	110	225	30	18.47
13	165	110	225	165	20.34
14	165	110	225	165	18.84
15	165	110	225	165	19.53
16	165	110	225	165	20.21
17	165	110	225	165	20.77
18	165	110	225	165	19.59
19	165	110	225	300	19.96
20	165	110	250	165	19.91
21	165	200	225	165	20.00
22	173	65	213	98	18.52
23	173	65	213	233	20.29
24	173	65	238	98	19.44
25	173	65	238	233	19.05
26	173	155	213	98	19.94
27	173	155	213	233	19.95
28	173	155	238	98	20.30
29	173	155	238	233	20.24
30	180	110	225	165	18.83

reaction time of the hydrolysis stage, and subsequently at the designed temperature and reaction time of the carbonization stage (Table 1). At the end of each experiment, the reactor was rapidly cooled to the ambient temperature with water in a cooling jacket at the cooling rate of about 45 °C/min to quench the reaction. After collection of the gas samples, the carbonized FS remaining in the reactor was separated for 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, liquid, and gas samples were analyzed for their characteristics as described in the following section.

2.3. Analytical methods

Energy content of the produced hydrochar was determined by a bomb calorimeter (AC500, Leco, USA), while energy consumption during the HTC operating was measured by a watt-hour meter (Mitsubishi, Thailand). The proximate analysis (moisture, volatile matter (VM), fixed carbon (FC), and ash contents) and ultimate analysis (carbon, hydrogen, nitrogen, and sulfur) of the produced hydrochar were measured using a thermogravimetric analyzer (TGA701, Leco, USA) and CHNS analyzer (Truspec, Leco, USA), respectively. Total organic carbon (TOC), chemical oxygen demand (COD) concentrations, total nitrogen (TN), and total phosphorus (TP) of liquid samples were analyzed using high temperature combustion method (TOC-V CPH, Shimadzu, Japan), closed dichromate reflux method, persulfate method, and colorimetric method (APHA, 2005), respectively. Gas samples were analyzed for; CO_2, CH_4, O_2, and N_2 using a gas chromatograph instrument (GC 7890A, Agilent, USA) equipped with FID detector.

3. Results and discussion

3.1. Effects of process parameters

Based on these experimental results (Table 1), surface and contour plots of the energy contents of the produced hydrochar vs the process parameters were developed as shown in Fig. 3. The analysis of variance (ANOVA) showed p-values of process parameters such as the hydrolysis temperature, hydrolysis reaction time, carbonization temperature, and carbonization reaction time to be 0.62, 0.01, 0.05, and 0.30, respectively, which indicated the significances of the hydrolysis reaction time and carbonization temperature on the energy content of the produced hydrochar. The effects of process parameters on energy content of the produced hydrochar and the optimum conditions of the two-stage HTC are discussed in the following sections.

3.1.1. Hydrolysis stage

Process parameters of the hydrolysis stage in the two-stage HTC include temperature and reaction time. Fig. 3(a) indicated that increasing the hydrolysis reaction time from 20 to 200 min resulted in the increased energy content of the produced hydrochar. The energy contents of the produced hydrochar were greater than 20 MJ/kg at hydrolysis temperatures and reaction times of 150–175 °C and 150–200 min, respectively. Results of the hydrolysis stage of HTC operation indicated that the VM contents were reduced from 60% in the initial FS to about 50% in the produced hydrochar at the hydrolysis reaction times of ⩾150 min, while the FC contents were relatively constant at all the hydrolysis reaction times.

At the hydrolysis temperature range of 150–180 °C, lignocellulosic biomass as VM content in FS was hydrolyzed. Operating the hydrolysis stage at reaction times longer than 150 min might allow more production of oligomers and glucose which would be subsequently dehydrated and polymerized in the carbonization stage giving the products such as HMF, other soluble products and hydrochar (Sevilla and Fuertes, 2009).

3.1.2. Carbonization stage

The effects of the carbonization temperature and reaction time on energy content of the produced hydrochar are shown in Fig. 3(b). It can be seen that increasing the carbonization temperature from 200 to 250 °C resulted in the increased energy contents of the produced hydrochar. Fig. 3(b) indicates the energy contents of the produced hydrochar to be greater than 20 MJ/kg at the carbonization temperature range of 230–250 °C. With respect to the carbonization reaction time, energy contents of the produced hydrochar tended to decrease with increasing the reaction time. If the energy contents of the produced hydrochar were expected to be greater than 20 MJ/kg, the carbonization reaction times should be 100–250 min.

At the carbonization stage, the VM contents were further degraded from 50% to about 40% while the FC contents in the produced hydrochar were increased from 10% to about 15% which were attributed to the carbonization of the hydrolyzed VM. It could be hypothesized that reduction of the VM was due to the hydrolysis reaction and the hydrolyzed products were subsequently dehydrated and polymerized to become hydrochar, soluble products and gases. The increase of FC and decrease of VM contents during the two-stage HTC resulted in the increased energy content of 13.8 MJ/kg in the dry initial FS to about 20.0 MJ/kg in the produced hydrochar.

Previous researchers working on conventional (or single-stage) HTC found that increasing temperature resulted in increased dehydration and hydrochar formation reactions (Falco et al., 2011;
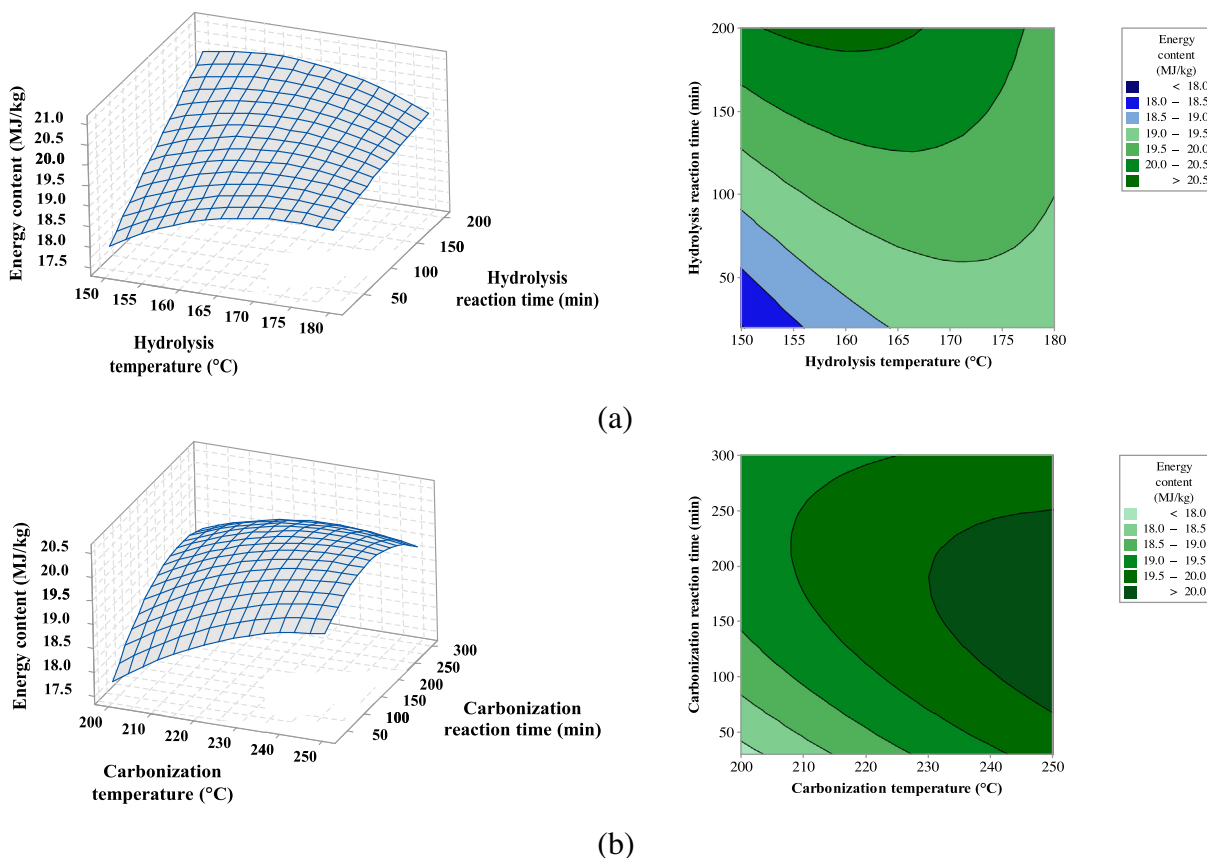
Fig. 3. Surface and contour plots of energy content vs process parameters: (a) hydrolysis temperature and hydrolysis reaction time, and (b) carbonization temperature and carbonization reaction time.

Sevilla and Fuertes, 2009), hence energy contents of the produced hydrochar were found to correspondingly increase. Similar effects of the increased temperature on the conventional HTC of various feedstocks were also reported in the literatures (Danso-Boateng et al., 2013; Liu et al., 2013; Lu et al., 2013; Parshetti et al., 2013).

3.2. Optimum conditions of two-stage HTC

In this study, the optimum conditions of the two-stage HTC were based on the normalized energy yield which is defined as the energy of the produced hydrochar per mass of the dry initial feedstock (Li et al., 2013), as show in Table 2 (Eq. (1)). It could be deduced from the results in Fig. 4 that optimum conditions to produce the highest normalized energy yields of 13.9 MJ/kg-FS were: hydrolysis temperature of 170 °C, hydrolysis reaction time of 155 min, carbonization temperature of 215 °C, and carbonization reaction time of 100 min. To verify these optimum conditions, 3 replicates of the two-stage HTC experiments using different FS samples were conducted. These experimental results showed energy contents of the produced hydrochar and hydrochar yield to be 19.7, 19.9 and 20.8 MJ/kg and 72.8%, 70.7% and 71.2%, respectively, while the normalized energy yields of about 14.4 MJ/kg were achieved. Further evaluations of these optimum conditions with pilot- or full-scale two-stage HTC reactors treating FS or other biomass materials are recommended.

3.3. Mass balance and carbon distribution

Mass balance and carbon distribution of the two-stage HTC, shown in Fig. 5, were carried out at the optimum conditions

indicated in section 3.2. The carbon content of the initial FS was 38.1%wt and the other elements (e.g. hydrogen, nitrogen, oxygen, and sulfur) were 61.9%wt. The hydrothermally carbonized products, being hydrochar, liquid and gas, were found to be 72.8, 23.7 and 3.5%wt, respectively. The carbon distribution data indicated that 74.6% of carbon in the initial FS (38.1%wt) retained within the hydrochar (28.4%wt). The rest of carbon was shifted into either the liquid or gaseous products.

The liquid products still contained high concentrations of organic matters and nutrients as indicated by COD, TOC, TN, and TP concentrations (Table 3). The TOC concentration was used to calculate the carbon content in the liquid product which was 7.8%wt of the initial FS. Analysis of HTC gas samples showed CO_2 to be the main component (64.1%v), similar to results of the conventional HTC of FS (61.9%v) and other literatures (Berge et al., 2011; and Funke et al., 2013). From the mass balance analysis, about 5.0% of carbon in the initial FS was transferred into gas products (1.9%wt). It is apparent that these liquid and gas products need to be further treated to minimize environmental pollutions, odor and greenhouse gas emissions. The liquid products could be treated by anaerobic digestion (Oliveira et al., 2013; Poerschmann et al., 2014) to produce the useful biogas, or applied to farmlands as liquid fertilizer (Polprasert, 2007).

3.4. Comparison to conventional HTC and thermal conversion processes

This comparison of the available information and the experimental results focuses on the operating conditions and product distribution (Table 4), as well as energy efficiency (Table 5) for

Table 2
Summary equations.

Equations	
Normalized energy yield $= E_{HC} \times M_{HC}/M_{dFS}$	(1)
Energy efficiency $= E_{output} \times M_{product}/E_{input}$	(2)
$E_{input} = E_{drying} + E_{heating} + E_{operating}$	(3)
$E_{drying} = M_{FS} \times W \times [(C_{p,water} \times \Delta T) + \Delta H_{vap}] + [M_{FS} \times (1 - W)] \times C_{p,FS} \times \Delta T$	(4)
$E_{heating} = M_{dFS} \times Cp_{FS} \times \Delta T_{operating}$	(5)
$E_{heating,HTC} = M_{FS} \times W \times (C_{p,water} \times \Delta T_{heating}) + [M_{FS} \times (1 - W)] \times C_{p,FS} \times \Delta T_{heating}$	(6)

Notations	
E_{HC}	is the energy content of the hydrochar
E_{output}	is the energy content of the objective product
E_{input}	is the energy required to produce the objective product
E_{drying}	is the energy required for drying the wet FS from initial temperature to 105 °C
$E_{heating}$	is the energy required for heating the dried FS from 105 °C to the operating temperature for pyrolysis and gasification processes
$E_{heating,HTC}$	is the energy required for heating the FS from initial temperature to the operating temperature for HTC process
$E_{operating}$	is the energy required for operating the process at the operating temperature and time
M_{HC}	is the mass of the hydrochar
M_{dFS}	is the mass of dry initial FS
$M_{product}$	is the mass of the objective product
M_{FS}	is the mass of initial FS
W	is the moisture content in FS
ΔH_{vap}	is the latent heat for vaporization of water (2260 kJ/kg)
$C_{p,water}$	is the heat capacity of water (4.186 kJ/kg/°C)
$C_{p,FS}$	is the heat capacity of solids in FS (1.95 kJ/kg/°C)
ΔT	is the temperature difference between initial temperature of FS and 105 °C
$\Delta T_{operating}$	is temperature difference between 105 °C and the operating temperature

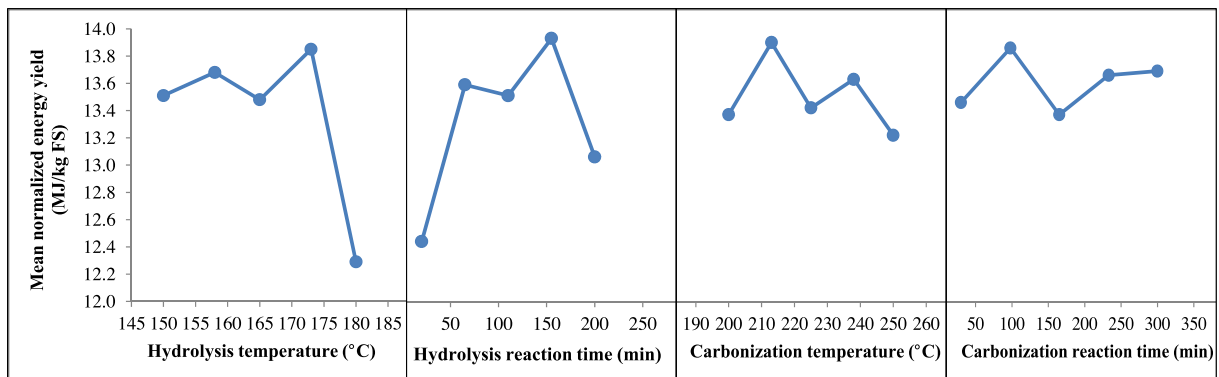Adapted from Li et al. (2013), Xu and Lancaster (2008) and Kim and Parker (2008).

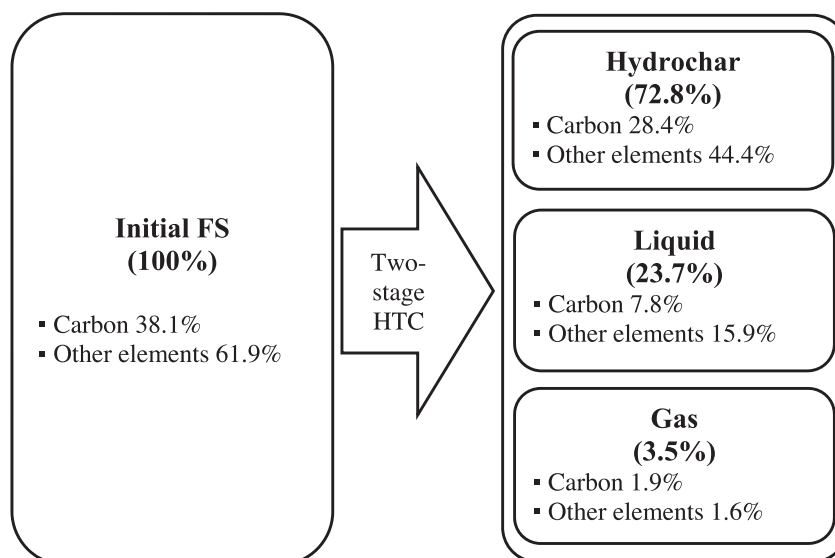**Fig. 4.** Mean normalized energy yields at each process parameters of two-stage HTC of FS.

Fig. 5. Mass balance and carbon distribution for two-stage HTC of FS.

Table 3
Characteristics of FS and liquid products.

Parameters	Unit	FS[a]	Liquid products	
			Conventional HTC	Two-stage HTC
TOC	g/L	16–40	12–16	29–30
COD	g/L	43–50	25–31	26–32
TN	g/L	5.5–7.5	7.0–8.5	5.0–6.2
TP	mg/L	100	0.78	1.50

[a] FS with moisture content of 80%wt.

the thermal conversion processes such as pyrolysis, gasification, HTC and two-stage HTC, with the intent to examine the potential technology options for treating FS and producing valuable products. In general, the two-stage and conventional HTC processes could be operated at relatively lower temperatures and higher moisture contents of the feedstock than the two thermal conversion processes, but operating times of the HTC processes were relatively longer. The main advantage of the HTC processes is to produce hydrochar in the range of 50–80%wt while the pyrolysis yielded only 12–35%wt. Energy contents of the char product from these thermal conversion processes were in the same range of 11–36 MJ/kg.

Energy efficiency can be defined as the ratio of the energy content of the product to the energy input (Xu and Lancaster, 2008). Based on 1 kg of dewatered FS feedstock at 80% moisture content, the energy efficiency of these thermal conversion processes could be determined using Eq. (2) in Table 2 and the results were compared in Table 5. Total energy inputs of pyrolysis and gasification (Table 5) were higher than the HTC processes because operations of pyrolysis and gasification processes require the dried feedstock which utilizes high energy for drying wet FS (80% moisture content) during the pre-drying process. With respect to the HTC processes, the energy input of the two-stage HTC was about 25% less than the conventional HTC. The highest energy efficiency of 1.59 could be observed at the two-stage HTC which was higher than those for conventional HTC, pyrolysis and gasification processes.

The experimental results obtained from this study proved the advantages of the two-stage HTC over the conventional HTC, pyrolysis and gasification, such as the relatively high hydrochar yield and low energy required for heating the feedstock in the reactor to reach the desired temperatures and reaction times. To reduce the energy input for the HTC process, solar energy could be used in a drying bed technology for reducing the moisture content in feedstock prior feeding into HTC reactor and drying wet hydrochar produced after filtration process. The produced hydrochar can be used as solid fuels, soil amendment, energy storage, water purification and other value-added products (Libra et al., 2011; Titirici and Antonietti, 2010). Energy contents of the produced hydrochar

Table 5
Comparison of energy efficiency for thermal conversion processes.

Process	Energy input (MJ)				Energy output (MJ)	Energy efficiency
	Pre-drying	Operating	Post-drying	Total		
Pyrolysis[a]	2.13	1.07	–	3.20	3.38	1.06
Gasification[b]	2.13	1.45	–	3.58	3.18	0.89
Conventional HTC[c]	–	1.92	0.46	2.50	2.74	1.10
Two-stage HTC[c]	–	1.41	0.46	1.87	2.97	1.59

Notes: (1) based on 1 kg of dewatered FS feedstock (80% moisture content) and (2) original FS (about 95% moisture content) could be pre-dewatered before feeding into the reactors by sedimentation, thickening, or drying bed, which were not included in this comparison.
[a] Data from Kim and Parker (2008); pyrolysis of digested sludge at 500 °C.
[b] Data from Hamilton (2000); gasification of dried sewage sludge with a circulating fluidized bed at 850 °C.
[c] Data from this study.

could be further increased with the addition of some catalysts (Lynam et al., 2011, 2012) and biomass (Heilmann et al., 2010; Oliveira et al., 2013).

With respect to scale-up, an increase in volume or capacity of production is usually an increasing investment cost but decreasing operation cost. In case of the HTC reactor, increase in size or volume of the reactor may affect heat transfer efficiency which might require longer operation time to complete the reactions. To avoid these scale-up effects on the HTC reactor, the following recommendations could be considered: (1) applying numbering-up (increasing number of rectors, not size of reactor) (Titirici, 2013) is a way to increase hydrochar production and avoid the effects of large-scale reactor; (2) determining optimal heating rate for the HTC operation, because too fast heating could lead to high difference of temperatures inside the reactor; (3) mixing of the reactor content to make the uniform heat distribution; and (4) heating the reactor from inside could be applied in the large-scale reactor for improving the heat transfer and reducing heat loss. However, it would be desirable to further evaluate cost-benefit analysis of full-scale two-stage HTC reactors treating FS or other biomass materials.

4. Conclusions

Based on the results obtained from this study, the optimum conditions for the two-stage HTC of FS were: hydrolysis temperature of 170 °C, hydrolysis reaction time of 155 min, carbonization temperature of 215 °C, and carbonization reaction time of 100 min.

Energy input of the two-stage HTC was about 25% less than the conventional HTC. Energy efficiency of the two-stage HTC using FS as feedstock was higher than those of conventional HTC, pyrolysis

Table 4
Comparison of operating condition, energy content and product distribution for thermal conversion processes.

Process	Operation		Feed stock	Product distribution					
				Char		Liquid		Gas	
	Temp (°C)	Time		Dist. (%wt.)	Energy (MJ/kg)	Dist. (%wt.)	Energy (MJ/kg)	Dist. (%wt.)	Energy (MJ/m³)
Pyrolysis[a,b,c]	300–500	Sec–week	Dry	12–35	11–35	30–75	10–35	13–35	5–30
Gasification[b,c]	800–1400	10–20 s	Dry	10	NA	5	NA	85	2–20
HTC[b,c]	180–250	1–72 h	Wet	50–80	18–36	5–20	NA	2–5	NA
HTC of FS[d]	250	300 min	Wet	70–74	18–20	19–21	Not analyzed	7–9	Not analyzed
Two-stage HTC of FS[d]	170 and 215	155 and 100 min	Wet	70–73	20–21	21–23	Not analyzed	3–7	Not analyzed

NA = not available.
[a] Depends on process (slow, intermediate and fast).
[b] Libra et al. (2011).
[c] Lu et al. (2012).
[d] Data from this study.

and gasification processes. Therefore, the two-stage HTC could be considered as a potential technology for treating FS and producing hydrochar.

Acknowledgements

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