

Pretreatment and usage of pulp and paper industry residues for fuels production and their energetic potential

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Abstract. This paper gives an overview about Pulp and Paper Industry (PPI) residues, their properties and some solutions for converting those materials into fuels. The main leftovers are bark, sludge of aerobic digestion, primary floto sediment (PFS) and pulp rejects (PR). PFS and PR after applying dewatering (press fluids) have considerable biogas potential. Bark and press cake of PR are a good resource for briquetting. Ethanol potentials of bark and PR cake are presented.

Keywords: briquetting, dewatering, press cake, press fluids, bark, biogas, pulp and paper, residues, ethanol.

Introduction

It has been estimated that by the year 2020, paper mills will produce almost 500 million tons of paper and paperboard per year (Wyatt, 2007). Pulp and paper is the third largest industrial polluter to air, water, and soil and releases well over 100 million kg of toxic pollution each year (Environment Canada, 1996). Worldwide, the pulp and paper industry is the fifth largest consumer of energy, accounting for four percent of the entire world's energy use. The pulp and paper industry uses more water to produce a ton of product than any other industry (Earth Greetings Co 2010). The used process water from a pulp mill contains a lot of organic material such as lignin and other organic material from the wood (including chlorinated organic material) resulting in high biochemical oxygen demand (BOD) and dissolved organic carbon (DOC) values. It also contains alcohols, chelating agents and some inorganic materials. Due to this, different wastewaters from a pulp mill may be considered as potential substrates for biogas production. A modern kraft pulp mill is more than self-sufficient in its electrical generation and will normally provide a net flow of energy to the local electrical grid (Jeffries, 1997). Additionally, bark and wood residues are often burned in a separate power boiler to generate steam. Mechanical (ground wood) pulping physically shreds trees into pulp with grindstones and/or heat. These processes use about 90% of the tree (Tilman, 2008). One of the possibilities to use lignocellulosic material is briquetting (Kers et al., 2010). Briquetting has some advantages over

straight burning technologies (Križan et al., 2010). Briquettes have a certain bulk density resulting in convenient stove automation and dosing (Menind et al., 2012).

The other possibility to use lignocellulosic material is to convert it to bioethanol or biogas. Cellulosic ethanol production is a complex process compared to first generation grain or sugarcane ethanol production. The cellulose in the biomass can be degraded to sugar monomers only after the lignin seal and hemicellulose sheathing over the cellulose has been broken and the crystalline structure of the cellulose has been disrupted. This disruption is achieved by the pretreatment process which is usually followed by enzymatic hydrolysis to convert the cellulose fibres and hemicellulose to fermentable sugars (Dwivedi et al., 2009; Kim et al., 2011). Hydrolysis is carried out by a complex mixture of cellulose enzymes which are usually produced by cellulose degrading bacteria or fungi, for example *Trichoderma reesei*. The main factors that affect the hydrolysis rate of cellulose are the accessibility of cellulose fibers to enzymes, crystallinity of cellulose and hemicellulose, and lignin content (Sun et al., 2002). Presence of lignin and hemicellulose makes the access of enzymes to cellulose fibres difficult. Therefore, the removal of lignin and hemicellulose as well as the increase of porosity during the pretreatment process increases the hydrolysis rate significantly (Dwivedi et al., 2009). Enzymatic hydrolysis can be carried out with total solid loadings up to 20%. If solid loading is higher, the constant stirring and equal distribution of enzymes in the mixture becomes difficult to achieve.

In this paper the main focus is on primary floto sediment or primary sludge (PFS), sludge of aerobic digestion (SAD), bark and separates from tape type separator or pulp rejects (PR). PFS, SAD and pulp rejects press fluids (PRPF) are used to analyze their biomethane potential (BMP) applying anaerobic digestion (AD). Bark and PR were pretreated (ground and dried) before they were used in experiments.

Materials and methods

Four different materials chosen from PPI residues were used in the study. All materials differed in nutrition value, fibre and organic matter content. Two samples (PFS and SAD) were used as they were for biogas potential analyses. Bark and PR were pretreated in order to achieve an appropriate particle size and humidity for briquetting. Dewatering screw press Vincent CP4 was used to separate the PR into two fractions: liquid fraction (PRPF) for biogasification and press cake (PC) for briquetting. For PFS and SAD chemical analyses were performed.

Biomethane potential tests (BMP) were carried out using plasma bottles with a volume of 550 ml. Incubated (for 48 hours on 36°C) and sifted (sieve 1 mm) inoculum (150 ml) was used 3 times for each test material (0.3 gTS (total solids) per bottle) and for the blank. During a 45 day period batch raw data was measured. Equipment RS06 with side screen 45 mm was used for bark grinding. Briquetting tests were carried out on briquetting press Weima C150. Energy consumption measurements for processing operations were measured. For determining energy losses during thermal drying and its economic expression, the theory of realistic drying was used (Treier & Hovi, 1997).

During ethanol potential tests, dilute sulfuric acid solution was used for pretreatment. The sample size was 100 g of dried (moisture content <10%) and milled bark and PR cake to which 1,000 ml of 1% acid or alkali solution was added. All

samples were heated for $t = 60$ minutes at a temperature $T = 130 \pm 3^\circ\text{C}$ and pressure of $p = 3$ bar. Samples were then rinsed with distilled water to remove dissolved hemicellulose and lignin. As enzymes are inactivated on temperature $T > 70^\circ\text{C}$ or $\text{pH} > 7$, the sample was cooled to a temperature below 50°C and K_2CO_3 or HCl was added to neutralize the pH. Pretreatment was followed by enzymatic hydrolysis with the enzyme complex Accellerase 1,500. Enzyme mixture was added to the sample at a ratio of 0.3 ml per g of biomass. Hydrolysis lasted for $t = 24$ hours under constant stirring and at a temperature $T = 50^\circ\text{C}$. After the hydrolysis process, glucose concentrations in all the samples were measured reflectometrically by using RQflex 10 reflectometer and Reflectoquant glucose & fructose test.

In order to start the fermentation process, 2.5 g of dry yeast *Saccharomyces cerevisiae* was added to all of the samples. The fermentation process was carried out for 7 days under low oxygen conditions in 1,000 ml glass bottles, sealed with a fermentation tube. No glucose was detected in the samples after fermentation. Ethanol concentration was measured by a gas chromatograph.

At least 3 parallel samples were analyzed with each pretreatment method. Averaged results are used in figures and standard deviations are shown by vertical lines. Data were processed with the programs Microsoft Excel and GraphPad Prism 5.

Results and discussion

Dewatering and drying

Moisture content of PR was about 85% in raw material. After dewatering with screw press Vincent CP4 cakes humidity decreased to 47%. The amount of water that was removed with the mechanical dewatering process was calculated by the following equation (1.1).

$$\Delta m = \frac{m \cdot (w' - w'')}{100\% - w''} \quad (1.1)$$

where, m is primary mass of the material, w' humidity before and w'' humidity after the mechanical dewatering. Therefore, from one ton of PR it was possible to separate 717 kg of PRPF and 283 kg of PC with a humidity content of 47%. Energy consumption for dewatering of PR was 22.53 kWh per ton. As the maximum allowed humidity for briquetting in this study was taken as 12%, the material required additional drying. In order to lose the necessary 35% of humidity, thermal convective drying was used. In this process 112.6 kg of water was separated, which is calculable by using the same equation. About 280 MJ of energy is needed to vaporize 112.6 kg of water.

After reducing the humidity of raw material to the desired level there is 170 kg of material (from one ton of raw material) left that is suitable for briquetting. By using the same principles it is possible to find respective values for bark. Bark had approximate humidity of 50%. By using humid air diagram (Fig. 1.) it is possible to determine energy consumption for various drying conditions from the difference in enthalpies. Because of losses, the real consumption of thermal energy was 422.1 MJ t^{-1} , which is about 50% higher than the theoretical need for energy (280 MJ t^{-1} for PR).

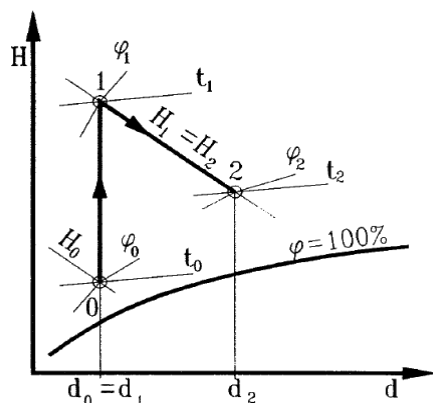


Fig. 1. Air heating (0–1) and drying (1–2) on humid air diagram.

The flow data of theoretical drying of materials at different temperatures are presented in Table 1. Energy consumption of drying is much higher when using the hot air input at 75°C because the air drying potential decreases by half. In this case 538.5 MJ t⁻¹ of energy would be needed (Fig. 1). Therefore, it would be advantageous to use higher temperatures in the drying process.

Table 1. Flow data of theoretical drying

Process Flow data: Air-10 m ³ ·s ⁻¹ ; Density-1.2 kg·m ⁻³ ; Atmosphere pressure-1,013 mbar						
Nr	Name	Temp (°C)	Relative humidity (%)	Specific humidity (g kg ⁻¹)	Enthalpy (kJ kg ⁻¹)	
1	0	10	70	5.32	23.4	
2	1	75	2.2	5.32	89.4	
3	2	40	41	19.12	89.4	

Briquetting

Briquettes from both materials were a good shape and stable as it is common in briquettes made of wooden materials. Moisture and ash content are presented in Table 2. Ash content of PR (1.56%) is little higher than in normal firewood. It may be due to the content of chelating agents and some inorganic materials as described in introduction. Chemical analyses for PR briquettes in this study are not performed. Ash content of 4.49% for bark is an expected result because of bark's normally higher ash content compared to firewood. Energy consumption of briquetting operation was 118.67 kWh per ton of bark briquettes.

Table 2. Experimental and test results of bark and PR

Material	Moisture %	Ash %	Briquettes density t·m ³	Glucose yield (g kg ⁻¹)	Ethanol yield (g kg ⁻¹)	Fermentation efficiency (%)
PR	87.43	1.56	753.0	142.0	34.7	47.8
Bark	89.68	4.49	954.3	251.0	78.9	61.5

Ethanol potential tests

Results show that the highest cellulose to glucose conversion rate of 251.0 g kg⁻¹ of biomass was given by pulp rejects (PR) samples (Fig. 2). As could be expected from glucose yields, the samples of PR also gave the highest ethanol yield of 78.9 g kg⁻¹. The more sugars there are available for yeast, the more ethanol they can produce. Samples of bark gave an ethanol yield of only 34.7 g kg⁻¹. PR samples had 13.7% higher fermentation efficiency than bark samples (Table 2), which indicates that high lignin content of bark has a negative effect not just on hydrolysis, but also on the fermentation process.

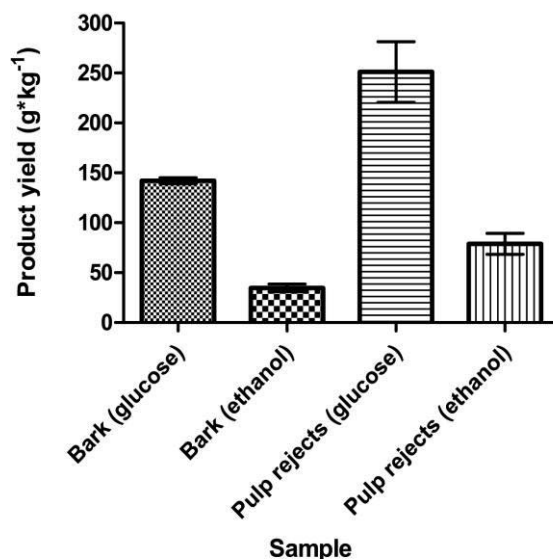


Fig. 2. Glucose and ethanol yields (g kg⁻¹) of bark and PR samples.

Biogasification

Biomethanization tests (methane yield and process parameters) are based on plant's chemical composition for SAD and PFS data (Table 3). No chemical composition analyses were performed for PRPF but total and volatile solids.

Table 3. Chemical composition of SAD and PFS

Material	pH	TS %	NO ₃ -N mg kg ⁻¹	NH ₄ -N mg kg ⁻¹	N %	P %	K %	Ca %	Mg %
SAD	7.37	3.02	0	547.17	0.648	0.049	0.05	0.576	0.035
PFS	6.17	2.34	0	0	0.025	0.003	0.009	0.037	0.005

The preliminarily BMP tests for PRPF gave promising results – 333 liters of methane per one kg of total solids (LCH₄·KgTS⁻¹), which is comparable to biomethane potential of PFS 351 LCH₄·KgTS⁻¹. BMP experiments for SAD produced less methane and resulted in 216 LCH₄·KgTS⁻¹.

Process activity, duration parameters and summarized methane yields are presented in Fig. 4.

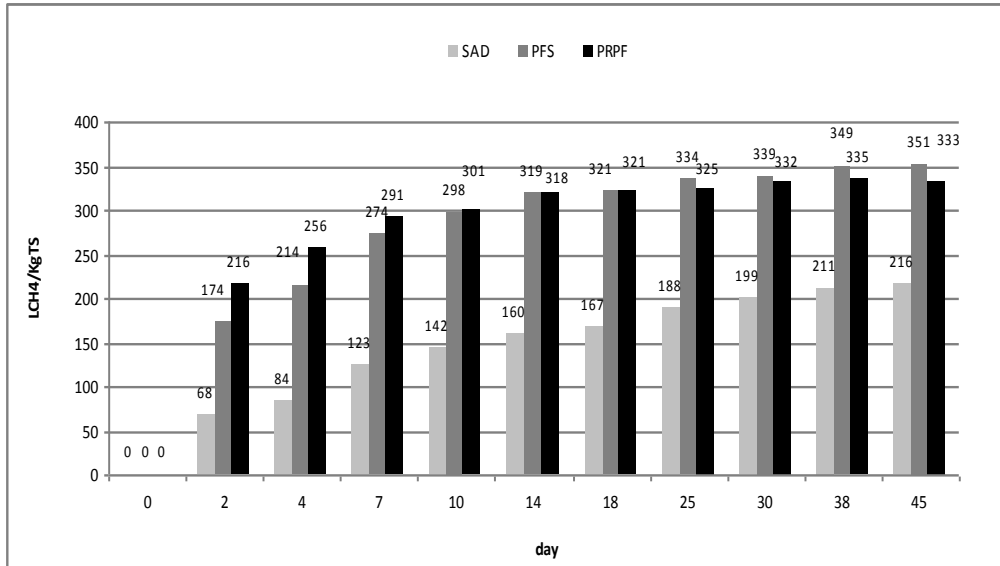


Fig. 4. Methane yield test results and process activity of SAD, PFS and PRPF.

Process activity is comparably high for both PFS and PRPF. 80% of methane potential is achievable during 7 to 8 days. This is advantageous for short retention time plants. Mixture of PFS and PRPF which reflects proportionally the amounts of residues emerging in the factory is not used for BMP test together in this study. Additional analyses are needed to receive realistic data about BMP and process performance of PFS and PRPF mixture.

Conclusions

1. Thermal drying of materials is a process with high energy demand. When producing the thermal energy it would be possible to achieve the energetic independence of the production by using part of the product for drying.
2. On higher drying temperatures the total energy consumption of the drying process decreases.
3. Based on ethanol potential tests results we can conclude that PR could effectively be used for bioethanol production, but bark is a very poor feedstock for bioethanol production.
4. Briquettes from bark and PR are stable and have good shape. Briquettes from bark normally have higher ash content than briquettes from wooden residues.
5. PFS and PRPF have similar BMP, 333 and 351 LCH₄·kgTS⁻¹, respectively. 80% of methane potential is achieved during 7 to 8 days.
6. SAD has lower biomethane potential than PFS and PRPF (216 LCH₄·kgTS⁻¹). 80% of methane potential is achieved during approximately 20 days.

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