Bioresource Technology 235 (2017) 265–273

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

New alternative energy pathway for chemical pulp mills: From traditional fibers to methane production

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HIGHLIGHTS

- Brown, oxygen delignified and bleached pulp were tested for methane potential.
- Highest methane yields correspond to fiber samples, particularly of bleached pulp.
- Degradability was found to be in the following order: bleached > brown > delignified.
- Energy and cost estimations were evaluated.

ARTICLE INFO

Article history:
Received 4 February 2017
Received in revised form 17 March 2017
Accepted 22 March 2017
Available online 25 March 2017

Keywords:
Anaerobic digestion
Biochemical methane potential
Chemical pulp
Microcrystalline cellulose

ABSTRACT

Chemical pulp mills have a need to diversify their end-product portfolio due to the current changing bio-economy. In this study, the methane potential of brown, oxygen delignified and bleached pulp were evaluated in order to assess the potential of converting traditional fibers; as well as microcrystalline cellulose and filtrates; to energy. Results showed that high yields (380 mL CH_4/gVS) were achieved with bleached fibers which correlates with the lower presence of lignin. Filtrates from the hydrolysis process on the other hand, had the lowest yields (253 mL CH_4/gVS) due to the high amount of acid and lignin compounds that cause inhibition. Overall, substrates had a biodegradability above 50% which demonstrates that they can be subjected to efficient anaerobic digestion. An energy and cost estimation showed that the energy produced can be translated into a significant profit and that methane production can be a promising new alternative option for chemical pulp mills.

1. Introduction

Bio-economy markets are rapidly changing worldwide, therefore new alternative energy pathways, which use bio-based natural resources in a sustainable way will be needed in the future. European Union (EU) environmental regulations and energy directives have made renewable energy production an important topic to address. This ongoing trend can give a new potential to existing forest companies to also develop as significant biofuels producers in addition to producers of cellulose based products. Nowadays chemical pulp mills typically produce fibers for paper, board and viscose production and at the same time harvest great amount of bioenergy in the form of heat and power. So far fiber products have a good share in the market of traditional cellulose products, but due to global increasing capacities, the situation can dramatically change leading small production plants into financial difficulties. For these mills, the production of renewable energy in the form of biogas could become a potential alternative to the application/use of different types of pulps.

In recent years most of the anaerobic digestion (AD) studies in the forest industry have focused on primary and secondary sludge from the aerobic treatment of wastewaters mainly from paper industries (Bayr and Rintala, 2012; Hagelqvist, 2013; Lin et al., 2011). Sludge is produced in great amounts and disposal is costly; this is why studies have concluded that it is more effective to reduce sludge formation by changes in the wastewater treatment (such as including AD) than reducing the amount of sludge by post-treatment (Stoica et al., 2009). Little attention has been focused on the direct AD of streams of chemical pulping wastewater. Gavrilescu and Puitel (2007) describe the different processes and water flows in a chemical pulping line. Effluent emissions are generated in wood handling, debarking and chip washing, wood cooking, pulp washing and pulp bleaching. Bleaching efflu-

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http://dx.doi.org/10.1016/j.biortech.2017.03.140
0960-8524/

ents are the most important discharge of pollutants to water in a pulp mill. They are generally the main source of wastewater and chemical oxygen demand (COD) load (around 50–60% of the total load) in a chemical pulp mill, this underlines their potential for AD. However, they also contain many inhibiting compounds for methanogenic bacteria such as degradation products of lignin, polysaccharide, wood extractives and most importantly chlorine compounds that can produce absorbable organic halides (Monje et al., 2010). Different treatment processes of bleaching effluents have been reviewed and AD has been found to be most promising with COD removals ranging from 28 to 50% and maximum dechlorinating (Rintala and Puhakka, 1994; Savant et al., 2006). Ekstrand et al. (2013) elaborated a comprehensive study of the methane potentials of many different effluent streams in the pulping industry finding that kraft pulp effluents from the cooking and condensates had high yields at or above 50% of the theoretical potential. Larsson et al. (2015) also state that alkaline bleaching effluents from a kraft pulp mill were suitable for AD application, however significant lower yields were found when using softwood as raw material rather than hardwood.

Due to some of the challenges mentioned above, different sources for biogas production were assessed in order to improve the implementation of AD in chemical pulping. In this study, the biochemical methane potential (BMP) of brown, oxygen delignified and bleached pulp were evaluated in mesophillic batch reactors. The anaerobic degradability was monitored for each pulp fiber, acid hydrolyzed microcrystalline cellulose (MCC) manufactured from fibers, MCC + hydrolysis filtrate mixture and for filtrates alone. This research could provide an assessment of an alternative option to diversify the end-product portfolio of chemical pulp mills.

2. Materials and methods

2.1. Raw material

Softwood pulp fibers used in this study were collected from a kraft pulp mill located in north west Finland. The mill's cooking stage is done at 1000 H-factor and the bleaching stage works with elemental chlorine free (ECF) technique. Pulp fibers were taken after pulp mill digester, after oxygen delignification (O_2) stage and after final bleaching stage; from now on denoted as BRFiber, O2Fiber and BLFiber respectively. Fibers were washed prior to further use with distilled water in large Büchner funnel to attain wash filtrate conductivity value of 5 μS, subsequently they were centrifuged to dry consistency. Centrifuged pulps were used as raw material in MCC manufacturing and also employed in BMP tests.

MCC materials were manufactured using an acid hydrolysis procedure called AaltoCell™ described in Vanhatalo and Dahl (2014). In short, a defined amount of pulp was loaded in tube-like 2.5 dm^3 metal reactor using H_2SO_4 as hydrolyzing agent. The hydrolyzation was done with a 2.0% acid charge (calculated for oven dry cellulose weight) at 160 °C, 30 min, with a 10% pulp consistency. After reaction, reactor was cooled down to room temperature in cold water bath for 15 min. Content of reactor was poured to filter bag and liquid fraction was separated using a laundry centrifuge (UPO, Finland) at 4500 rpm. Liquid fractions were used as such in digestion experiments and denoted as BRFiltrate for brown pulp, O2Filtrate for oxygen delignification, and BLFiltrate for bleached pulp. Solid MCC fraction was washed three times using dilution thickening washing with dilution factor 10. Washed MCC's were used in BMP experiments and denoted as BRMCC, O2MCC, and BLMCC. Fourth material used for BMP denoted as BRMix, O2Mix, and BLMix was the reactor content after hydrolyzing procedure, but without filtrate separation and washing. Distilled water was used in all experiments, H_2SO_4 was 1 M and analytical grade.

2.2. Substrates and inoculum

The fractions from the production of the different MCC qualities were used as substrates for the BMP experiments. For each type of MCC: brown (BR), oxygen delignified (O_2) and bleached (BL); four substrates were tested for methane production. The substrates were namely Fiber which was used as a control, MCC, Mix (MCC + Filtrate) and the separated Filtrate. Each substrate was characterized (Tables 1 and 2) using average values of triplicates and subsequently stored at 4 °C prior to its use. Filtrates were stored at −20 °C to avoid any carbohydrate degradation before the beginning of experiments.

Fresh digested sludge from a mesophillic anaerobic digester of Suomenoja municipal wastewater treatment plant located in Espoo, Finland was used as inoculum for all the experiments. The inoculum was collected and degassed for 4 days prior to the start of each of the experiments. Using average values of triplicates, characterization of the inoculum resulted in total solids (TS) of

Table 2
Initial characteristics of pulp filtrates. Values represent the average of triplicate samples and their standard deviation when indicated.

Parameter	BRFiltrate	O2Filtrate	BLFiltrate
pH	1.9	1.8	1.4
TS (g/L)	14.8 ± 0.2	16.2 ± 0.2	8.4 ± 0.1
VS (g/L)	12.3 ± 0.2	14.6 ± 0.2	8.1 ± 0.1
Arabinose (mg/L)	483.1	268	704.4
Rhamnose (mg/L)	0	0	0
Galactose (mg/L)	297	164	260.9
Glucose (mg/L)	1962.7	3445.4	1165
Xylose (mg/L)	3373.9	2459.9	3404.9
Mannose (mg/L)	1262.3	1224.5	1155.8
Total carbohydrates (mg/L)	7379	7561.8	6691
COD (mg/L)	14,765.5 ± 97	18,514.3 ± 44	9187 ± 48
Soluble lignin (mg/L)	363	532	406
VFA (g/L)	38.1 ± 0.1	39.9 ± 0.3	2.7
Formic acid (mg/L)	4057.4	8800.2	113.7
Furfural (mg/L)	215.7	1649.2	46.9
Hydroxymethylfurfural (mg/L)	52.7	853.5	12.2

Table 1
Initial characteristics of solid substrates. Values represent the average of triplicate samples and their standard deviation when indicated.

Parameter	Brown pulp			Delignified pulp			Bleached pulp		
	Fiber	MCC	Mix	Fiber	MCC	Mix	Fiber	MCC	Mix
Carbohydrates (% DW[a])	95.4	95.0	94.6	97.6	96.8	96.2	99.2	99.4	97.8
Extractives (% DW)	0.3	0.8	0.3	0.1	0.2	0.3	0.2	0.1	1.4
Total Lignin[b] (% DW)	4.2	4.6	4.8	2.3	3.2	3.2	0.7	0.5	0.9
TS (%)	29.9 ± 0.2	31.2 ± 0.1	10.5 ± 0.5	33.4 ± 0.2	31.5 ± 0.1	9.8 ± 0.1	44.7 ± 0.2	44.4 ± 0.3	10.4 ± 0.2
VS (%)	29.7 ± 0.1	31.2 ± 0.1	10.3 ± 0.5	33.4 ± 0.2	31.4 ± 0.1	9.6 ± 0.1	44.7 ± 0.2	44.4 ± 0.3	10.4 ± 0.2

[a] DW: Dry weight.
[b] Reported as the sum of acid soluble and insoluble lignin fractions.