Alkaline subcritical-water treatment and alkaline heat treatment for the increase in biodegradability of newsprint waste

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Abstract This work describes two alkaline semicontinuous processes for the conversion of refractory organic materials into biodegradable substances. Newsprint was used as a lignocellulosic waste. Methane conversion efficiencies and cellulose removals were investigated for the two following processes: alkaline subcritical-water treatment (ASWT) coupled with methane fermentation and alkaline heat treatment (newsprint heated with steam in an autoclave; AHT) coupled with methane fermentation with a neutral subcritical-water treatment (NSWT) recycle. Results showed that for ASWT coupled with methane fermentation higher methane conversion efficiencies and higher cellulose removals were achieved as HRT increased. At HRT = 20 days, average CH_4 conversion efficiency and average cellulose removal reached 26% and 44%, respectively. After a final HRT of 40 days, average CH_4 conversion efficiency and average cellulose removal reached 50% and 60%, respectively. On the other hand, for AHT coupled with methane fermentation, methane conversion efficiencies did not show a greater improvement using this pretreatment process. Average conversion reached 9% with an average cellulose removal of 20%. In order to improve the yield of the reactor, approximately one-third of the effluent was recycled using NSWT (150°C; neutral pH). Methane conversion efficiency of this process increased as more recycles were performed. For the fifth operation, the total average methane conversion efficiency was 44% with a total average cellulose removal of 55%.

Keywords Alkaline pretreatment; cellulose degradation; heterocyclic compound; methane fermentation; newsprint biodegradability; phenolic derivative

Introduction

In Japan, new technological efforts are necessary to reduce the volume of the organic fraction of solid waste and to be able to apply treatment technologies or to find viable policies for the renewable handling of municipal and industrial wastes. A great variety of usable biological and thermal processes are available for the conversion of biomass to energy resource. Anaerobic digestion is a useful process that can recover renewable energy from biowaste (Noike, 2001).

In general, thermal treatments are applied to organic wastes that are difficult to degrade biologically with the objective to soften them with the high temperatures and to make them accessible to later treatments. They are also to be used to hydrolyze and generate organic soluble compounds for later fermentation technologies. Subcritical-water treatment or wet oxidation is a subcritical physico-chemical process in which oxygen from air allows oxidization of organic substances. In lignocellulosic materials, this process solubilizes or oxidizes holocellulose and lignin to CO_2, H_2O, organic acids and several soluble compounds.

The objective of performing this work was to increase the biodegradability and hence methane production from newsprint as a waste refractive organic material by thermal pretreatments.

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Methods

Material for ASWT and AHT. Newsprint in Japan is composed of cellulose (54%) and lignin (17%) (Fox, 2000).

Procedures. Using a blender machine hand shredded newsprint was added together with sodium carbonate (Na_2CO_3) to 2-litre of distilled water. Alkali was added in order to avoid the natural acidification of both processes. Initial and final pH values are shown in Table 1. For the subcritical-water treatment process, pressurized air was fed from a compressor and during the tests, the vessel internal pressure was maintained above the vapor pressure of water in order to ensure that the reaction would only occur in the liquid phase. For the heat treatment process, an autoclave model Yamato SP-50 was filled with the newsprint alkaline solution and pressurized at 1.5 kg/cm^2 and heated at 128°C for 1 hr.

Semi-continuous experiment design. Two 4 litre volume laboratory-scale semicontinuous reactors were operated in an environmental box maintained at 35°C. The reactors were fed with the newsprint pretreated by alkaline subcritical-water treatment and alkaline heat treatment; loading rates are shown in Table 2. The flowsheets of the two processes are shown in Figure 1.

Both processes are independent and each one possesses a methanogenic reactor Reactor-1 (R-1) and Reactor-2 (R-2). R-1 treats newsprint waste pretreated thermically by alkaline subcritical-water at different hydraulic retention times (20 to 40 days). R-2 treats alkaline heat-treated newsprint at a hydraulic retention time (HRT) of 20 days. Processes were compared for methane production and newsprint biodegradabilities. In a further step, the incidence of a recycle stream treated with subcritical water at 150°C on R-2 was investigated.

Substrate composition and procedure. The composition of the phosphate–vitamin–mineral solution was adopted from Khan (1977). One litre medium solution was added to two litre of pretreated newsprint to form three litre of substrate solution. The substrate solution was semicontinuously added (100 ml every day) by a roller pump and reactor contents completely mixed with a magnetic stirrer. The reactor effluents were removed manually every day and checked weekly for fiber, COD, protein, and every two weeks for cellulose, lignin, phenol derivatives and heterocyclic compounds. The generated biogas was collected using

Table 1 Pretreatment conditions and pH behavior for both processes

T°C	Na_2CO_3 (g/l)	Newsprint (g/l)	Pressure (kg/cm^2)	Reaction time (min)	pH	
					Before treatment	After treatment
190	5	20	40.9	60	11.0	6.97
128	5	20	1.50	60	11.0	10.5

Table 2 Loading rates for R-1 and R-2

Parameter	Loading rates(kg/m^{3}reactor-day)					
	R-1					R-2
	HRT:20	HRT:25	HRT:30	HRT:35	HRT:40	HRT:20
Wet oxidized newsprint	0.428	0.342	0.285	0.245	0.214	0.578
Cellulose	0.290	0.232	0.193	0.165	0.145	0.320
Lignin	0.008	0.007	0.005	0.005	0.004	0.089
TCOD	0.627	0.502	0.418	0.359	0.314	0.786

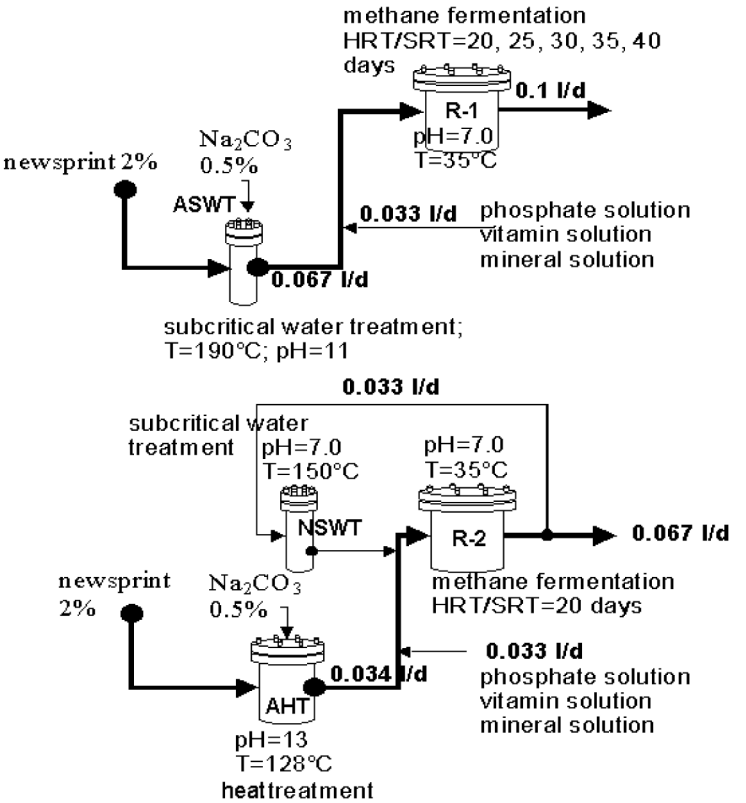

Figure 1 Pretreatments for newsprint waste. Alkaline subcritical-water treatment (ASWT) and alkaline heat treatment (AHT) combined with neutral subcritical-water treatment (NSWT)

a measuring cylinder by displacement of this in acidified water to prevent the carbon dioxide dissolving.

Analytical methods. Lignin contents were determined by the Klason 72% sulfuric acid digestion procedure. Cellulose concentrations were determined according to the Updegraff (1969) colorimetric method. COD and suspended solids (SS) concentration were determined according to the procedures described in the Standard Methods (APHA, 1995). Total and soluble protein was measured according to the Folin phenol reagent (Lowry *et al.*, 1965).

Furfural, hydroxymethylfurfural (HMF), phenolic compounds or soluble lignin derivatives were analyzed at 55°C using an Aminex HPX-87H column (60°C). Furans (F) were defined as the arithmetic sum of furfural and HMF. Total phenolics (TP) were defined as the sum of individual peaks eluting in the regions corresponding to the compounds being determined. These compounds were separated using the same mobile phase as for furfural and HMF at an elution rate of 0.35 ml/min.

Methane and carbon dioxide were measured with a gas chromatograph (GC, Shimadzu 8A) equipped with a thermal conductivity detector (TCD) and 2-m stainless column packed with Porapak T (50/80 mesh). Helium at a flow rate of 30 (mL/min) was used as carrier gas.

Results and discussion

Lignocellulose biodegradability can be improved by alkaline thermal treatments (Fox *et al.*, 2001). The basic condition for an effective pretreatment process is to remove the

refractory fraction (lignin) and to leave stable or free render the holocellulose fraction for biological degradation.

In this study, alkaline conditions (Na_2CO_3) were selected since they had already produced high methane conversion efficiencies in batch reactors. Also, the effectiveness of the addition of alkalinity showed that high solubilization ratios for ASWT were achieved compared to NSWT at the same temperatures.

As an alternative pretreatment to remove and dissolve lignin, an alkaline newsprint solution was heated with steam in an autoclave (initial conditions are shown in Table 1). Solubilization ratios for ASWT and AHT were 0.26 and 0.10, respectively. Likewise, for ASWT and AHT, approximately 93% and 21% lignin was removed, respectively. Although the degradation of cellulose for these two pretreatments shows similar values (20%-ASWT and 11%-AHT), lignin removal showed a notable difference. From the point of view of the effectiveness of the pretreatments, the ASWT is more favorable since it degrades a greater amount of lignin leaving an amount of cellulose for the later anaerobic treatment similar to AHT. The nature of the soluble fraction produced in ASWT and AHT had a phenolic and heterocyclic characteristic. Monomeric phenolic compounds are formed from lignin under alkaline and heat conditions (McCarty *et al.*, 1976).

In previous alkaline subcritical-water treatment batch tests, newsprint produced several lignin derivatives identified as hydroquinone, vanillyl alcohol, 4-methylcatechol, p-hydroxybenzaldehyde, vanillin and syringaldehyde. Posterior batch methane fermentation tests elucidated that almost complete degradation of these compounds was achieved (Noike and Niigata Eng., 2001).

On the other hand, heterocyclic compounds like furfural and 5-hydroxymethylfurfural (HMF) were formed during the thermal decomposition of cellulose and hemicellulose in an acid medium (Fox and Noike, submitted). These compounds were less expected to be produced during ASWT and AHT. Indeed, the production of furan compounds was approximately three times greater for the NSWT than for the alkaline process (ASWT). Concentration of furans for subcritical-water treatment and heat treatment are shown in Table 3.

Methane conversion efficiencies. In order to evaluate the effect of the thermal treatments on the biodegradability of newsprint, R-1 has been operated from an initial HRT of 20 days to a final HRT of 40 days. R-2 was operated with a constant HRT of 20 days. The digesters were initially incubated with digested sludge from an anaerobic reactor treating municipal wastewater.

In order to ensure certain stability in methane production in R-1 and to compare methane conversion efficiencies in its different HRTs, periods of more than 50 days were considered after every period of increase of hydraulic volume. Figure 2 shows the average values for methane conversion efficiency, percentage of methane in biogas and methane production rate in every period of HRT. As shown here, the optimization of R-1 depended upon the increase in the HRT. Analyzing these semicontinuous results with those obtained in previous batch experiments, it can be mentioned that batch tests of newsprint without thermal pretreatment gave methane conversion efficiencies of 36% in a period of 30 days. Using

Table 3 Production of furans and soluble lignin derivatives

Process	T (°C)	Furans (F) (g/l) (280 nm)	Total phenolics (TP) (g/l) (210 nm)
ASWT	190	0.007	0.451
AHT	128	0.018	0.008
NSWT	150	0.025	0.352

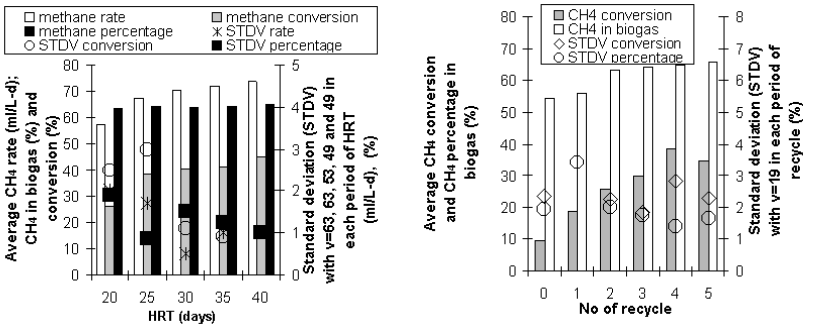

Figure 2 Average methane rate, methane in biogas, and conversion eff. in R-1 at several HRT. Average methane conversion eff. and methane in biogas in R-2 at (0): AHT coupled with methane fermentation and (1–5): AHT coupled with methane fermentation with NSWT

thermal pretreatments, the highest conversion efficiencies were obtained in AWST at 190°C (75%) followed by neutral subcritical-water treatment (NSWT) (59%) and nitrogen subcritical-water treatment (NiSWT) (50%). AWST at 190°C overestimated the value of the methane conversion efficiency in R-1 at HRT = 40 days (45%). Nevertheless, a conversion of 45% is higher than the value obtained by newsprint without pretreatment (36%). Moreover, results from previous works on semicontinuous conversions of newsprint without pretreatment were of the order of 15%. If this fact is taken into account, the renewable energy value for methane production of newspaper increases almost 4.5 times with this alkaline pretreatment.

Regarding the pretreatment of newsprint with AHT coupled with R-2 and its recycling operation using NSWT, it can be mentioned that there was a notorious change in the methane conversion efficiency. Figure 2 shows this change before recycling and during the recycling operations. In a first stage, the alkaline solution pretreated with steam or preheated in an autoclave with water at 128°C was treated anaerobically in R-2. For comparison purposes with the second or later stage of recycling, a period of 50 days for the evaluation of methane conversion was considered 100 days after start-up. An average value of approximately 10% was found for methane conversion efficiency; very low if AHT was applied as a pretreatment technology to improve biodegradation of newsprint. Probably, a hydraulic retention time of 20 days is very short to allow a suitable degradation or the temperature of 128°C is insufficient to obtain some degree of solubilization and softening of the fiber of newsprint. Starting from the 150 days, R-2 was operated with a recycle at 150°C-30 bar with one third of the effluent (Figure 1). Each recycling from the first to the fifth operation lasted between 20 and 25 days. The average methane conversion efficiency in every period is shown in Figure 2. Conversion efficiency increased gradually up to 45% in the fourth operation and decreased in the fifth operation to approximately 35%. It seems reasonable to suppose that methane production was improved with the operation of NSWT. With the purpose of hydrolyzing the newsprint fiber being recycled a low temperature in NSWT was used. Solubilization ratios through the recycling operations varied between 3% and 6%. It is believed that the effect of recycling on R-2 caused some degree of improvement in methane production. Indeed, the HRT/SRT for the recycled flow increases to 60 days. This effect and the one of solubilizing occupying NSWT made this process attractive to ASWT coupled with R-1. For R-1, methane conversion efficiencies during HRT = 20, 25, 30 and 35 fluctuated between 25% and 40%, which gives similar results in R-2 for the fourth and fifth operation of recycling (35% and 39%). However, R-1 with a HRT of 40 days showed a conversion near 45%. If R-2 is to be optimized, conditions for NSWT should be more oxidative; this is, increasing the temperature to more than 190°C. In these conditions a

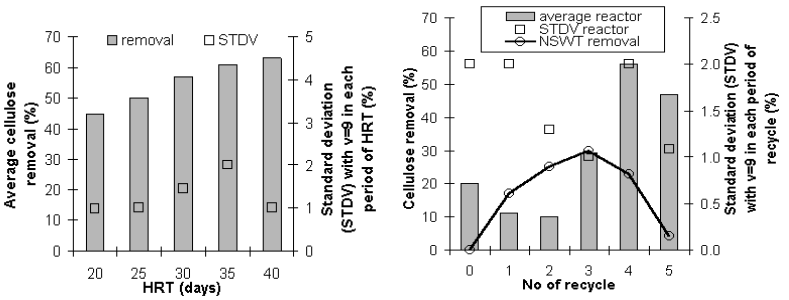

Figure 3 Average cellulose removal in R-1 at several HRT. Average cellulose removal in R-2 at (0): AHT coupled with methane fermentation and (1–5): AHT coupled with methane fermentation with NSWT and cellulose removal in NSWT

solubilization rate of 24% is produced (Fox and Noike, submitted). A disadvantage of this process is that the fraction of the effluent that is not recycled does not receive the benefit of NSWT.

Cellulose removal efficiencies. Results are shown in Figure 3. Average cellulose removals in R-1 increased with greater hydraulic retention time (HRT). A stable removal of cellulose was observed in every period of HRT. Thus, standard deviations (STDV) values varied between 1% and 2%. A maximum cellulose removal of approximately 60% was reached in the period of HRT = 40 days. The incidence of the HRT in cellulose removal shows a certain linear dependency in periods 20, 25 and 30 days. In periods 30, 35 and 40 days, this incidence becomes nonlinear and reveals that cellulose removal could, with HRT greater than 40 days, increase only marginally. Probably, it would be not practical to increase the HRT more than 40 days. Changes in the HRT may not show a substantial change in the cellulose removal. The average removals of cellulose in R-2 in each operation of recycle are shown in Figure 3. No of recycles = 0 represents the process without NSWT and numbers up to 5 represents the recycling operations using NSWT. It is observed that in recycles 1 and 2, the removal average was lower compared to the process without NSWT. This depression could be caused by the adverse effect of NSWT in the reactor. Phenolic compounds and furans are produced in this type of process. Although these soluble compounds may affect the bacterial behavior, these can be almost completely degraded. Probably, to start cellulose degradation, some kinds of acclimatization to NSWT should occur before the real potential of degradation started. The trend of cellulose removal in NSWT showed a maximum in the third operation and minimum in the fifth operation; approximately 30% and 5% of cellulose were removed, respectively. On the other hand, analyzing the removals of TCOD in NSWT, it was observed that these values reached 5%, 15%, 17% and 1% in the recycles from 2 to 5. The low COD removal rates may indicate that NSWT did not have an oxidative role. It is believed that the cellulose removed in NSWT was transformed mainly into soluble compounds.

Lignin derivatives and furans degradation. Through ASWT and AHT, some of the refractory lignin in newsprint was converted into several aromatic or phenolic-like compounds. Some were identified as vanillin, vanillyl alcohol, 4-methylcatechol, p-hydroxybenzaldehyde and syringaldehyde. Likewise, cellulose and hemicellulose solubilization generated heterocyclic compounds identified as furfural and 5-hydroxymethylfurfural (HMF). Total phenolics and furans were considered as the sum of the aromatic compounds previously mentioned, and the sum of furfural and HMF, respectively (Table 3). The ASWT process

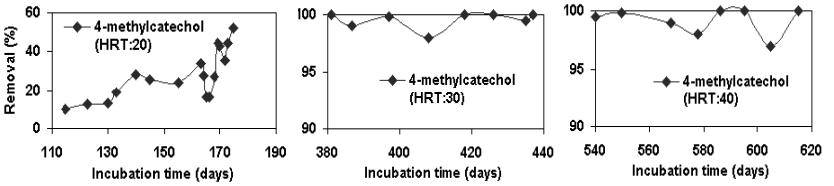

Figure 4 4-methylcatechol removal trends in R-1

coupled with R-1 showed nearly 100% degradation of these aromatic and furan compounds. Only 4-methylcatechol showed a strong refractory characteristic. The removal varied between 15% and 97% after 600 days of incubation (see Figure 4).

Conclusions

Although newsprint waste can be recycled 100% as raw material for papermaking it can only be used up to 4 times since its fiber loses its structural strength. That fraction of paper that is not recycled must be incinerated and the ashes destined for landfilling. Viable alternatives for the renewable recovery of energy are the processes presented in this work. Two alkaline thermal treatments were investigated for their effectiveness in converting refractory newsprint by semicontinuous digesters into methane gas. ASWT solubilization ratio was about 0.26 which means that 26% of the initial total COD was converted into soluble compounds. AHT solubilized only 10% and its performance destroying lignin was considerably low compared with ASWT. By recycling one third of the effluent using NSWT solubility in the recycle stream increased up to 6%.

In the anaerobiological treatments, 35%–45% methane gas was recovered from the newsprint waste. Likewise, cellulose as the main carbohydrate contributor in newsprint waste was anaerobically degraded up to 60%. Phenolic and heterocyclic compounds were completely degraded. Among these compounds, 4-methylcatechol showed a strong refractory characteristic. Acclimation occurred approximately after 200 days of semicontinuous incubation.

Finally, further work is being performed in order to recover methane gas from the remaining COD by co-digestion experiments using cattle slurry.

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