

Impact of thermal pretreatment and MSW origin on composition and hydrolysability in a sugar platform biorefinery

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Abstract. Municipal solid waste (MSW) is a widely available large volume source of lignocellulosic material containing a waste paper/cardboard mixture which can be converted into fermentable sugars via cellulolytic enzyme hydrolysis in a sugar platform biorefinery. Thermal pre-treatments are generally applied to MSW to facilitate the extraction of the lignocellulosic material from recyclable materials (plastics, metals etc.) and improve the paper pulp conversion to sugars. Applying high temperature might enhance food waste solubilisation but may collapse cellulose fibre decreasing its hydrolysability. Low temperature pre-treatment will reduce the energy demand but might result in highly contaminated pulp. Preliminary results showed that the enzymatic hydrolysis performances were dependent on the MSW origins. Using 8 different samples, the impact of thermal pretreatment and MSW origin on pulp composition and hydrolysability was assessed in this work. Low pre-treatment temperature produced pulp which contained less lignocellulosic material but which hydrolysed to a higher degree than MSW treated at high temperatures. High temperature pre-treatment could have exposed more of the inhibiting lignin to cellulase. This information would have a significant economic impact on a commercial plant as expensive autoclave could be advantageously replaced by a cheaper process. Glucan conversions were also found to vary depending on the region, the recycling rate possibly because of the lower recycling rate resulting in the use of less paper additive in the material or the difference in paper production technology (chemical VS mechanical pulping). This could also be explained by the differences in paper composition.

1. Introduction

Many efforts are currently made to reduce fossil fuel dependence while ensuring worldwide food supply to cope with increasing population. In the meantime, waste generation inevitably associated to society development, is raising as a priority concern for municipalities [1].

Municipal solid waste (MSW) represents a large amount of lignocellulosic material which can be enzymatically converted into monosaccharides (mostly glucose from cellulose) in a platform biorefinery. This raw material has the advantages of not being in competition with crops for arable land, it does not require additional energy supplementation to be grown, is widely available and poorly exploited.



To extract the lignocellulosic fraction, mainly constituted of wastepaper and cardboard, it is commonly accepted that a thermal pre-treatment must be applied [2-5]. Preliminary results also indicated that the MSW origin impacted upon these performances. These issues were addressed in this work. These results are confidential and were therefore expressed as percentages of the maximum conversions or autoclave temperatures.

2. Materials and Methods

2.1. Material collection and pre-treatment applied

Eight different MSW samples were collected (Table 1) and thermally pre-treated at different temperatures and a constant material/water ratio (confidential). The material was then washed and the paper pulp was extracted using a patented process (Fiberight). Office papers, newspapers, magazines and cardboards were collected from local recycled paper collections. They were shredded or manually cut into small pieces. A mix stream was also created based on UK waste paper composition [6-8].

Table 1. Summary table of all sample characteristics and pre-treatment conditions.

Designation	Region	Paper recycling rate	Pulping process	Pre-treatment temperature (% of the maximum applied)
Sample 1	Region 1	Low	Chemical	70
Sample 2-4	Region 2	Medium	Mechanical	75-100
Sample 5-6	Region 2	Medium	Mechanical	60-75
Sample 7-8	Region 3	South Wales	Mechanical	50-75

2.2. Composition analysis

All compositional analyses were carried out on dried and ground material. Structural carbohydrate and Acid Insoluble Material (AIM) were analysed based on the NREL method [9]. Pseudo lignin, which is a non-lignin acid insoluble organic fraction [10], was determined by applying an Acid Detergent Fibre (ADF) followed by an Acid Detergent Lignin (ADL) on AIM (see [11]). Food waste content was evaluated by measuring lipid [12], protein by TKN determination [13, 14] and by measuring carbohydrate from lignocellulose using the NREL method after washing the pulp with Neutral Detergent Fibre (NDF) [15], and applying the following equation:

$$\% \text{Food waste (TS)} = \% \text{Lipid} + \% \text{TKN} \times 6.25 + (\% \text{sugar before NDF} - \% \text{NDF} \times \% \text{sugar after NDF})_{(1)}$$

2.3. Enzymatic hydrolysis

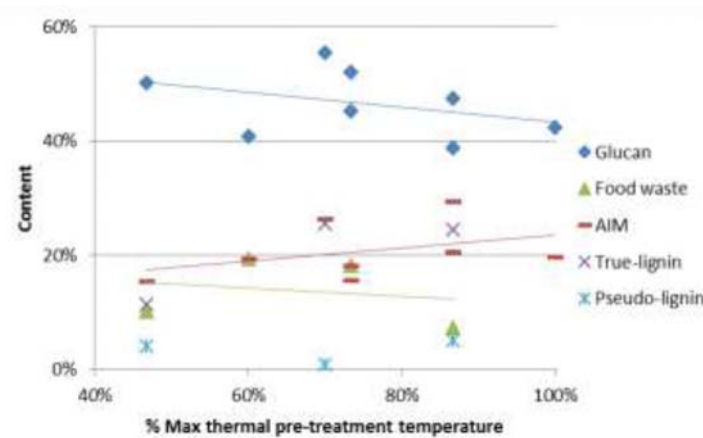
All materials were enzymatically hydrolysed at 5 % total solids (TS) using 2 % commercial cellulase enzyme on a TS basis for 72 h in a 50°C tumbler mixer. Sugars were measured by HPLC at the end of the reaction. To assess the impact of recycling on pulp hydrolysis, filter papers were soaked and mixed for 4 h at 60% in presence of 2 different paper additives.

3. Results and discussions

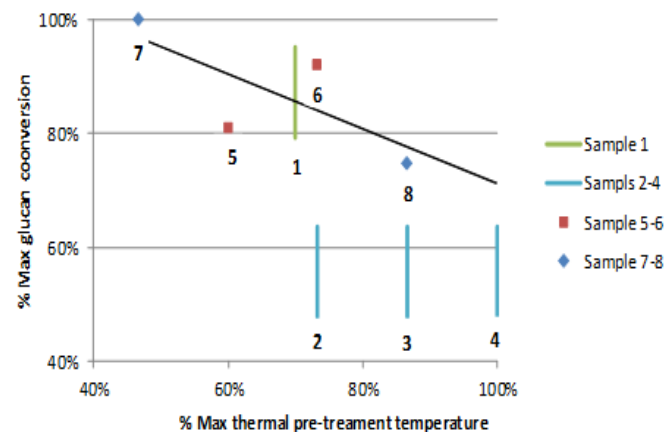
3.1. Impact of thermal pre-treatment temperature on composition

High pre-treatment temperature seemed to decrease the glucan content and increase the AIM percent in pulp (Figure 1a). This had a negligible effect on the content of food waste and pseudo lignin associated with the pulp.

The lignocellulosic content of the material increases when using higher temperature treatments, most probably due to a higher degree of material solubilisation during the pre-treatment, enhancing pulp separation (lab scale observation).



a)



b)

Figure 1. Impact of thermal pre-treatment temperature on a) pulp composition and b) glucan conversion. Vertical bars correspond to ranges of conversion. For linear regression, averaged values were taken.

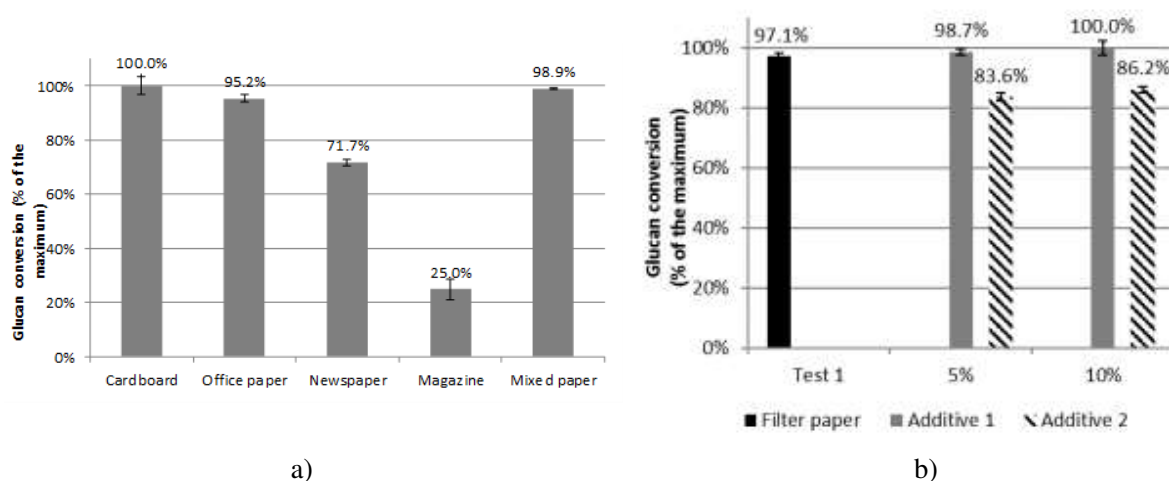
3.2. Comparison between different paper streams

Results from compositional analysis of the different paper streams are presented in Table 2. As can be seen, the composition varies quite a lot depending on the type of paper, especially the glucan content, AIM, and ash (which includes CaCO_3) content. Missing mass could be ink or any acid soluble lignin or additives. Note that the high missing mass in magazines could be caused by the application of organic filler used in coated paper products to provide high gloss and brightness [16].

Table 2. Composition of different paper streams used in this experiment.

All %TS	Glucan	Xylan	Mannan	Galactan	Arabinan	AIM	Ash	CaCO ₃	Missing mass
Newspaper	47.1 (0.9)	5.6 (1.0)	5.2 (0.2)	0.7 (0.1)	0.4 (0.1)	17.3 (1.0)	17.3 (0.1)	9.6 (0.5)	6.5
Cardboard	46.2 (0.7)	7.7 (0.2)	4.2 (0.0)	0.6 (0.0)	0.4 (0.0)	15.6 (0.0)	11.4 (0.1)	3.6 (0.1)	13.9
Magazine	42.4 (0.8)	7.6 (0.3)	0.7 (0.0)	0.2 (0.0)	0.1 (0.0)	5.9 (1.8)	17.2 (0.2)	10.7 (0.1)	26.1
Office paper	66.8 (0.8)	9.00 (0.3)	1.2 (0.0)	0.0 (0.0)	0.1 (0.0)	1.2 (0.0)	20.5 (0.2)	15.1 (0.1)	0.2
Mixed paper	46.4 (2.9)	7.2 (0.3)	3.7 (0.5)	0.6 (0.1)	0.3 (0.1)	10.6 (0.2)	23.9 (0.8)	19.9 (0.7)	7.4

Results from enzymatic hydrolyses of the different paper streams can be found in Figure 2a. Glucan conversions differ depending on the type of paper. Office paper and cardboard show similar hydrolysis performances with virtually the same glucan conversions. The glucan conversion of newspaper was approximately 30 % lower, while that of magazines was only 25.0 ± 3.1 %. Surprisingly, the paper mixture showed very good conversion, close to that of office paper and cardboard, while it should theoretically be equal to the weighted average of 68.3 %. This may indicate the difficulty of obtaining representative samples at laboratory scale.

**Figure 2.** Impact of a) paper stream and b) different paper additive on enzymatic hydrolysis

Waste paper found in MSW from region 1 contains a much higher proportion of easily hydrolysable office paper compared to MSW wastepaper from region 2&3 which contain approximately 40% poorly hydrolysable newspaper and magazine [6-8, 17]. This could partially explain differences in pulp glucan conversions.

3.3. Impact of paper recycling and paper pulping process on enzymatic hydrolysis

The impact of 2 paper additives on enzymatic hydrolysis is shown Figure 2b. Additive 1 appeared not to have any impact on the glucan conversion of filter paper while additive 2 decreased the conversion by around 20%. Paper additives generally used in the paper recycling industry to cope with short fibres might coat the cellulose fibrils and therefore limit the access of cellulolytic enzymes to the fibres. SEM comparison of virgin softwood fibres and recycled newsprint (not shown) seemed to confirm this hypothesis.

The different paper recycling rate within the different regions might therefore contribute to differences in hydrolysability. Paper from region 1 is mostly made from chemical pulping processes which target lignin removal while only mechanical processes are currently operating in region 2&3. Lignin is known to negatively influence enzymatic hydrolysis by physically limiting the access of cellulose to cellulase and by unproductively binding to cellulolytic enzymes [18]. Differences in pulping process can therefore impact the hydrolysability of the various pulps tested.

4. Conclusion

This preliminary study shows that low pre-treatment temperatures produce pulp which contains less lignocellulosic material but which hydrolyses to a higher degree than MSW treated at high temperatures. The composition of the wastepaper stream in MSW has also an impact on the enzymatic hydrolysis: Office paper and cardboard give the highest conversion while newspaper and magazine give the lowest.

Some paper additives typically used in the paper recycling industry was found to reduce enzymatic conversion of paper to sugars possibly due to fibre coating. The different pulping processes are also likely to influence MSW pulp hydrolysability. All these aspects could contribute to the large differences in glucan conversion reported in this work.

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