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Digestibility Improvement of Sorted Waste with Alkaline Hydrothermal Pretreatment*

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Abstract: The digestibility of sorted municipal solid waste (MSW) is often limited by the high content of structured green waste. The objectives of this study are to investigate the effect of alkaline hydrothermal pretreatment on the anaerobic digestion of sorted waste and to analyze the biogas production of different parts of the waste. The waste was hydrothermally pretreated in a dilute alkali solution. The hydrolysis product was then incubated in a 500 mL saline bottle to determine the biochemical methane potential (BMP) under mesophilic anaerobic conditions. The optimum hydrothermal condition was 170℃ at 4 g NaOH/ 100 g solid for one hour. The concentration of chemical oxygen demand (COD) was 13 936 mg/L and the methane yield was 164 mL/g volatile solid (VS) for 6 days incubation at the optimum conditions. The biogas production was increased more than 50% over the control, with the methane conversion ratio on a carbon basis enhanced to 30.6%. The organic part of the sorted waste was mainly kitchen garbage and leaves. Model kitchen garbage completely liquified at 130℃ for one hour had a methane yield of 276 mL/g VS. The alkali addition slightly enhanced the hydrolyzation rate and methane yield. The biogas potential of leaves was improved by pre-treatment at above 150℃ under alkaline conditions.

Key words: mechanically-sorted waste; anaerobic digestion; biochemical methane potential; kitchen garbage; hydrothermal liquidization; green waste; alkaline hydrolysis

Introduction

According to the Chinese Statistical Yearbook[1], the total weight of collected and transported municipal solid waste surpassed 0.155 billion tons in 2006. This tremendous quantity of municipal solid waste (MSW), together with organics from wastewater treatment and agriculture, are mostly disposed of insanitary land-fills, which produce methane (an explosive, "green house" gas) and toxic leachate over long periods of time.

Anaerobic digestion of the putrescible fraction of municipal solid waste (PFMSW), which accounts for nearly 40% of the MSW, has been intensively studied for years. The total treatment capacity for solid waste organics in Europe, excluding the tonnage used for sewage sludge and manures, increased from 122 000 tons per year in 1990 to 1 037 000 tons available or under construction by 2000 in 53 plants across Europe, an increase of 750%[2]. Anaerobic digestion is generally considered to be a four-step process: hydrolysis, fermentation, acetogenesis, and methanogenesis. Hydrolysis, the first step, is the limited step in the process, especially for green wastes that are composed of cellulosic and lignocellulosic materials.

High temperature alkaline treatment of sewage sludge not only enhanced the hydrolysis but also improved the dewatering properties of the remaining

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solids by destroying the bacteria cell walls[3]. The advantages of thermo-alkaline hydrolysis of cellulosic and lignocellulosic materials have been recognized for a long time. Many researchers have investigated thermochemical pretreatment to enhance the hydrolysis of cellulose[4,5] and biowaste[6,7]. The molecular weight is significantly reduced when the cellulose is boiled with dilute sodium hydroxide, a problem observed many years ago with respect to the scouring of cotton for textile use[8]. However, little is known about the thermochemical pretreatment of mechanically-sorted waste. The purpose of this study is to improve the anaerobic digestion of medium-size sorted waste from MSW, which has a high organic content, through thermochemical pretreatment. The study investigates the effects of operating parameters, the temperature, reaction time, and alkali dose, on the organics solubilization and the anaerobic biodegradability. The leaves and model kitchen garbage were separately hydrolyzed to investigate which part of the waste contributes the most to gas generation after pretreatment.

Table 1 Characteristics of the sorted waste, leaves, and model kitchen garbage

	Mass balance (%)		
	Sorted waste	Leaves	Model kitchen garbage
Moisture	51.0	10.5	88.0
Volatile solid/dry matter	55.9	79.4	92.1
Ash/dry matter	44.1	20.6	7.9
Elemental composition of dry matter			
Carbon	28.5	40.3	46.2
Hydrogen	3.7	5.7	4.8
Nitrogen	1.2	1.4	3.1

Table 2 Main components of aspen leaves (on an oven-dried basis) (%)

Cellulose	Hemicellulose	Lignin	Others	Ash
30.4	15.5	14.7	18.8	20.6

1 Methods

1.1 Substrate

Three kinds of substrates were used in the experiments. Mechanically-sorted municipal solid waste was taken from the Majialou Screening Center, with the medium size waste, 15-60 mm, chosen for its high organic content. The waste was transported to the Nangong Compost Plant in Beijing after screening to produce refuse derived fertilizer. The composition of the waste changes seasonally, being characterized by fruit waste in the summer, green waste in the fall, and ash in the winter and spring. The organic part of the selected waste is mainly kitchen garbage (about 30 wt.%) and leaves (about 10 wt.%). The waste characteristics are listed in Table 1. The second substrate was model kitchen garbage which consisted of boiled rice (49.1 wt.%), cabbage (32.9 wt.%), meat (14.0 wt.%), and bean curd (4.0 wt.%). The third type was dry fallen aspen leaves (Table 2). All the waste was smashed to the proper size (5-10 mm) and individually mixed.

1.2 Thermochemical hydrolysis

Experiments were run at temperatures ranging from 90℃ to 190℃ for 60 min. After that, the tests were based on an orthogonal experimental design method. The waste was hydrothermally pretreated with sodium hydroxide, 1-4 g / 100 g solid, at 130-170℃ with a retention time of 30-90 min. The sample (10 g) and distilled water (100 mL) were placed into a 700 mL stainless steel container after purging with nitrogen gas and then placed in a 5 L autoclave. The autoclave was heated with an electric furnace to the set temperature. When the reaction was finished, liquid fraction was centrifuged at 5000 r/min for 5 min and the supernate was taken as the sample (5 mL). The hydrolysate (liquid and solid) was transferred to a saline bottle for digestion. To compare the results, the volatile solid (VS)/water ratio was kept constant for the hydrolysis of all the selected waste.

1.3 BMP assays

The seed sludge for anaerobic digestion was obtained from a wastewater treatment plant in Beijing. Each sample was added to the seed sludge and incubated in a 500 mL saline bottle at 35℃ in a water bath after purging with nitrogen gas. The food to microorganism ratio was 0.45-0.50, and the pH of the feed sludge was adjusted to 7±0.1 with sodium hydroxide. Blank sludge was incubated to correct the results and raw material was fed as a control.

1.4 Analytical measurements

The elemental composition (carbon, hydrogen, and nitrogen) of the waste was determined using a CE-440 elemental analyzer (EAI Company, USA). The cellulose and hemicellulose contents were measured using acid hydrolysis with the lignin content measured by the Klason method. The moisture content was measured from the difference between the sample weight prior to and after heating at 105℃ for 24 h. The VS content and the ash content were determined from the difference between the sample weight prior to and after heating at 600℃ for 2 h. The pH was measured by a pH meter. The chemical oxygen demand (COD) was determined by the potassium dichromate-ferrous ammonium sulfate method in accordance with standard methods. The total organic carbon (TOC) was measured by a total organic carbon analyzer (Shimadzu, Model TOC-5000A). The gas production yield from the bioreactor was measured in terms of the displacement of a saturated sodium chloride solution. The biogas composition was determined by an Infrared Gas Analyzer (Huayun company, error <0.1%).

2 Results and Discussion

The raw material showed poor anaerobic biodegradability. The hydrothermal product of the MSW was digested quickly with favorable biogas production. The hydrolysate had a beige color, which was a function of the temperature and alkali concentration.

2.1 Effect of temperature on COD and methane production

Temperature has an important effect on the hydrolysis of the MSW material. Low temperatures do not significantly enhance the solubilization, while high temperatures require too much energy. The effects of pretreatment temperature on the particulate COD solubilization are presented in Fig. 1. The concentration of COD increased from 1812 mg/L at 90℃ to 7549 mg/L at 190℃. For temperatures between 90℃ and 150℃, the curve is essentially linear and increasing rapidly. The organic part of the MSW waste is split up in the first step into short-chain fragments that are easily dissolved, which also facilitates the digestion step. The effects of temperature on the specific methane yield (amount of methane produced per amount of VS added) are shown in Fig. 2. Significant methane gain was observed at temperatures above 130℃. The hydrolysate at 90℃ showed similar biodegradation characteristics as the raw material.

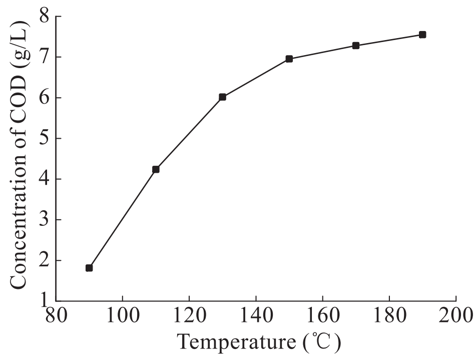

Fig. 1 Influence of temperature on the organics solubilization

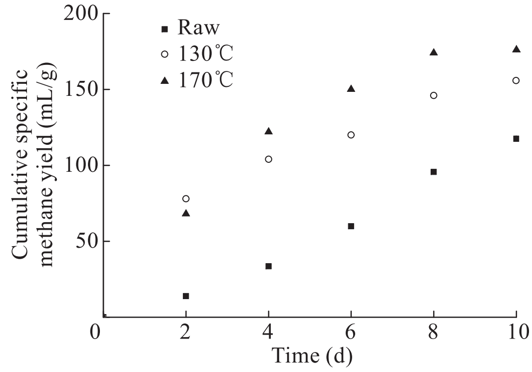

Fig. 2 Methane yield of hydrolysate at different temperatures

Several previous studies have reported high biogas yield of MSW, depending on the waste composition. The methane yield of biomass waste is significantly lower than that of food waste, as will be discussed later. The carbon ratio and the biodegradability of waste are the most important factors influencing the biogas yield.

2.2 Effect of alkali dose on COD and methane yield

Orthogonal experiments were designed for the heterogeneity of the selected waste. The concentration of COD increased with the addition of sodium hydroxide (Fig. 3). The data are the means of the COD and methane yields at various temperatures. The mean concentration of COD increased from 5931 mg/L at 1 g NaOH/ 100 g solid to 12 007 mg/L at 4 g NaOH/ 100 g solid. As shown in Fig. 3, the methane production over 6 days digestion gradually increased for these alkali doses. The alkali dose has the largest effect on the hydrolysis, with the biogas yield increased by more than 50% over the control at 4 g NaOH/ 100 g solid. Further organics solubilization could be achieved at higher alkali concentration, but the methane production was inhibited by the high alkalinity.

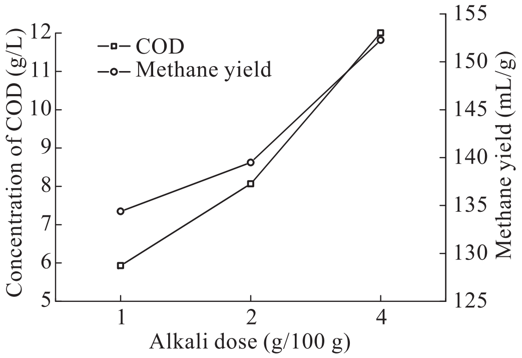

Fig. 3 Effect of alkali dose on COD and methane yield

The pH decreased followed by the increase of temperature during the hydrothermal reaction of the organic material. The lowest pH was 4.76 at 170℃. The optimum pH range for digestion, however, was found to be 6.5-7.5. The alkali buffer could be added to adjust pH for anaerobic digestion. Sodium hydroxide could also serve as a catalyst for the hydrothermal reaction. The alkaline degradation of carbohydrates has been intensively studied[9,10].

2.3 Liquidization and digestion of model kitchen garbage and leaves

Kitchen garbage can be readily hydrolyzed and biodegraded. The model kitchen garbage which was completely liquidized at 130℃ for one hour, had a concentration of COD of 12 412 mg/L. Addition of the alkali slightly enhanced the hydrolyzation rate. The methane yields of the kitchen garbage are shown in Fig. 4. The methane yield of the untreated material with 4 days digestion was 102 mL/g. A significant part of the garbage was still in its original shape after digestion. This methane yield was quite low due to the inefficient

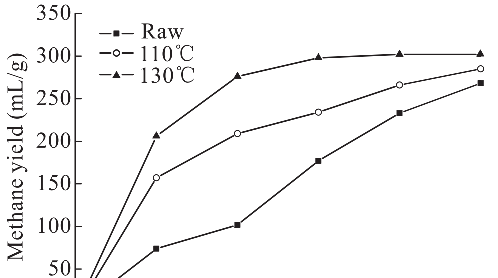

Fig. 4 Methane yield of kitchen garbage liquified at different temperatures

liquidization, so that only the surface of the garbage was utilized by the anaerobic microorganisms without mixing. Liquidized garbage at 130℃ had an excellent methane yield of 276 mL/g VS, the highest yield in the batch experiments.

Although the hydrolysis rate of the kitchen garbage was found at lower temperatures, the biogas production from the leaves was only measured at temperatures above 150℃ and a sodium hydroxide concentration of 0.05 mol/L. The concentration of COD was 12 733 mg/L (TOC 8021 mg/L) at 150℃ after hydrothermal pretreatment of the leaves, but the methane yield was still essentially zero after 20-day digestion in the batch system. The digestion performance under alkaline condition was shown in Fig. 5. The hydrolysates at 150℃ and 170℃ display similar methane potentials. Leaves are a cellulosic biowaste, and the hydrolysis of cellulose is caused by the dissolution of short-chain fragment detached from the reducing ends of the cellulose molecules (generally known as "peeling" or "unzipping")[11]. Much greater weight losses are obtained by scission at temperatures above 170℃ than by alkaline degradation at lower temperatures, although alkaline degradation of amorphous hydrocellulose has been observed at temperatures lower than 100℃[12]. Although the solubilization of the organics occurred as soon as the hydrothermal processes began, methane production was only observed at higher temperatures above 150℃.

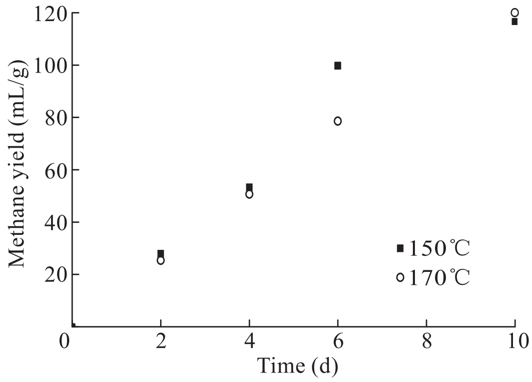

Fig. 5 Biogas production of leaves hydrolysate with alkaline conditions

Lissens et al.[13] enhanced the anaerobic biodegradability and methane yield of various biowastes (food waste, yard waste, and digested biowaste already treated in a full-scale biogas plant) by using thermal wet oxidation. Extrapolation of the experimental results to a full-scale DRANCO plant (50 000 t of organic waste per year) in Belgium must balance the gain in methane yield expressed as the electrical power produced against the estimated costs of the wet oxidation pretreatment of the raw waste or intermediate treatment of primary digested waste.

3 Conclusions

Hydrothermal alkaline pretreatment is an effective method to enhance solubilization of organics and hydrolysis of polymers for anaerobic digestion. The optimum reaction conditions obtained in the study were 170℃ at a dose of 4 g NaOH/ 100 g solid for one hour. The concentration of COD was then 13 936 mg/L and the methane yield was 164 mL/g VS at the optimal conditions. Methane production during 6-day digestion was greatly increased at liquidization temperatures above 130℃. The alkali dose was found to be the most important factor affecting the hydrolysis and methane production of sorted waste in orthogonal tests.

The specific methane yield of mechanically sorted MSW is much lower than the model kitchen garbage. The low methane yield of green waste and other materials in the sorted waste result in the low biogas production. Alkali can be added to enhance the hydrolysis and methane production, but the effect of accumulating sodium cation on the methane yield needs to be investigated for use in continuous digestion systems.

The biogas yield of the liquidized model kitchen garbage at 130℃ was higher than that of the liquidized sorted waste and the leaves. The methane conversion ratios on a carbon basis of 31.7% for the model garbage were higher than that of 18.2% for sorted waste and leaves for 6 days of incubation at the same conditions. The biogas yield of leaves was only significant after pretreatment at temperature above 150℃ in an alkaline solution. Microbial hydrolysis of natural lignocellulose is a slow and difficult process due to the chemical and physical construction of lignocellulose. Thermochemical pretreatment, therefore, is necessary to improve the energy production from the biomass in waste. The COD and TOC, which were thought to describe the hydrolysis rate, could not be used to accurately determine the methane potential. Hydrothermal alkaline pretreatment can be used to shorten the digestion period of both kitchen garbage and green waste. The critical temperature, however, differs for the different wastes. Degradation of the kitchen waste contributes most to the methane production. The production increase after pretreatment of the MSW is partially due to the digestion of the green waste.

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