

Comparison of photocatalytic and hydrolytic pre-treatment of paper-industry lignocellulosic residues to enhance methane yield during anaerobic digestion

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1. Introduction

Wastes generated during the production and processing of cellulose, paper and cardboard represent a potentially available source of organic matter for energy recovery (Meyer and Edwards, 2014). In practice, however, their direct treatment in biogas plant technology often faces operational constraints resulting from their specific composition. Typical barriers include (i) a lignocellulosic structure with limited biological accessibility, and (ii) a high share of mineral impurities, which may lead to the accumulation of inert particles, equipment fouling and a reduced proportion of biodegradable organic matter (Kamperidou and Terzopoulou, 2021). Therefore, the project focuses on verifying suitable pre-treatments that can improve the processability of selected materials, support stable anaerobic digestion and enhance the utilisation of these waste streams in the downstream process chain.

The aim of this study was to compare the effectiveness of selected pre-treatments for two representative waste streams from the pulp and paper sector and to evaluate their impact on biochemical methane potential (BMP) under mesophilic batch conditions.

2. Materials and methods

2.1 Substrates

Two types of feedstocks (Fig. 1) that are also realistically available for industrial practice were assessed: (A) **Cigarette paper production waste** (trimmings and rejects) a material with a substantial mineral fraction, mainly due to calcium carbonate used as a filler. A high inert content may limit practical use in biogas technology through the accumulation of non-degradable solids, increased fouling risk and a reduced share of biodegradable organic matter. (B) **Residual lignocellulosic fraction** from wood preparation for pulp production (e.g., fine chips/sawdust fractions) – a typical lignocellulosic substrate rich in structural polysaccharides. The main limitation is low bioavailability of organic matter and potentially slow degradation kinetics, which may result in low anaerobic conversion efficiency without pre-treatment.

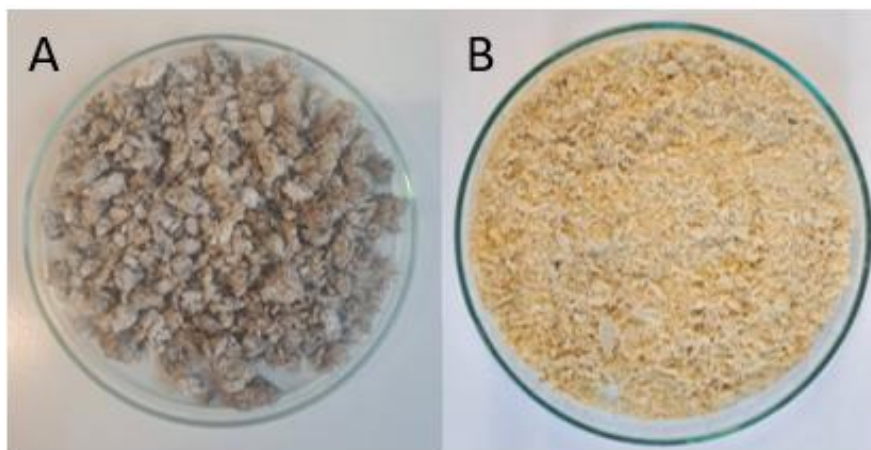


Figure 1. Substrates before pre-treatment.

(A) Cigarette paper production waste; (B) Residual lignocellulosic paper waste

2.2 Pre-treatments

Pre-treatment was applied prior to anaerobic digestion to disrupt biomass structure, increase accessibility of degradable fractions and improve processability:

- **Hydrolytic pre-treatment** in a laboratory autoclave was applied to the lignocellulosic fraction (and also tested on selected variants of materials with challenging properties). Two regimes representing milder and more severe conditions (lower vs higher temperature and longer exposure time) were evaluated to assess the effect of pre-treatment intensity on subsequent anaerobic biodegradability.
- **Photolytic and photocatalytic pre-treatment** of the lignocellulosic material was tested as an additional approach beyond the original project plan, aiming to verify whether surface/oxidative modifications could increase organic matter accessibility and enhance methane production.
- **Chemical alkaline pre-treatment (NaOH)** was selected for the cigarette paper waste due to its specific composition and the need to mitigate negative impacts on anaerobic processing.

2.3 BMP tests

BMP assays were conducted as mesophilic batch anaerobic tests in accordance with VDI 4630 and DIN 38 414-S8. Untreated and pre-treated substrates were incubated with active inoculum (biogas plant digestate), with inoculum-only blanks used to quantify endogenous gas production. Biogas volume was recorded continuously by volumetric measurement, and gas composition was determined by a portable biogas analyser and process gas chromatography once sufficient volume had accumulated. All results were normalised to standard conditions and dry gas. Each variant was run in duplicate for approximately one month.

3. Results

3.1 Cigarette paper production waste

Pre-treatments increased biogas and methane yields versus the untreated reference and accelerated the start-up phase, indicating improved substrate availability. Hydrothermal/hydrolytic treatment provided a small–moderate benefit (slightly higher when using a process-relevant medium), while alkaline pre-treatment delivered the strongest improvement, achieving the highest methane yield and the fastest production profile. Overall, the results suggest that a suitable chemical/thermochemical strategy can reduce composition-related limitations and enhance energy recovery.

3.2 Residual lignocellulosic fraction

The untreated lignocellulosic residue showed very low biodegradability. Mild hydrothermal treatment had little effect on total biogas but improved methane formation, whereas a more severe regime increased both biogas and methane, confirming the role of treatment intensity. The best performance was achieved with photocatalytic pre-treatment, which markedly boosted yields (about twofold) and sustained gas production later in the test, suggesting improved accessibility of otherwise recalcitrant fractions.

Meyer, T., Edwards, E.A. Anaerobic digestion of pulp and paper mill wastewater and sludge. *Water Research* 2014, 48, 321–349. <https://doi.org/10.1016/j.watres.2014.07.022>

Kamperidou, V., Terzopoulou, P. Anaerobic Digestion of Lignocellulosic Waste Materials. *Sustainability* 2021, 13 (22), 12810. <https://doi.org/10.3390/su132212810>