Subcritical Solutions to Enhance the Recovery of Renewable Methane from Paper Waste(亜臨界域における可溶化による紙類のメタン発酵に関する研究)

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論文内容要旨

Introduction and objectives

The amount of municipal and industrial waste is increasing year by year. As a result, existing landfill sites are rapidly running out of space and secondary pollution is becoming a serious problem. Recycling, incineration and other pre-treatment and treatment processes are necessary to reduce the volume of municipal and industrial solid wastes. Although, the cost of recycling or zero waste operations is becoming competitive with that of such traditional waste disposal methods as landfilling and incineration, recycling must be improved through technological developments and for papers, by a social agreement to prefer paper made with recycled papers. The utilization of recycled fibers in Japan is about 53% and is expected to increase up to 55%. Almost 90% of raw materials for paperboard production are derived from recycled fibers. However, incineration processes such as a disposal route are applied to reduce those fractions of discarded waste paper which are not recyclable anymore. The ashes generated are then filled into a landfill.
New technological efforts are necessary to reduce the volume of the organic fraction of solid waste. A variety of biological and thermal processes are available for the conversion of biomass to energy resource (Jerger et al. 1982), and research on mesophilic anaerobic bioconversion of agricultural and wood residues has contributed to much of the advancement in the understanding of applying bioconversion to lignocellulosic wastes (Clarkson and Xiao, 1999). Crystallinity and lignification are by far the most important factors of the susceptibility of cellulosic materials to enzymatic and bacterial conversions (Cowling and Kirk, 1976). Therefore, enhancement of the total accessible surface area of cellulosic substrates can contribute to creation of more effective pretreatments for lignocellulosic materials.
The process in which organic material is oxidized with gaseous oxygen of air in water at low temperature and pressure is called 'subcritical water oxidation'. In the case of lignocellulosic materials, this process disrupts and solubilizes cellulose and lignin to intermediate products (Fox and Noike, 2002). The objectives of this work were: (1) to investigate the anaerobic biodegradability of paper waste i.e.: toilet paper and newsprint, in terms of methane production potential and cellulose degradabilities; (2) to investigate subcritical solutions (subcritical water treatment; SWT) as a thermal pretreatment process for paper waste solubilization; (3) to evaluate this pretreatment step in terms of anaerobic biodegradability and conclude which temperature of pretreatment is the optimum; (4) to investigate and to assess the technical feasibility of two semicontinuos treatment systems to treat newsprint waste; (5) to investigate the viability of co-digestion of the effluent of the semicontinuos process with cattle manure, and (6) recommend and propose a general flowsheet diagram process for the recovery of renewable methane from lignocellulosic waste.

Background

Anaerobic digestion of municipal solid waste is a controlled process of microbial decomposition where, under anaerobic conditions, a consortium of microorganisms convert organic matter into methane, carbon dioxide, inorganic nutrients, and humus. For the final production of biogas the digestion processes involves numerous interactions between several metabolic groups, namely hydrolytic fermentative bacteria, proton-reducing acetogenic bacteria, aceticlastic methanogens, and hydrogenotrophic methanogens (Griffin et al. 1998). These microorganisms catalyze the mineralization of waste components to carbon dioxide, methane, and water through a cascade of biochemical reactions.

Subcritical solutions

Domestic and industrial waste solutions at high temperatures (subcritical, 150-370°C, or critical above 370°C) and pressures (5-30 Mpa) are transformed into inorganic salts and simpler forms of biodegradable and non-biodegradable compounds. The basic principle of this method is to enhance contact between oxygen of air and the aqueous solution containing the organic pollutants.

Chapter 3: Methane recovery from paper waste-a basic study

Cellulose from wastepaper is capable of being converted to methane gas. The effect of substrate concentration on cellulose degradation was investigated to assess the capability and activity of a mixed culture to produce methane in batch conditions. The presence of ink in newsprint was also studied while performing the sets of experiments. Toilet paper and newsprint waste were mixed with anaerobic digested sludge and incubated at 35°C for 30 and 60 days, respectively. Toilet paper reactors were filled with 5 g/l, 10 g/l, 20 g/l, 30 g/l and 40 g/l whereas newsprint reactors were filled with 1 g/l, 5 g/l and 10 g/l printed and blank paper samples (with and without ink).

Regarding to the experimental results obtained in the sets of reactors degrading toilet paper, it could be indicated that the threshold for inhibition due to solid content may lie between 5 g/l and 10 g/l. Indeed, cumulated methane production in the reactors treating 10 g/l to 40 g/l revealed a depressed capability for potential of methane production compared to the control vial (<200-ml) due to acetate toxicity. The solid content in the sets of reactors degrading newsprint also led to the conclusion that this condition may be inhibitory for cellulose degradation. As in toilet paper, 10 g/l newsprint also revealed a lower capability compared to the control reactor (<200 ml). However, the reason for inhibition may be different since acetate levels never reached toxic values (<0.6 g/l). Vials treating 1 g/l and 5 g/l newsprint showed a diauxic growth figure less remarkably than in the toilet paper case indicating that when holocellulose (cellulose plus hemicellulose) is combined with lignin as in newsprint, the decomposition process becomes more complicated. A first-order rate model described well the methane fermentation process for newsprint, but was a poor model for soluble substrates (i.e.: glucose).

Chapter 4: Solubilization of paper waste in alkaline and neutral aqueous solutions under subcritical conditions and its technical evaluation as a pretreatment technology for methane recovery

Lignin limits the anaerobic bacterial availability for cellulose. Aqueous solutions under subcritical conditions (SWT) were investigated as a pretreatment technology to enhance anaerobic degradation of paper waste i.e.: newsprint. SWT was driven under two conditions: alkaline (addition of sodium carbonate to avoid the natural acidification of the aqueous solution) and neutral (from neutral to acid range).

SWT was carried out at 170°C, 190°C, and 210°C, with a retention time of 1 hr. Air and nitrogen gas were compressed into the SWT-vessel to support subcritical conditions.

Results showed that using compressed air, the maximum solubilization rate was 29% at 210°C whereas for compressed nitrogen was 18% at 190°C. In general terms, air provided a better support for solubilization and oxidation of the newsprint fiber. The addition of alkalinity enhanced lignin solubilization and prevented cellulose depletion.

Neutral conditions did not prevent the aqueous newsprint solution from its natural acidification. Thus, pH values dropped drastically down to 3. This process made the holocellulose more vulnerable to acid hydrolysis and hence, more depletion occurred and less cellulose available for methane recovery was attained.

Batch methane fermentation of newsprint pretreated at 170°C, 190°C, 210°C at alkaline conditions gave better methane conversion efficiencies compared to those without Na_2CO_3.

Table 4.1. Incubation time, total methane production and conversion efficiencies (%).

Batch N°	Incubation time (days)	CH_4 (S.T.P) (Liter) Nc[a]	To[b]	Ce (%)[c]
		Neutral		
B-1	60	2.4	4.7	51
B-2	60	2.3	3.9	59
B-3	62	1.8	3.6	50
		Alkaline		
B-4	79	3.1	4.6	67
B-5	58	3.1	4.3	72
B-6	36	2.3	3.6	64
		Nitrogen		
B-7	30	0.12	0.29	41
B-8	30	0.15	0.31	48
B-9	30	0.16	0.29	55
N-1	30	0.12	0.34	35

a: net cumulated volume was corrected for the methane production attributable to the seed.
b: theoretical maximum methane production.
c: conversion efficiency (Nc/To*100)

Newsprint pretreated at 190°C at alkaline condition gave the highest methane conversion efficiency. Seventy two percent (72%) of the initial COD was recovered as methane gas after 58 days of incubation (Table 4.1).

Chapter 5: Alkaline subcritical-water treatment and alkaline heat treatment for the increase in biodegradability of paper waste-semicontinuos studies

This chapter describes two alkaline pretreatment processes combined with semicontinuos reactors for the conversion of refractory paper waste (i.e. newsprint) into biogas. Methane conversion efficiencies, cellulose and soluble lignin derivatives (SLD) removals were investigated for the two following processes: air-alkaline subcritical-water treatment (A-ASWT) coupled with methane fermentation (R-1) and alkaline heat treatment (newsprint heated with steam in an autoclave; AHT) coupled with methane fermentation (R-2) with a air-neutral subcritical-water treatment (A-NSWT) recycle. Results showed that for A-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 45%, respectively. After a final HRT of 40 days, average CH_4 conversion efficiency and average cellulose removal reached 45% and 63%, 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 A-NSWT (150°C; neutral-pH). Methane conversion efficiency of this process increased as more recycles were performed. To the fifth operation, the total average methane conversion efficiency was 34% with a total average cellulose removal of 48%.

The technical achievements attained by ASWT-R1 and AHT-R2-NSWT were similar in terms of cellulose degradation and methane production. The later can be optimized in order to take advantage of the subcritical thermal treatment process for a second methanogenic reactor with the whole effluent drawn off from the first reactor (R2-SWT-R2). From a comparison of the control results and the results of NSWT and recycle, the improvement in biodegradability from NSWT can be calculated. Such calculation indicates that subcritical water treatment off all the effluent and subsequent digestion in a second-stage digester would result in 25% destruction of the NSW treated volatile solids.

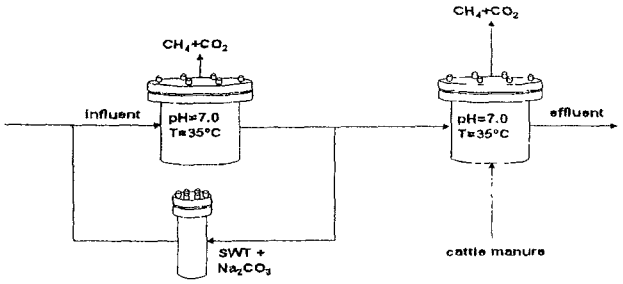

Figure 5.1. A possible combined process anaerobic system. The effluent of the first stage is co-digested with cattle manure.

Using this value along with the two-stage system indicates in comparison with the newsprint control reactor (C-N) that NSWT and subsequent digestion should increase volatile solids destruction by 292% (the new system should result in 51% VS removal compared to 13% removal of the control reactor), probably increase methane production by about the same percentage, and should result in 44% less volatile solids for final disposal. These appear to be substantial benefits. To choose any other viable alternative before final disposal, volatile solids removal should have similar values to biowaste treatment facilities (50%~80%) or in this case, be higher than 51%. The volatile solids removal of the combined process (R2-recycle SWT-R2) resulted in 27% destructed which left 73% volatile solids for final disposal (the AHT step can be withdrawn from the process since no important advantages pro anaerobic biodegradability were observed during the experiments; the economic impact of this step is approx. 0.32 $/batch at 128°C-1 hr). Therefore an attractive alternative should consider the use of manure and the effluent of the combined process (Fig. 5.1). The next chapter presents a basic study concerning the feasibility of co-digestion of filtered cattle manure from a dairy herd and the effluent from the combined process studied through this chapter.

An estimation of the operational cost concerning subcritical water treatment (SWT) at 190°C-40 bar-1 hr is approximately 0.68 $/Liter 2% newsprint solution. This cost can be lowered considerably if temperatures are increased to higher values (230°C~250°C) that may allow the generation of a self-sustainable process in terms of energy production (in these conditions more than 70% COD removal can be achieved with higher net heat releases).

Chapter 6: Feasibility of co-digestion of filtered cattle manure and thermally-anaerobically treated newsprint

In the previous chapter two digestion systems were investigated as viable alternatives for the recovery of methane gas from paper waste. The improvement or optimization of one of these two systems led to a possible two-stage anaerobic system with calculated volatile solids destruction of about 51%. The second technically feasible system which was previously mentioned, pointed out the idea of adding a co-digestion step in order to have less volatile solids before final disposal. To evaluate the feasibility of this system it was necessary to investigate the co-digestion process in terms of volatile solids (VS) reduction and methane conversion efficiency (%). Ammonia, volatile fatty acids, protein and cellulose were determined in order to understand better the synergic relationship between mixtures.

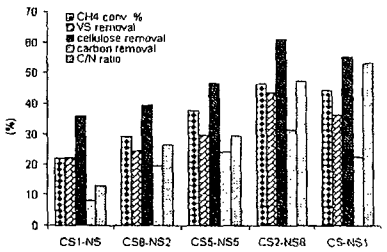

Figure 6.1. Characterization of the co-digestion process through methane conversion efficiency, volatile solids removal, cellulose removal, organic carbon removal and carbon to nitrogen ratio.

Through this chapter, the technical feasibility of co-digestion was assessed in order to recommend a treatment process for lignocellulosic or refractory waste (i.e.: paper waste and wood waste). Fig. 6.1 shows a summary of the characteristics of this step including methane conversion efficiency, volatile solids removal, cellulose removal, organic carbon removal and carbon to nitrogen (C/N) ratio of each mixture.

It can be clearly confirmed that the optimum mixture for co-digestion is 20% cattle slurry and 80% newsprint slurry (CS2-NS8). As shown in Fig. 5.1, the volatile solids removal of the combined process resulted in approximately 27% destructed. Making an overall calculation with the addition of the codigestion step, the new system should result in 59% VS removal. In the next and final chapter, final conclusions of this thesis will be drawn.

Likewise, a general flowsheet with a putative amount of lignocellulosic waste (i.e.: the amount of industrial lignocellulosic solid waste discarded in the FY 1999) for treatment and the total methane recovered as a renewable source for heat will be calculated.

Chapter 7: Conclusions and recommendations

- Cellulose is the major biopolymer present in the fraction of organic solid wastes. Conversion of cellulose to methane by means of microbial fermentation has a considerable potential to reduce organic waste accumulation and hydrocarbon fuels depletion. Experimental results indicated that the microbial ecosystem that exists in municipal waste treatment plants maintained its activity and degraded toilet paper into methane and carbon dioxide under defined conditions. Vials treating newsprint showed a growth figure less remarkably than in the toilet paper case indicating that when holocellulose (cellulose plus hemicellulose) is combined with lignin as in newsprint, the decomposition process becomes more complicated.
- Due to a complex association of physical type between lignin and holocellulose, the biodegradability of newsprint is remarkably low compared with other substrates used for methane fermentation. As an attractive alternative to incineration and landfilling and as renewable source of energy, its low biodegradability had to be improved with effective thermal pretreatments in the mitigation of lignin without destroying or degrading the fraction of sugars (carbohydrates) present in the paper fiber. Subcritical water treatment process (SWT) was a pretreatment technically viable for the fragmentation and solubilization of newsprint.
- Two alkaline thermal treatments were investigated and compared for their effectiveness in converting refractory newsprint by semicontinuos digesters into methane gas. Up to 45% methane gas was recovered from the newsprint waste. Cellulose as the main carbohydrate contributor in newsprint waste was anaerobically degraded up to 63%. For the combined process with R-2 the optimum was achieved in the fourth operation of recycle (64%).
- Two digestion systems were investigated as viable alternatives for the recovery of methane gas from paper waste. The improvement or optimization of one of these two systems led to a possible two-stage anaerobic system with calculated volatile solids destruction of about 51%. The second technically feasible two-stage system pointed out the idea of adding a co-digestion step in order to have less volatile solids before final disposal. Making an overall calculation with the addition of the codigestion step, the new system should result in 59% VS removal.

Paper waste and wood waste are important energy sources. The yields of recovered methane per ton COD produced in the treatment processes proposed in this thesis were utilized to evaluate a potential methane production per year in terms of oil liters. Methane recovered from the organics contained in municipal wastewater, nightsoil and agricultural waste corresponds to 9(10^6) kl/year of crude petroleum. As about 200(10^6) kl/year of crude petroleum is imported and from this amount 4.5% corresponds to energy recovered by methane fermentation (Noike, 2001); through the evaluation made some 1.43~2.45% would correspond to methane production from lignocellulosic wastes. Therefore, further development for methane recovery from biowastes is needed in order to improve the reason of its energy substitution for oil. To finalize, Fig. 7.1 shows a summary flowsheet diagram of the recommended alternative for the integral treatment of the fraction of lignocellulosic waste.

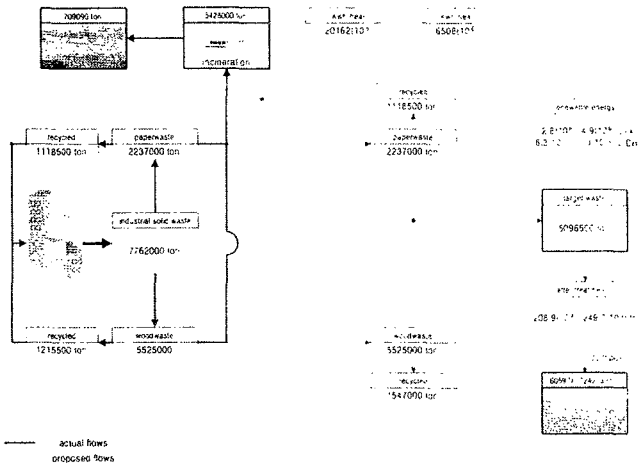

Figure 7.1. Integrated flowsheet diagram of the recommended alternatives for the treatment of the fraction of lignocellulosic waste.

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論文審査結果の要旨

循環型社会の形成のためには、都市および産業廃棄物の再生可能な処理が求められている。紙類は再生紙製造のための材料として、100%のリサイクルが可能であるが、繊維がその強度を失うために、４倍量の材料が必要とされ、再生のために利用されない部分は焼却処理されなければならない。本論文は、新聞紙からのバイオガス回収のために、亜臨界域における可溶化による前処理によるメタン発酵について検討したもので、全編７章からなる。

第１章は総論であり、本研究の背景および目的について述べている。

第２章では、メタン発酵の原理および亜臨界域における可溶化等に関する既往の研究について文献調査を行い、研究課題の整理を行っている。

第３章では、トイレットペーパーおよび新聞紙のメタン発酵の可能性について、35℃における回分実験を行い、前者では基質濃度 5g/L および 10g/L の間に、揮発性脂肪酸の蓄積による阻害が生ずるが、後者ではセルロース中のリグニンの存在により、加水分解が阻害されるため揮発性脂肪酸の蓄積は生じない。新聞紙のメタン発酵のためには、前処理としてセルロースおよびヘミセルロースと堅く結合したリグニンの分解が重要であることを見いだしている。また、ink はメタン発酵に影響を及ぼさない。これは重要な知見である。

第４章では、190℃における亜臨界域可溶化によって前処理を行った新聞紙のメタン発酵を回分実験で行い、72%の最も高いメタンへの転換率が得られた。セルロース除去率は、74%から 93%であり、リグニンは嫌気的分解を受けなかった。これは重要な成果である。

第５章では、新聞紙のメタンへの転換に対するアルカリ熱処理および亜臨界域可溶化処理を組み合わせたプロセス効果について半連続実験によって検討され、新聞紙より 45%のメタンガスが回収された。セルロースが新聞紙の主な炭水化物であり、63%まで嫌気的に分解された。溶解性リグニンおよび複素環化合物は完全に分解され、分解生成物の中に強固な難分解性の性質を有する 4-methylcatechol が見いだされた。これも重要な知見である。

第６章では、固形物の減少およびメタン生成量の増大を目的として行った亜臨界域可溶化処理された新聞紙および畜産廃棄物の混合メタン発酵は、新聞紙と畜産廃棄物の混合比 80 : 20 において、44%の最大固形物減少率および 47%の最大メタン転換率（COD ベース）が得られた。これは有用な知見である。

第７章は結論である。

以上要するに本論文は、生物学的に難分解性の新聞紙のメタン発酵において、亜臨界域における可溶化による前処理によって、固形物の減少およびメタン生成の増大のための基礎的検討を行い、新たなメタン発酵プロセスを提案したもので、環境工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。