

Simultaneous pretreatment and acidogenesis of solid food wastes by a rotational drum fermentation system with methanogenic leachate recirculation and andesite porphyry addition

著者別名	北村 豊
journal or publication title	Bioresource technology
volume	138
page range	101-108
year	2013-06
権利	(C) 2013 Elsevier Ltd. NOTICE: this is the author's version of a work that was accepted for publication in Bioresource Technology. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Bioresource Technology, VOL138, June 2013. DOI:10.1016/j.biortech.2013.03.166
URL	http://hdl.handle.net/2241/119525

Simultaneous pretreatment and acidogenesis of solid food wastes by a
rotational drum fermentation system with methanogenic leachate
recirculation and andesite porphyry addition

Jingwen Lu¹, Dawei Li¹, Ling Chen², Yutaka Kitamura³, Weizhong Jiang^{1*} and

Baoming Li¹

¹Key Laboratory of Agricultural Engineering in Structure and Environment, Ministry
of Agriculture, China Agricultural University, Qinghua Donglu 17, Beijing 100083,
China

²Institute of Energy and Environmental Protection, Chinese Academy of Agricultural
Engineering, Maizidian 41, Beijing 100125, China

³Graduate School of Life and Environmental Sciences, University of Tsukuba,
Tsukuba, Ibaraki 305-8572, Japan

*Corresponding Author. Tel: +86 10 62737992; Fax: +86 10 62736413

E-mail address: jiangwz@cau.edu.cn (W.Z. Jiang).

1 **Abstract**

2 A simultaneous pretreatment and acidogenesis process was developed by
3 recirculating methanogenic leachate and adding andesite porphyry (WRS) powder to a
4 rotational drum fermentation system to enhance the anaerobic digestion of solid food
5 wastes. In the continuous operations, methanogenic leachate recirculation
6 significantly increased hydrolysis rates and volatile solids (VS) degradation. The VS
7 degradation ratio and the hydrolysis rate constant at a higher leachate recirculation
8 ratio (2:1 weight ratio of methanogenic leachate to substrate) were increased by 2.1-
9 and 1.4-fold, respectively, compared to those of the lower ratio (1:1 leachate
10 recirculation ratio). A 10% (weight ratio of WRS to substrate solid content) WRS
11 addition assisted the biochemical reactions in the process at the higher leachate
12 recirculation ratio was employed. The hydrolysis rate constant and VS degradation
13 were elevated by 54.7% and 63.9%, respectively, with the WRS addition. Besides, the
14 WRS addition enhanced the VA formation and its conversion to biogas.

15 **Highlights**

- 16 • A simultaneous pretreatment and acidogenesis process for solid wastes was
17 developed.
- 18 • The methanogenic leachate considerably enhanced the hydrolysis of solid food
19 wastes.

1 • The biochemical reactions significantly happened due to the mineral clay
2 addition.

3 ***Key words:***

4 Leachate recirculation, andesite porphyry, simultaneous pretreatment and
5 acidogenesis, solid food waste, rotational drum fermentation system

6

1 **1. Introduction**

2 Bioenergy from solid organic wastes is an excellent alternative to traditional fossil
3 fuels when considering greenhouse gas emission control. Solid food wastes,
4 comprising large fractions of municipal solid wastes, are amenable to bioenergy
5 recovery by anaerobic conversion due to their large biodegradable fractions and
6 moisture. The anaerobic conversion of solid food wastes to the end products CH₄ and
7 CO₂ proceeds in a series of complex biochemical steps due to the lignin content of the
8 solid food wastes (Converti et al., 1999). Hydrolysis is the rate-limiting step in the
9 overall anaerobic conversion of solid substrates (Fdez-Guelfo et al., 2011). The
10 hydrolysis rate mainly depends on the biodegradability of the substrate and the
11 availability of microbes/enzymes (Veeken and Hamelers, 1999), and influenced by
12 many other factors such as rheological properties (Kedziora et al., 2006).

13 Pretreatments by mechanical, chemical, thermal and combined treatments have
14 been used for decades in the food industry and for biofuel production. Pretreatment
15 contributes to both the reduction of particle size and the rearranging/breaking of some
16 chemical bonds (McIntosh and Vancov, 2011; Seehra et al., 2012). Ball milling is
17 traditionally applied as a mechanical pretreatment for its ability to rapidly reduce
18 particle sizes and m Among the different ball milling pretreatments, wet milling is
19 preferred to dry milling due to the higher pulverization efficiency (Charkhi et al.,
20 2010) and lower energy consumption (Fuerstenau and Abouzeid, 2002) of wet ball

1 [milling](#). In the wet ball milling process, the pulverization is usually enhanced by
2 increasing the moisture of the feedstock or by adding extra water ([Fuerstenau and](#)
3 [Abouzeid, 2002](#)). Wet ball milling also meets the requirements for pretreating solid
4 food wastes for anaerobic digestion.

5 In the anaerobic digestion process, the addition of a methanogenic process
6 leachate instead of extra water during the wet ball milling process is conducive to
7 water conservation ([Shahriari et al., 2012](#)). Using leachate recirculation to enhance the
8 anaerobic digestion of solid food wastes ([Chen et al., 2008](#)) resulted in a similar VA
9 yield (0.13 g-VA/g-VS) to that (0.11 g-VA/g-VS) of water flushing ([Gan et al., 2008](#)).
10 Leachate recirculation improves the rheological properties of substrates and supplies
11 enzymes and microbes to the pretreatment process. The enzymes and microbes also
12 biochemically pretreat the solid substrates. Recycled leachate lowers the acidogenic
13 product concentrations and buffers its inhibition to the hydrolysis and acidogenesis
14 processes as the biochemical pretreatment occurs ([Sponza and Agdag, 2004](#)).
15 Pretreatment using leachate recirculation ([Zhang et al., 2009](#)) and wet ball milling has
16 been reviewed recently ([Chen et al., 2007](#)).

17 Although wet ball milling with leachate recirculation enforces the stabilization of
18 food waste, the acidogenic products are prone to accumulation when low recirculation
19 ratios are used. The accumulated acidogenic products caused the pH decrease and the
20 increase of unionized volatile acid (UVA) . The extremely low pH and UVA inhibited
21 the activity of methanogens and acidogens and may even lead to a failure of the entire

1 anaerobic process (Wang et al., 1999). Many experimental efforts have aimed to
2 alleviate this inhibition, including lowering the product concentrations (Gan et al.,
3 2008), electro dialysis (Yi et al., 2008), pervaporation (Cui et al., 2004) and removal of
4 the products in situ (Cheng et al., 2010). Adsorptions by porous media such as zeolite
5 (Wang et al., 2011), activated carbon (Pyrzynska and Bystrzejewski, 2010) and resin
6 (Lin and Juang, 2009) are an interesting method for in-situ removal. In recent years,
7 andesite porphyry (known as wheat-rice-stone, WRS, in Asia), a kind of natural clay
8 mineral, has been applied as a candidate to remove the acidogenic products in situ and
9 thereby assist hydrolysis and acidogenesis (Cheng et al., 2010). WRS not only
10 adsorbs the accumulated acidogenic products due to its unique tetrahedral structure
11 with micro- and nano-channels, but also dissociates and releases cations, including
12 Ca^{2+} , Mg^{2+} and Na^+ , during the acidogenesis of solid food wastes (Li et al., 2009;
13 Cheng et al., 2010). The dissociated cations provide nutrition required by the
14 microbes (Cheng et al., 2010). The acidogenic product adsorption and cation
15 dissociation contribute positively to the anaerobic digestion of solid food wastes.

16 In this study, a rotational drum fermentation (RDF) system with methanogenic
17 leachate recirculation has been developed. The objectives of the work were to (1)
18 pretreat and simultaneously acidify solid food wastes as part of anaerobic digestion by
19 an RDF system with methanogenic leachate recirculation and (2) enhance
20 pretreatment and acidogenesis of solid food wastes by methanogenic leachate
21 recirculation and WRS addition.

1 **2. Materials and methods**

2 *2.1. Materials*

3 *2.1.1 Substrate and seeding sludge*

4 Fresh soybean meal (approximately 24.1% total solids, TS) was collected from a
5 dining hall of the China Agricultural University (Beijing, China) to be used as the
6 substrate. The composition of the dry soybean meal was as follows: protein (22.6%),
7 lipid (19.6%), sugar (37.0%), cellulose (14.5%), ash (6.1%) and other constituents
8 (0.2%). The initial mean particle size of the raw material was 673 μm .

9 Anaerobic digestion sludge was taken from a municipal wastewater treatment
10 plant (Beijing, China) for use as the seeding sludge. The TS, VS and of the sludge
11 were 2.6%, 1.4% and 7.8, respectively. The initial volatile fatty acids of the substrate
12 and the sludge were 0 and 0.04 g/L, respectively.

13 *2.2.2. Andesite porphyry*

14 Andesite porphyry (WRS) was collected from the Changping Mine (Beijing,
15 China) for use as an additive during the hydrolysis and acidogenesis of the solid food
16 wastes. The chemical composition of the WRS used was as in Li et al (Li et al., 2009).
17 The WRS was washed 2-3 times with distilled water and then dried in an oven at 105
18 $^{\circ}\text{C}$ to constant weight.

1 2.1.3. *Methanogenic leachate*

2 The methanogenic leachate was obtained from a sound mesophilic (35-37 °C)
3 methanogenic process. The methanogenic process was fed daily with acetic acid and
4 synthetic wastewater (Chang et al., 1982) and run well for over 2 years. The
5 methanogenic effluent was centrifuged at 3000 rpm for 3 min, and the supernatant
6 was recycled into the acidogenic process as the methanogenic leachate. The average
7 pH of the leachate was 7.2.

8 2.2. *Experimental apparatus*

9 The RDF system developed by Jiang et al (Jiang et al., 2005) was employed to
10 perform the simultaneous pretreatment and acidogenesis of the solid food wastes. The
11 RDF system consisted of six drum fermentors, and each fermentor's working volume
12 was 3.6 L. The mechanical pretreatment was mainly performed by rotating the
13 fermentor with 26 aluminum oxide milling balls (diameter=30 mm), taking up 10% of
14 each fermentor (in volume). Each fermentor was rotated automatically for 15 min
15 every 45 min at 12 rpm and 35 ± 1 °C during the experimental period.

16 2.3. *Experimental procedure*

17 2.3.1. *Batch operation*

18 In batch operation, two fermentors, LB1 and LB2, were used to evaluate the effect
19 of leachate recirculation on the simultaneous pretreatment and acidogenesis of solid

1 food wastes, while the other four fermentors, B11, B12, B21 and B22, were used to
2 evaluate the effect of leachate recirculation with the addition of WRS. The seeding
3 sludge was considered as the methanogenic leachate in the batch operation. The
4 leachate recirculation ratio (the weight ratio of methanogenic leachate to substrate)
5 was 1:1 for LB1, B11 and B12 and 2:1 for LB2, B21 and B22. Five percent WRS (the
6 weight ratio of WRS to substrate solid content) was added to B11 and B21, and 10%
7 to B12 and B22. The detailed feeding conditions were shown in Table 1

8 The batch operations lasted for 10 days. Samples were withdrawn for the analysis
9 of pH, TS (total solids), TDS (total dissolved solids), VS (volatile solids), TVA (total
10 volatile acids), volatile acids (VA) spectra, mean diameter (MD), cation concentration
11 (CC) and ATP concentration on alternate days.

12 *2.3.2. Continuous operation*

13 Fermentors LC1, LC2, C11, C12, C21 and C22 were used for continuous
14 operation. Their detailed feeding conditions are shown in Table 2.

15 **Table 2 Daily operation conditions for the continuous operation experiment**

16 The hydraulic retention time (HRT) of the continuous operation was 10 days. The
17 continuous operation was maintained with daily feedings and withdrawals for at least
18 3 HRTs before reaching pseudo-steady state. The pH was tested every day, while other
19 parameters were measured on alternate days during the pseudo-steady state as for the
20 batch operation.

1 *2.4. Measurements and analyses*

2 The pH, TS, TDS, VS and VA levels were measured using the sewage test
3 procedure (APHA, 2005). MDs were measured using a laser particle size analyzer
4 (LS230, COULTER). ATP concentrations, used to quantify the microbe populations,
5 were determined using an ATP analyzer (AF-100, DKK-TOA). The sample was
6 centrifuged at 6000 rpm for 5 min, and then the supernatant was filtered through a
7 0.45 µm membrane filter to assess VA spectra by a high-performance liquid
8 chromatograph (LC-10AVP, SHIMADZU) with an Atlantic dC column (18.5µm,
9 4.6×150mm, WATERS) at 30 °C.

10 *2.5. Parameter calculations for the degradation of anaerobic solid waste*

11 *2.5.1. Hydrolysis rate constant*

12 The hydrolysis of a solid substrate can be represented by the surface based
13 kinetics (SBK) model (Sanders et al, 2000). The hydrolysis rate constant can be
14 expressed as follows:

15
$$K_{sbk} = \rho \frac{R_0 - R_t}{t} \quad (0)$$

16 where ρ (kg/m³) is the density of the substrate, R_0 (m) is the mean size of the substrate
17 particle at time 0, and R_t (m) is the mean size of the substrate particle at time t.

18 *2.5.2. Total dissolved solids generated (TDS_G)*

19 The TDS_G can be calculated using equation (2)

1
$$TDS_G = TDS_t - TDS_0 + VS_0 - VS_t \quad (0)$$

2 where TDS_t (g/L) and TDS_0 (g/L) are the total dissolved solids at time t and time 0,
 3 respectively and VS_0 (g/L) and VS_t (g/L) are the VS contents of the broth at time 0 and
 4 time t, respectively (Cheng et al., 2010).

5 *2.5.3. Unionized VA concentration*

6 UVA concentration can be determined using following equation:

7
$$UVA = VA \frac{10^{(pKa-pH)}}{1 + 10^{(pKa-pH)}} \quad (0)$$

8 where pKa is the dissociation constant of the acid in water; the pKa of acetic acid is
 9 4.762 at 35 °C (Weast, 1981).

10 *2.5.4. Specific growth rates of TDS_G , VA, and ATP*

11 The specific growth rates of ATP or the other parameters can be calculated using
 12 equation (4):

13
$$\mu = \frac{1}{t} \ln(X_t/X_{t-1}) \quad (0)$$

14 where μ (d^{-1}) is the specific growth rate of TDS_G , VA or ATP; X_t is the value of TDS_G ,
 15 VA or ATP at time t; X_{t-1} is the value of TDS_G , VA or ATP at time t-1 and t is the
 16 sampling interval.

17 *2.5.5. VS degradation ratio (R_{VS})*

18 The R_{VS} can be calculated using equation (5):

1
$$R_{vs} = \frac{VS_0 - VS_t}{VS_0} \cdot 100 \quad (0)$$

2 where R_{VS} (%) is the VS degradation ratio; VS_0 (g/L) is the initial concentration and
3 VS_t (g/L) is the concentration of a sample taken from the fermentor at time t.

4 2.5.6. Particle size distribution

5 The particle size distribution is characterized by the MD and the relative span (S_L)
6 (Igathinathane et al., 2009; Resch et al., 2011). The relative span is determined using
7 equation (6):

8
$$S_L = \frac{D_{90} - D_{10}}{D_{50}} \quad (0)$$

9 where S_L is the relative span; D_{10} , D_{50} and D_{90} are the diameters as the cumulative
10 volumes reached 10%, 50% and 90%, respectively.

11 2.5.7. VA yield

12 The VA yield is expressed by the equation as follow:

13
$$\eta = \frac{VA_t - VA_0}{VS_0 - VS_t} \quad (1)$$

14 where VA_t (g/L) and VA_0 (g/L) are the VA concentration of the sample at time t and
15 time 0, respectively; VS_0 (g/L) is the initial concentration and VS_t (g/L) is the
16 concentration of a sample taken from the fermentor at time t.

1 **3. Results and discussion**

2 *3.1. Effect of leachate recirculation on simultaneous pretreatment and acidogenesis of* 3 *solid food wastes*

4 *3.1.1 Batch operation*

5 The PSDs of broths in LB1 and LB2 are shown in Fig.1 (a and b). The curve of
6 the particle size distribution changed from one dominated by large particles to one
7 dominated by smaller ones (from right to left in the figure) over the operation time.
8 The S_L s obtained using equation (0) for LB1 and LB2 peaked at 2.70 and 3.16,
9 respectively, much higher than that of the original feedstock (1.53). The increases in
10 S_L suggest that substrate flocs were ground into finer particles. The calculated MDs of
11 substrate particles in the batch operations are shown in Fig. 2 (a). The MDs decreased
12 linearly in LB1 and LB2 from 673 to 567 and 96 μm , respectively. According to the
13 linear regression of Fig. 2 and equation (0), the calculated K_{sbk} values for LB1 and
14 LB2 were 11.4 and $50.0 \times 10^{-3} \text{ kg m}^{-2} \text{ d}^{-1}$, respectively. The K_{sbk} of LB2 was 4.4-fold
15 higher than that of LB1. The dramatically higher K_{sbk} of LB2 was ascribed to the
16 higher humidity that resulted from the increased leachate recirculation ratio. The
17 higher humidity reinforced the impact of the milling balls onto the substrate flocs, the
18 dispersion of flocs and the shear flow in the rheology (Izumi et al., 2010). Both the
19 higher impact and higher shear flow enhanced splitting of the substrate agglomerates
20 and broke crystal structures.

1 **Fig. 1 Particle size distributions in the batch operations**

2 **Fig. 2 Time courses for particle MDs in the batch experiments**

3 Enrichment with the enzymes and microbes in the leachate caused biodegradation
4 occur during the mechanical pretreatment. The VS degradation rate was determined
5 using a regression (Fig. 3 (a)). The VS degradation rates for LB1 and LB2 were 6.2
6 and $4.5 \text{ g L}^{-1} \text{ d}^{-1}$, respectively. The TDS_G grew logarithmically during the batch
7 operation. The specific growth rate of the TDS_G (μ_{TDSG}) was calculated using equation
8 (0) as 0.16 and 0.17 d^{-1} for LB1 and LB2, respectively. The higher TDS_G and the VS
9 degradation rate in LB1 were caused by the lower leachate recirculation ratio. Similar
10 results were obtained by Zhou et al (Zhou et al., 2011). In the lower leachate
11 recirculation ratio fermentor (LC1), the presence of more readily biodegradable
12 substrate (the initial total dissolved solids TDS_0 , 14.0 g/L) ensured the anaerobes'
13 growth during the initial period.

14 **Fig. 3 Time courses for TDSG and VS contents**

15 The specific growth rates of the anaerobes (represented by the ATP concentration
16 μ_{ATP} (APHA, 2005) in LB1 and LB2 were 5.40 and 5.04 d^{-1} , respectively. The growth
17 of the anaerobes not only accelerated VS degradation, but also enhanced the
18 formation of VAs. The specific growth rates (μ_{VAS}) for the TVAs in LB1 and LB2
19 were similar, with values of 0.29 and 0.28 d^{-1} , respectively. The yields of VA and
20 ionized VA (IVA) for LB1 and LB2 tended similar to the μ_{VAS} . The VA yields for LB1

1 and LB2 were 0.16 and 0.15 g-VA/g-VS, respectively. The IVA ratio of LB2 was
2 higher than that of LB1 during the batch operation, despite the finding that the IVAs
3 for both LB1 and LB2 were no more than 30% of the TVAs. Apparently, more
4 leachate recirculation had a greater effect on the mechanical than the biochemical
5 aspect of the in this work.

6 *3.1.2. Continuous operation*

7 **Fig. 4 Particle size distributions in the continuous operations**

8 The parameters in the continuous operation trials were obtained by averaging the
9 data obtained under steady state. The particle size distributions of LC1 and LC2 are
10 shown in Fig. 4. The particles spanned broader ranges in LC1 and LC2 than in the
11 feedstock. The S_L s of LC1 and LC2 were higher by 31.9% and 35.2% than that of the
12 feedstock (1.53), respectively. The higher S_L of LC2 indicated that substrates were
13 ground into finer particles in this fermentor. The pretreatment characteristics of the
14 continuous operations are summarized in Table 3. The MDs for LC1 and LC2 were
15 reduced from 744 μm in the feedstock to 662 and 491 μm , respectively. The
16 calculated K_{sbk} of LC2 was higher by 2.1-fold than that of LC1. Higher K_{sbk} and lower
17 MD were obtained at the higher moisture content (LC2), which coincided with the
18 results in the batch operation. The substrate particles were stressed mechanically by
19 the compression, impact and the friction of the milling balls in this work. The
20 breakage of substrate particles depended on the yield stress of itself and the stressing

1 intensity. The yield stress dropped at certain higher moisture content (Müller et al.,
2 2013), meaning particles were apt to be broken mechanically. In addition, the particles
3 were softened in the structure, thus the accessibility of the substrate was enhanced.
4 This was evidenced by the results and R_{VS} and TDS_G .

5 The R_{VS} of LC2 was 2.4-fold higher than that of LC1. Similar to the VS
6 degradation, the TDS_G for LC2 was more than 2-fold greater than that of LC1. The
7 finer particles presented larger surface area, and available for the microorganisms,
8 resulting a higher R_{VS} and TDS_G . The solubility of substrate were also enhanced by
9 the wet ball milling pretreatment (Izumi et al., 2010). In another word, these favorable
10 TDS_G s were generated by the combination of mechanical pretreatment with
11 biochemical reactions.

12 **Table 3 Pretreatment characteristics of the continuous operations under steady**
13 **state**

14 As shown in Table 4, the apparent VA yield of LC1 was 2.5-fold above that of
15 LC2 despite their similar TVAs. The IVAs predominated in both LC1 and LC2. The
16 IVA values were elevated significantly compared to those under continuous operation
17 without leachate recirculation (Chen et al., 2008). The higher IVAs favored higher
18 rates of methanogenesis.

19 The VA spectra appeared to be influenced by the leachate recirculation. The acetic
20 acid contents of LC1 and LC2 were 31.1% and 14.6%, respectively, while the
21 propionic acid contents were 20.7% and 36.5%, respectively. The ratio of propionic

1 acid to acetic acid (P/A) of LC2 greater than 1.4 or the was possibly considered as an
2 indicator of failure (Hill et al., 1987), however, the lower amount of acetic acid in
3 LC2 was caused by its conversion to biogas (methane and carbon dioxide) in this
4 work. The biogas emission was observed during daily operations, during which 70%
5 methane was generated from acetic acid. On the contrary, little biogas was observed
6 in LC1. The rich leachate in LC2 introduced more microbes and enzymes and favored
7 degradation of the acetate.

8 **Table 4 Acidogenesis characteristics of the continuous operations under steady**
9 **state**

10 *3.2. Effects of leachate recirculation and WRS addition on simultaneous pretreatment*
11 *and acidogenesis of solid food wastes*

12 *3.2.1. Batch operation*

13 Time courses for particle size distributions during the batch operations are shown
14 in Fig. 1 (c-f). The calculated $S_{L,S}$ for B11, B12, B21 and B22 were 3.0, 2.49, 3.44 and
15 2.98, respectively. The S_L for each run increased over the course of the reaction. The
16 time courses for MDs during batch operation are shown in Fig. 2 (b). The MDs for
17 B11, B12, B21 and B22 were 494, 294, 158 and 61 μm , respectively. The MDs for
18 B11 and B12 were lower by 12.8% and 48.1% than that of LB1, respectively. The MD
19 for B21 was higher than that of LB2, while the MD for B22 was 63.5% of LB2's.
20 Correspondingly, the K_{sbk} s obtained for B11 and B12 were 16.0 and 29.8 $\times 10^{-3}$ kg

1 $\text{m}^{-2} \text{d}^{-1}$, and 50.0 and $65.0 \times 10^{-3} \text{ kg m}^{-2} \text{ d}^{-1}$ for B21 and B22, respectively. The K_{sbkS}
2 for B11 and B12 were 1.4 and 2.6-fold higher than that of LB1 respectively. The K_{sbk}
3 for B21 was close to that of LB2 ($50.0 \times 10^{-3} \text{ kg m}^{-2} \text{ d}^{-1}$), while the K_{sbk} for B22 was
4 1.3-fold higher than that of LB2. Compared to LB1 and LB2, the WRS addition
5 significantly enhanced the substrate particle size reduction (except B21). Moreover,
6 the WRS addition led to a faster substrate particle size reduction in the case of the
7 higher leachate recirculation ratio. The WRS particles were much harder than the
8 substrate particles. The elasticities of the WRS and substrate mixtures were lower than
9 that of the substrate alone. With WRS addition, the substrate particles were more
10 easily broken when they were impacted by the milling balls. In addition, the large
11 amounts of cations such as Ca^{2+} , Na^{+} and Al^{3+} in the WRS are prone to dissociation
12 and formation of compounds such as CaCl_2 and CH_3COONa in acidic broth. In the
13 experiment, the compounds may have arranged their dipoles to reduce the flocs'
14 surface energies and thereby aided the fragmentation of the solid substrates.

15 The time course of VS degradation and TDS_G is shown in Fig. 3. The VS
16 degradation rates for B11, B12, B21 and B22 were 7.0 , 6.5 , 4.6 and $5.5 \text{ g L}^{-1} \text{ d}^{-1}$,
17 respectively. The VS degradation rates for B11 and B12 were higher by 11.7% and 4.8%
18 than that of LB1, respectively. The VS degradation rate for B21 was similar to that of
19 LB2, while that of B22 was higher by 22.2% than that of LB2. The TDS_G grew
20 logarithmically during the batch operation. The μ_{TDS_G} for B11, B12, B21 and B22
21 were 0.15 , 0.09 , 0.07 and 0.13 d^{-1} , respectively. Higher leachate recirculation and

1 more WRS addition were therefore favorable to the VS degradation.

2 The apparent VA yields for B11, B12, B21 and B22 were 0.09, 0.26, 0.16 and 0.31
3 g-VA/g-VS, respectively. Compared to LB1 and LB2, more WRS addition favored
4 more VA production (Li et al., 2009; Cheng et al., 2010). Formic acid predominated in
5 fermentor B11 and B21, while succinic acid did in fermentor B12 and B22 during the
6 initial period. Acetic acid predominated beginning on the 4th day in all the fermentors.
7 The specific growth rates for acetic acid in B11, B12, B21 and B22 were 0.31, 0.30,
8 0.24 and 0.31 d⁻¹, respectively. The occupation of acetic acid was elevated by the
9 WRS addition compared with LB1 and LB2. These results suggest that the WRS
10 addition promoted the conversion of long-chain VAs to short ones. Among the short
11 chain VAs, propionic acid is difficult to be converted to acetic acid by the
12 microorganisms compared to butyric acid. On the contrary, acetic acid was prone to
13 consumed by the methanogens. The higher acetic acid occupation implied a potential
14 for the biogas production.

15 The data for VS degradation and VA production demonstrate that the WRS
16 addition enhanced the biochemical reactions. These results were consistent with the
17 anaerobes' growth as the μ_{ATPS} for B11, B12, B21 and B22 increased by 5.9%, 24.5%,
18 21.0% and 2.4% compared to LB1 and LB2.

19 3.2.2. *Continuous operations*

20 The parameters of the continuous operations were obtained by averaging data
21 obtained under steady state. The particle size distributions are shown in Fig. 4.

1 Substrate particles smaller than 100 μm were 5.7%, 11.7%, 16.4% and 32.6% of the
2 totals, respectively, in comparison to those of LC1 (6.2%) and LC2 (8.7%). Aldin's
3 work (Aldin, 2010) suggested that most biodegradable matter ranged from 0.001-100
4 μm . In our work, the WRS addition contributed to the conversion from raw materials
5 to materials with high proportions of biodegradable constituents. The S_{LS} calculated
6 using equation (0) for C11, C12, C21 and C22 were 1.99, 2.36, 2.64 and 3.02,
7 respectively. The S_L of C11 was slightly lower than that of LC1, while the S_L of C12
8 was higher by 16.8% than that of LC1. The S_{LS} of C21 and C22 were higher by 27.5%
9 and 45.9% than that of LC2, respectively. These results suggest that more fine
10 particles were produced due to the WRS addition.

11 Characteristics of the pretreatments are shown in Table 2. The MDs of fermentors
12 C11, C12, C21 and C22 decreased from 673 μm to 656, 628, 518 and 351 μm ,
13 respectively. The MDs of C11 and C12 were slightly lower than that of LC1. The MD
14 of C21 was slightly higher than that of LC1, while the MD of C22 was lower by 39.8%
15 than that of LC2. Correspondingly, the K_{sbk} s for C11 and C12 were higher by 7.3%
16 and 41.5% than that of LC1, respectively. The K_{sbk} for C21 was close to that of LC2,
17 while the K_{sbk} for C22 was higher by 54.7% than that of LC2. The higher leachate
18 recirculation and WRS addition ratio led to the substrate particle shift from the large
19 to the micro range.

20 The R_{VSS} and the TDS_{GS} are shown in Table 3. The R_{VSS} of C11 and C12 were
21 close to that of LC1, whereas those of C21 and C22 were much higher than that of

1 LC2. The R_{VSS} of C21 and C22 were higher by 35.8% and 63.9% than that of LC2,
2 respectively. The WRS was prone to dissociate cations, including Fe^{2+}/Fe^{3+} , Ca^{2+} and
3 Mg^{2+} , and accelerated the oxidation/reduction reaction under the high leachate
4 recirculation ratio. On the contrary, the WRS dissociation and cation transfers were
5 perturbed in case of the lower leachate recirculation ratio. The leachate recirculation
6 contributed 64.8% and 64.5% to the VS degradation, while WRS addition contributed
7 35.2% and 35.5% to that in C11 and C12, respectively. The values for TDS_G showed
8 similar trends to those for the VS degradation ratio. The highest TDS_G achieved was
9 in C22, which was higher by 56.2% than that of LC2.

10 The TVA of C11 was higher by 8.7% than that of LC1, while the TVA of C12 was
11 lower by 2.9% than that of LC1. The VA formation seemed to be little enhanced by
12 WRS addition in the case of the lower leachate recirculation ratio, even though the
13 TVAs for C21 and C22 were supposed to increase. Interestingly, the TVAs of C21 and
14 C22 were lower by 14.4% and 28.8% than that of LC2, respectively. The decreased
15 VAs were converted to biogas. In our work, biogas emission was observed in C21 and
16 C22 during daily operations. The biogas emission should not only be ascribed to the
17 reduction of particle size (Zhang and Banks, 2013), but also resulted from the WRS
18 addition. As mentioned above, the cations dissociated from WRS had the enzyme and
19 microorganisms sparked and promoted the acidogenesis and even the methanogenesis
20 potentially.

21 Similar results were obtained for the distributions of the IVAs and UVAs and for

1 the VA spectra. The IVAs predominated in all the fermentors, which was possibly
2 conducive to biogas formation. Compared to LC2, the acetic acid occupation
3 decreased with the increased addition of WRS in C22. The decreased acetic acid was
4 possibly converted to biogas. Notably, the occupation of propionic acid varied in the
5 range of 29.2-58.5%. The TDSs were prone to conversion to propionate rather than to
6 other VAs (such as butyrate, acetate and lactate) by lower energy demand during the
7 biochemical reaction. However, propionate is more difficult to convert to acetate than
8 to butyrate and lactate (Azbar et al., 2001).

9 **4. Conclusion**

10 Methanogenic leachate recirculation and WRS addition were used to enhance
11 pretreatment and acidogenesis of solid food wastes in batch and continuous operations.
12 A higher leachate recirculation ratio from the methanogenesis to RDF system
13 improved the mechanical pretreatment such as particle size reduction and TDS
14 generation in anaerobic process. The 10% WRS addition at higher leachate
15 recirculation ratio considerably enhanced the VS degradation, particle size reduction,
16 VA formation and conversion to biogas.

17 **Acknowledgements**

18 This work was supported by the Fundamental Research Funds for the Central
19 Universities (2011JS121).

1 **Figure captions**

2 Fig. 1 Particle size distributions in the batch operations

3 Fig. 2 Time courses for particle MDs in the batch experiments

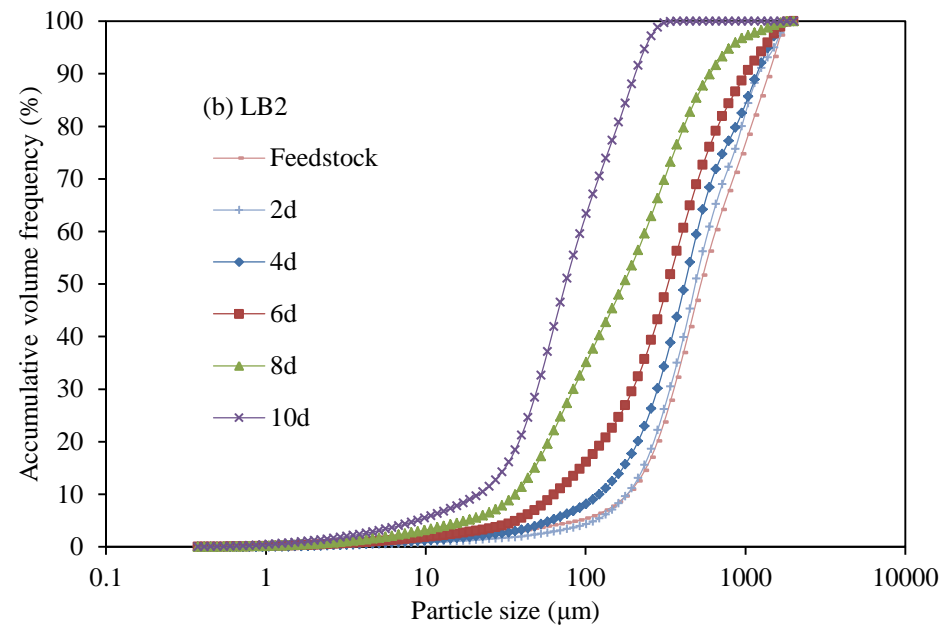
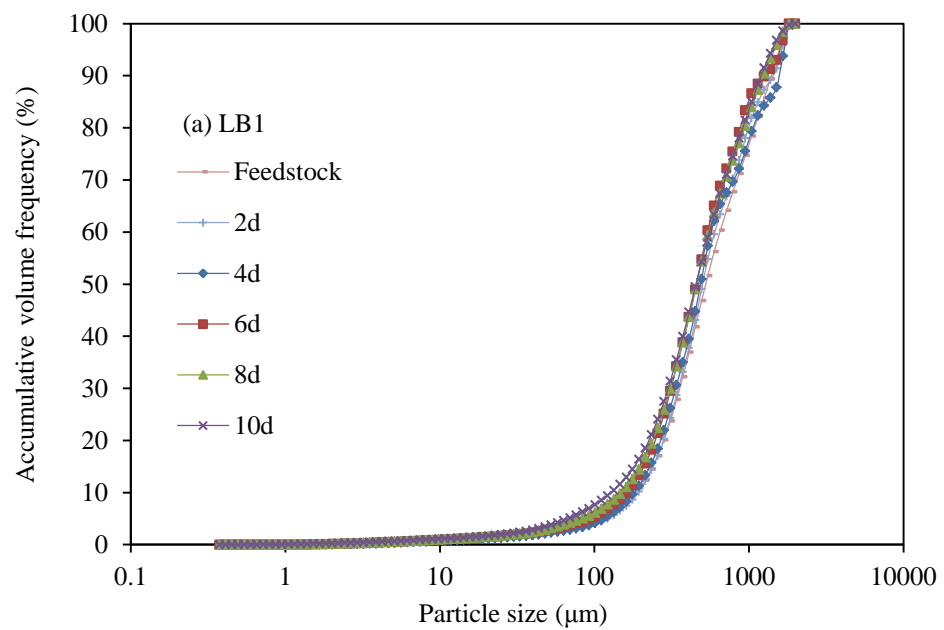
4 Fig. 3 Time courses for TDS_G and VS contents

5 Fig. 4 Particle size distributions in the continuous operations

6

7

Fig. 1



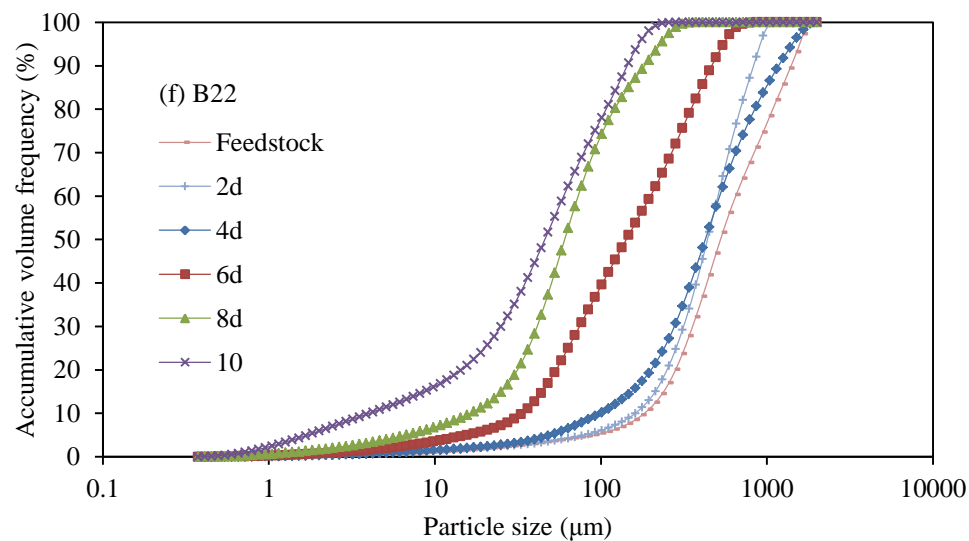
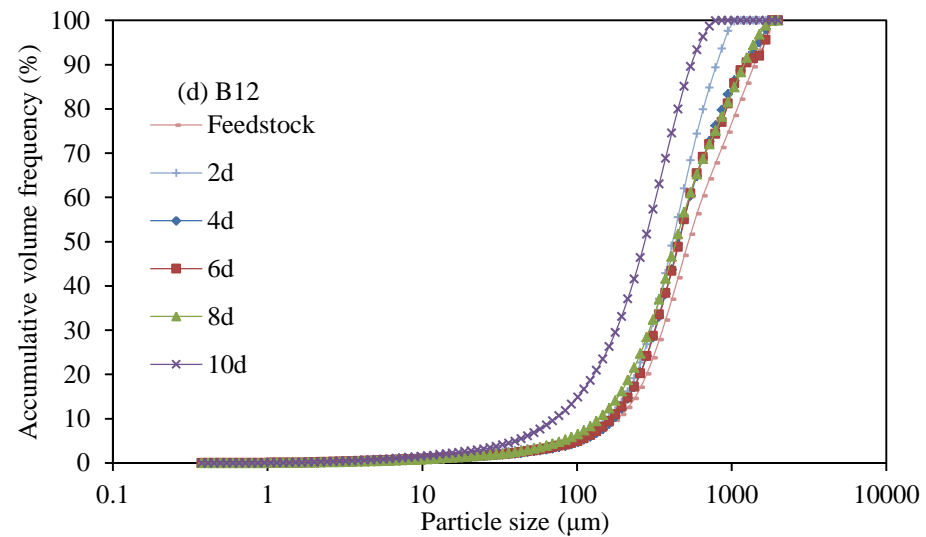
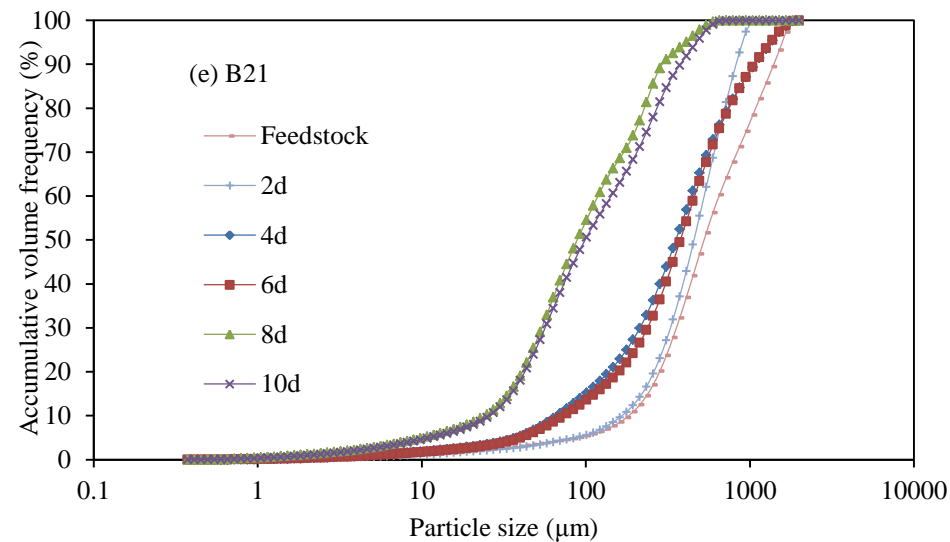
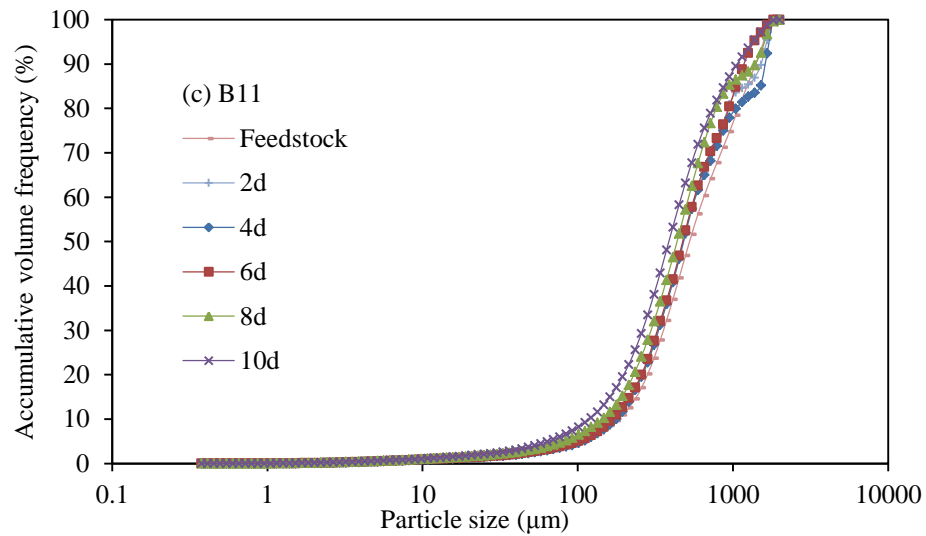


Fig. 1 Particle size distributions in the batch operations

Fig. 2

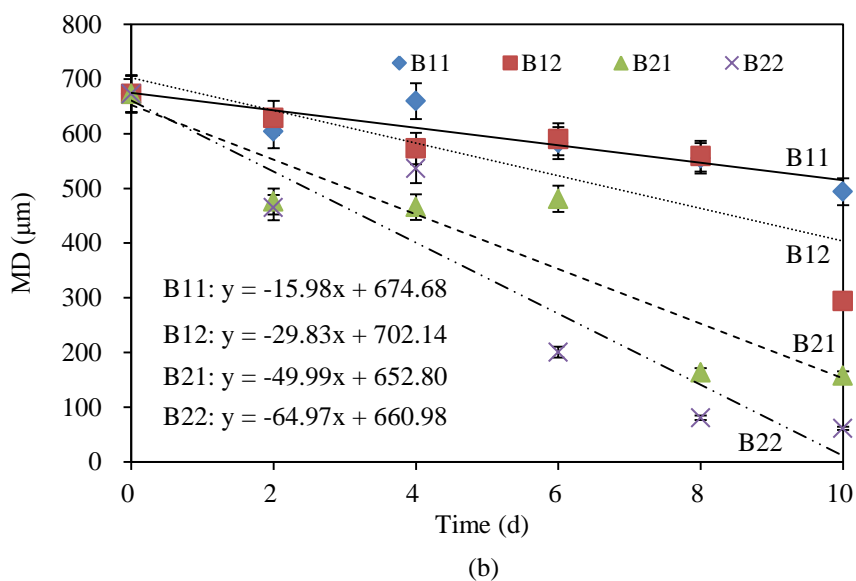
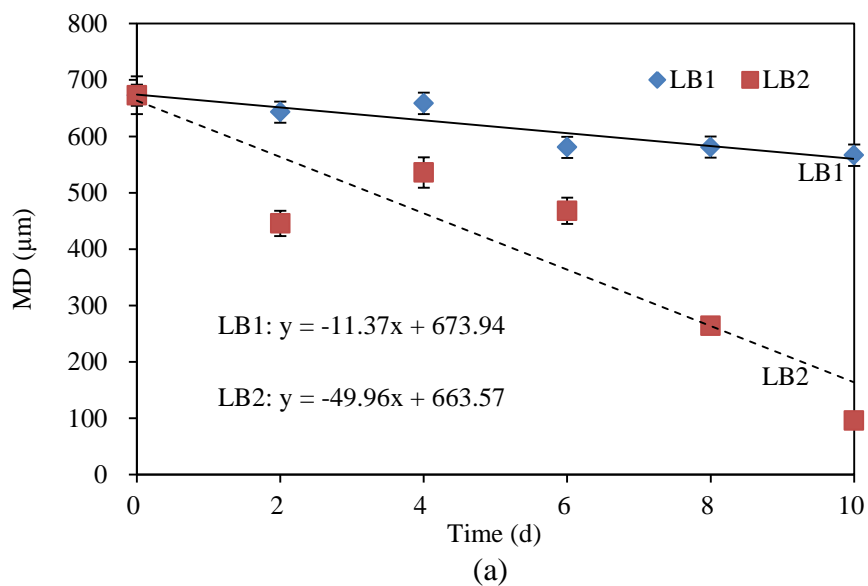


Fig. 2 Time courses for particle MDs in the batch experiments

Fig. 3

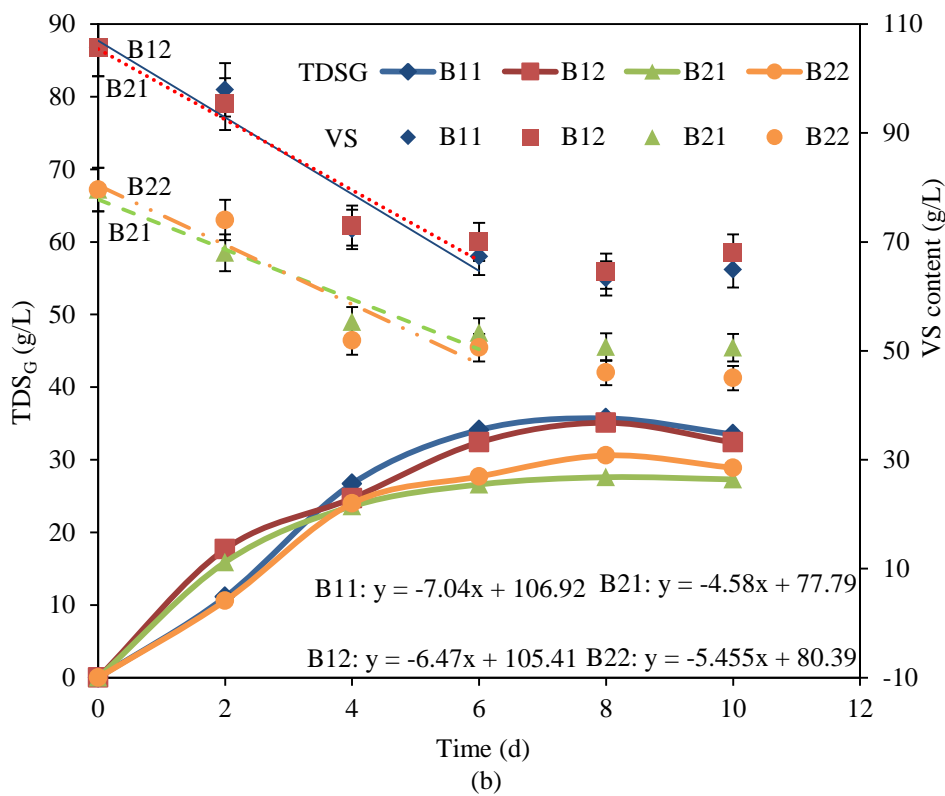
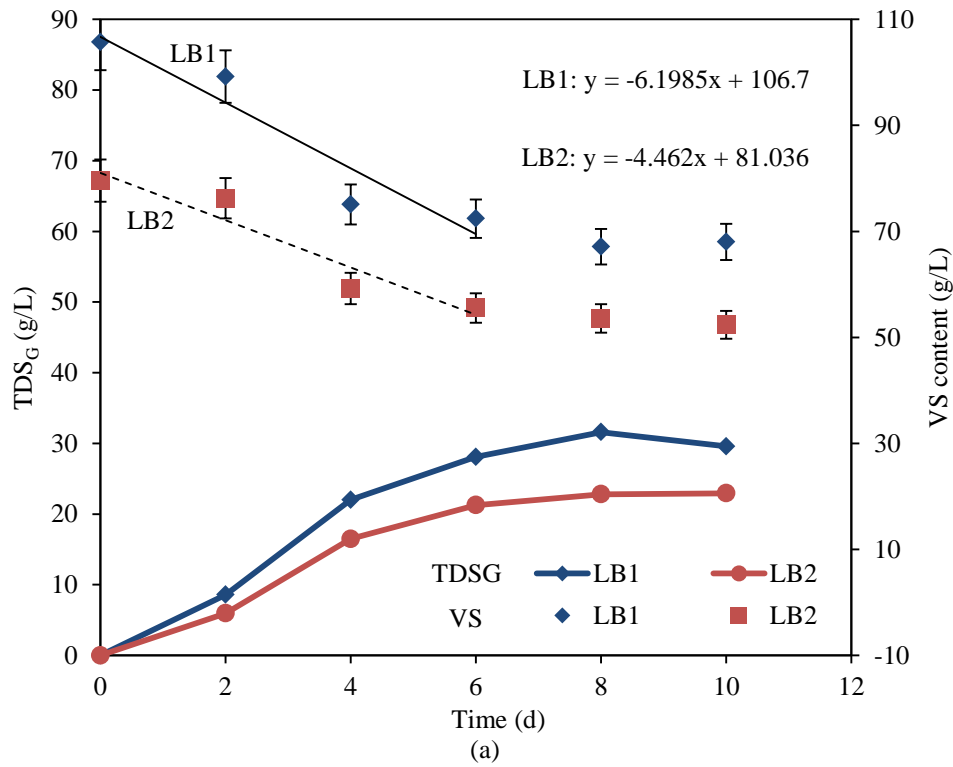


Fig. 3 Time courses for TDS_G and VS contents

Fig. 4

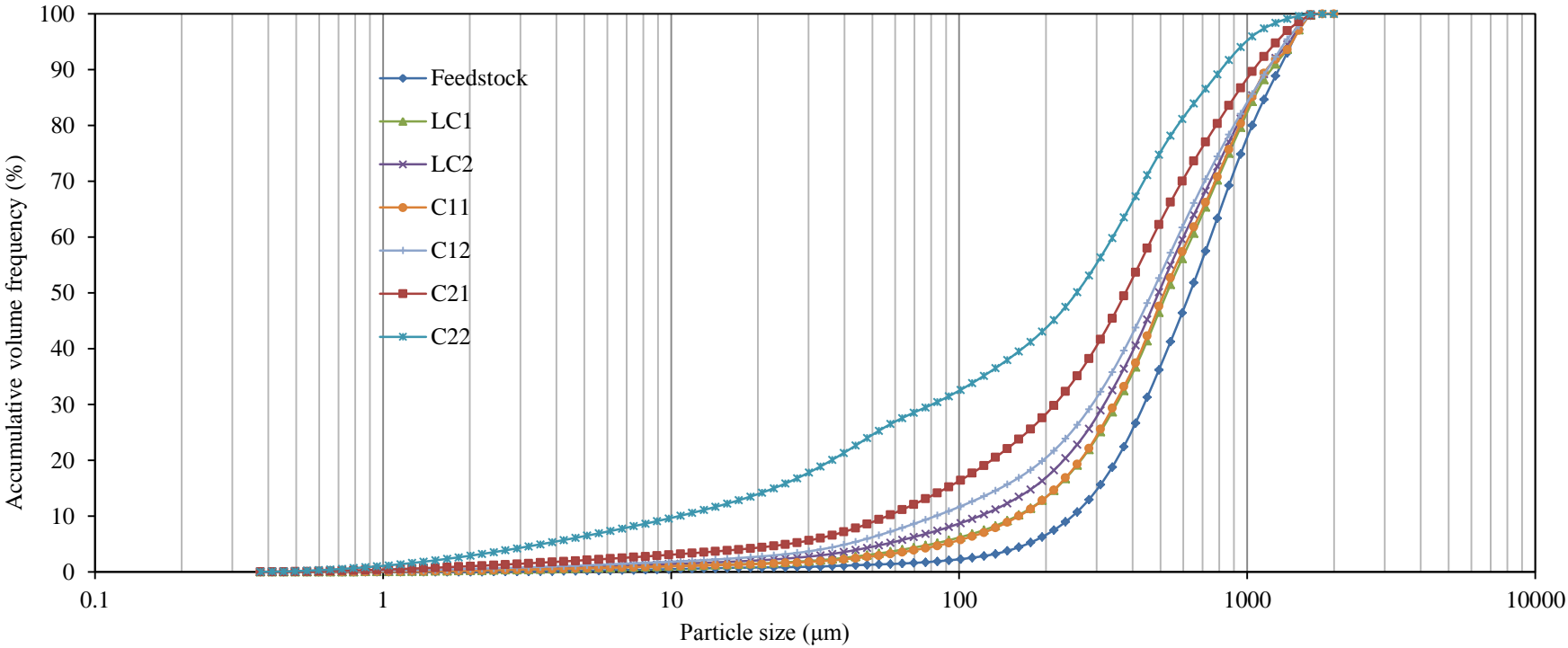


Fig. 4 Particle size distributions in the continuous operations

Table 1

Table 1 Operation conditions for the batch operation experiments

Fermentor	Substrate and methanogenic leachate			WRS addition	
	Weight of methanogenic leachate (g)	Weight of Soybean meal (g)	Weight ratio of methanogenic leachate to substrate	Weight (g)	Proportion (in substrate TS, %)
LB1	1200	1200	1:1	0	0
LB2	1600	800	2:1	0	0
B11	1200	1200	1:1	12	5
B12	1200	1200	1:1	24	10
B21	1600	800	2:1	8	5
B22	1600	800	2:1	16	10

Table 2

Table 2 Daily operation conditions for the continuous operation experiments

Fermentor	Substrate and methanogenic leachate			WRS addition	
	Weight of methanogenic leachate (g)	Weight of soybean meal (g)	Weight ratio of methanogenic leachate to substrate	Weight (g)	Proportion (in substrate TS, %)
LC1	90	90	1:1	0	0
LC2	120	60	2:1	0	0
C11	90	90	1:1	0.9	5
C12	120	120	1:1	2.4	10
C21	120	60	2:1	0.6	5
C22	140	70	2:1	1.4	10

Table 3

Table 3 Pretreatment characteristics of the continuous operations under steady state

Fermenter No.	PSD (μm)	K_{sbk} ($10^{-3} \text{ kg/m}^2 \text{ d}$)	R_{VS} (%)	TDS_G (g/L)	S_L -
LC1	662 \pm 12	8.2	17.1	20.8 \pm 0.2	2.02 \pm 0.01
LC2	491 \pm 11	25.4	41.6	42.9 \pm 0.1	2.07 \pm 0.02
C11	656 \pm 9	8.8	11.1	13.6 \pm 0.0	1.99 \pm 0.02
C12	628 \pm 15	11.6	16.2	21.4 \pm 0.1	2.36 \pm 0.03
C21	518 \pm 6	22.6	56.5	45.5 \pm 0.0	2.64 \pm 0.03
C22	351 \pm 15	39.3	68.2	67.0 \pm 0.0	3.02 \pm 0.03

Table 4

Table 4 Acidogenesis characteristics of the continuous operations under steady state

Fermenter No.	pH(-)		VA (g/L)	Apparent Y_{VA} g-VA/ g-VS	VA distribution		VA spectra (%)			
	In	Out			UVA (%)	IVA (%)	Acetic acid	Propionic acid	Butyric acid	Succinic acid
LC1	7.5	5.2	10.9	0.58	26.7	73.3	31.1	20.7	24.6	23.6
LC2	7.5	5.0	10.4	0.23	36.6	63.4	14.6	36.5	26.4	22.5
C11	7.4	5.1	11.7	0.97	31.5	68.5	-	-	-	-
C12	7.5	5.1	10.1	0.73	31.5	68.5	37.9	29.2	25.1	7.8
C21	7.4	5.0	8.9	0.21	36.6	63.4	17.3	58.5	23.1	1.1
C22	7.5	4.9	7.4	0.12	42.1	57.9	9.0	29.3	27.1	34.6

1 Reference

- 2 [1] Aldin, S., 2010. The effect of particle size on hydrolysis and modeling of
3 anaerobic digestion. PhD thesis, The University of Western Ontario.
- 4 [2] APHA, 2005. Standard methods for the examination of water and
5 wastewater, 21st ed. Washington, D.C., APHA.
- 6 [3] Azbar, N., Ursillo, P. and Speece, R. E., 2001. Effect of process
7 configuration and substrate complexity on the performance of anaerobic
8 processes. *Water Res.* 35, 817-829.
- 9 [4] Chang, J. E., Noike, T. and Matsumoto, J., 1982. Effect of retention time
10 and feed substrate concentration on methanogenesis in anaerobic digestion.
11 *Transaction of the Japanese Society of Civil Engineering.* 320, 67-76.
- 12 [5] Charkhi, A., Kazemian, H. and Kazemeini, M., 2010. Optimized
13 experimental design for natural clinoptilolite zeolite ball milling to
14 produce nano powders. *Powder Technol.* 203, 389-396.
- 15 [6] Chen, L., Jiang, W., Kitamura, Y., et al., 2007. Enhancement of hydrolysis
16 and acidification of solid organic waste by a rotational drum fermentation
17 system with methanogenic leachate recirculation. *Bioresource Technol.* 98,
18 2194-2200.
- 19 [7] Chen, L., Li, B., Li, D., et al., 2008. Ultrasound-assisted hydrolysis and
20 acidogenesis of solid organic wastes in a rotational drum fermentation

- 1 system. *Bioresource Technol.* 99, 8337-8343.
- 2 [8] Cheng, F., Li, M., Li, D., et al., 2010. Volatile organic acid adsorption and
3 cation dissociation by porphyritic andesite for enhancing hydrolysis and
4 acidogenesis of solid food wastes. *Bioresource Technol.* 101, 5076-5083.
- 5 [9] Converti, A., Del Borghi, A., Zilli, M., et al., 1999. Anaerobic digestion of
6 the vegetable fraction of municipal refuses: mesophilic versus
7 thermophilic conditions. *Bioprocess Eng.* 21, 371-376.
- 8 [10] Cui, Y., Kita, H. and Okamoto, K. I., 2004. Zeolite T membrane:
9 preparation, characterization, pervaporation of water/organic liquid
10 mixtures and acid stability. *J Membrane Sci.* 236, 17-27.
- 11 [11] Fdez-Guelfo, L. A., Alvarez-Gallego, C., Sales, D., et al., 2011. The use
12 of thermochemical and biological pretreatments to enhance organic matter
13 hydrolysis and solubilization from organic fraction of municipal solid
14 waste (OFMSW). *Chem Eng J.* 168, 249-254.
- 15 [12] Fuerstenau, D. W. and Abouzeid, A. Z. M., 2002. The energy efficiency
16 of ball milling in comminution. *Int J Miner Process.* 67, 161-185.
- 17 [13] Gan, J., Chen, L., Li, B., et al., 2008. A rotational drum fermentation
18 system with water flushing for enhancing hydrolysis and acidification of
19 solid organic wastes. *Bioresource Technol.* 99, 2571-2577.
- 20 [14] Hill, D. T., Cobb, S. A. and Bolte, J. P., 1987. Using Volatile Fatty-Acid
21 Relationships to Predict Anaerobic Digester Failure. *T Asae.* 30, 496-501.

- 1 [15] Igathinathane, C., Melin, S., Sokhansanj, S., et al., 2009. Machine vision
2 based particle size and size distribution determination of airborne dust
3 particles of wood and bark pellets. *Powder Technol.* 196, 202-212.
- 4 [16] Izumi, K., Okishio, Y. K., Nagao, N., et al., 2010. Effects of particle size
5 on anaerobic digestion of food waste. *Int Biodeter Biodegr.* 64, 601-608.
- 6 [17] Jiang, W., Kitamura, Y. and Li, B., 2005. Improving acidogenic
7 performance in anaerobic degradation of solid organic waste using a
8 rotational drum fermentation system. *Bioresource Technol.* 96, 1537-1543.
- 9 [18] Kedziora, P., Le Thanh, J., Lewandowicz, G., et al., 2006. An attempt to
10 application of continuous recycle membrane reactor for hydrolysis of
11 oxidised derivatives of potato starch. *J Membrane Sci.* 282, 14-20.
- 12 [19] Li, D., Zhou, T., Chen, L., et al., 2009. Using porphyritic andesite as a
13 new additive for improving hydrolysis and acidogenesis of solid organic
14 wastes. *Bioresource Technol.* 100, 5594-5599.
- 15 [20] Lin, S. H. and Juang, R. S., 2009. Adsorption of phenol and its
16 derivatives from water using synthetic resins and low-cost natural
17 adsorbents: A review. *J Environ Manage.* 90, 1336-1349.
- 18 [21] Müller, P., Seeger, M. and Tomas, J., 2013. Compression and breakage
19 behavior of γ -Al₂O₃ granules. *Powder Technol.* 237.
- 20 [22] McIntosh, S. and Vancov, T., 2011. Optimisation of dilute alkaline
21 pretreatment for enzymatic saccharification of wheat straw. *Biomass*

- 1 Bioenerg. 35, 3094-3103.
- 2 [23] Pyrzynska, K. and Bystrzejewski, M., 2010. Comparative study of heavy
3 metal ions sorption onto activated carbon, carbon nanotubes, and
4 carbon-encapsulated magnetic nanoparticles. *Colloid Surface A.* 362,
5 102-109.
- 6 [24] Resch, C., Worl, A., Waltenberger, R., et al., 2011. Enhancement options
7 for the utilisation of nitrogen rich animal by-products in anaerobic
8 digestion. *Bioresource Technol.* 102, 2503-2510.
- 9 [25] Seehra, M. S., Akkineni, L. P., Yalamanchi, M., et al., 2012. Structural
10 characteristics of nanoparticles produced by hydrothermal pretreatment of
11 cellulose and their applications for electrochemical hydrogen generation.
12 *Int J Hydrogen Energ.* 37, 9514-9523.
- 13 [26] Shahriari, H., Warith, M., Hamoda, M., et al., 2012. Effect of leachate
14 recirculation on mesophilic anaerobic digestion of food waste. *Waste
15 Manage.* 32, 400-403.
- 16 [27] Sponza, D. T. and Agdag, O. N., 2004. Impact of leachate recirculation
17 and recirculation volume on stabilization of municipal solid wastes in
18 simulated anaerobic bioreactors. *Process Biochem.* 39, 2157-2165.
- 19 [28] Veeken, A. and Hamelers, B., 1999. Effect of temperature on hydrolysis
20 rates of selected biowaste components. *Bioresource Technol.* 69, 249-254.
- 21 [29] Wang, Q. H., Kuninobu, M., Ogawa, H. I., et al., 1999. Degradation of

1 volatile fatty acids in highly efficient anaerobic digestion. *Biomass*
2 *Bioenerg.* 16, 407-416.

3 [30] Wang, Q. H., Yang, Y. N., Yu, C., et al., 2011. Study on a fixed zeolite
4 bioreactor for anaerobic digestion of ammonium-rich swine wastes.
5 *Bioresource Technol.* 102, 7064-7068.

6 [31] Weast, R. C., 1981. *Handbook of Chemistry and Physics*, 61st ed. Boca
7 Raton, CRC press.

8 [32] Yi, S. S., Lu, Y. C. and Luo, G. S., 2008. Separation and concentration of
9 lactic acid by electro-electrodialysis. *Sep Purif Technol.* 60, 308-314.

10 [33] Zhang, D. Q., He, P. J. and Shao, L. M., 2009. Effect of pH-neutralized
11 leachate recirculation on a combined hydrolytic-aerobic biopretreatment
12 for municipal solid waste. *Bioresource Technol.* 100, 3848-3854.

13 [34] Zhang, Y. and Banks, C. J., 2013. Impact of different particle size
14 distributions on anaerobic digestion of the organic fraction of municipal
15 solid waste. *Waste Manage.* 33, 297-307.

16 [35] Zhou, Y., Zhang, Z., Nakamoto, T., et al., 2011. Influence of
17 substrate-to-inoculum ratio on the batch anaerobic digestion of bean curd
18 refuse-okara under mesophilic conditions. *Biomass Bioenerg.* 35,
19 3251-3256.

20
21