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Electricity generation from rapeseed straw hydrolysates using microbial fuel cells

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HIGHLIGHTS

- Rapeseed straw has undergone a process of hydrolysis.
- Experiments were conducted with various hydrolysing media.
- The study demonstrates a significant impact of enzymes on the hydrolysis yield.

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ABSTRACT

Rapeseed straw is an attractive fuel material for microbial fuel cells (MFCs) due to its high content of carbohydrates (more than 60% carbohydrates). This study has demonstrated that reducing sugars can be efficiently extracted from raw rapeseed straw by combination of hydrothermal pretreatment and enzymatic hydrolysis followed by utilization as a fuel in two-chamber MFCs for electrical power generation. The most efficient method of saccharification of this lignocellulosic biomass (17%) turned out hydrothermal pretreatment followed by enzymatic hydrolysis. Electricity was produced using hydrolysate concentrations up to 150 mg/dm^3. The power density reached 54 mW/m^2, while CEs ranged from 60% to 10%, corresponding to the initial reducing sugar concentrations of 10–150 mg/dm^3. The COD degradation rates based on charge calculation increased from 0.445 g COD/m^2/d for the hydrolysate obtained with the microwave treatment to 0.602 g COD/m^2/d for the most efficient combination of hydrothermal treatment followed by enzymatic hydrolysis.

1. Introduction

Straw residues from rapeseed cultivation contain a diversity of plant organs including stems, pods and pedicels, and many tissue types, some highly lignified and some friable and unlignified. This abundant (Poland ca. 15 Mt/year), renewable and inexpensive source of lignocellulose is partly disposed of, in the form of briquettes or granules, by combustion.

On other hand, the cultivation residues, among them rapeseed straw, have long been identified as desirable source of sugars, which can be liberated by hydrolysis, and subsequently fermented to ethanol or methane. However, reports dealing with rapeseed straw as raw material for production of the second generation fuels are rare. Most often feasibility of ethanol production by a biochemical process including pretreatment (e.g. acidic, alkaline or hydrothermal), enzymatic hydrolysis and fermentation was studied (Wi et al., 2011; Mathew et al., 2011). Biogas production has also been reported (Vivekanand et al., 2012). We have not found any research reports aimed at exploiting the rapeseed straw residue as a potential fuel, neither raw nor digested (hydrolised and/or fermented), in a microbial fuel cell (MFC) technology, which is believed to allow a conversion of energy trapped in polymerised sugars (mainly glucose, and xylose) into electricity.

In recent years the MFCs have been tuned to deal with various cellulosic biomass (Ahmad et al., 2013). Two main approaches have been adopted to make electricity generation through cellulosic MFC economically feasible. The first is based on a consolidated bioprocessing approach to cellulosic biomass (CBP) (Elkins et al., 2010), i.e. cellulose hydrolysis and electricity generation processes proceed simultaneously in an anode compartment of the MFCs. This could be achieved by employing mixed microbial community consisting of naturally occurring cellulolytic microorganisms and exoelectrogenic microbial culture(s). For example electricity was generated from sodium carboxymethyl cellulose using a cellulose-degrading bacteria *Clostridium cellulolyticum* and the electrochemically active *Geobacter sulfurreducens* (Ren et al.,

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2007). Rismani-Yazdi et al. (2007, 2013), demonstrated that rumen microorganisms are capable of hydrolysing microcrystalline cellulose with concomitant electricity (2007) and methane production (2013). Cheng et al. (2011) were able to generate electrical power from pure cellulose using wastewater inoculum (2011). Rezaei et al. (2009) reported that *Enterobacter cloacae* could be used as the sole microorganism to accomplish both cellulose degradation and electricity generation (2009). Besides pure cellulose, electricity was also obtained from more complex lignocellulosic biomass, such as rice straw (Hassan et al., 2014), cornstalk (Wang et al., 2009), and corncob pellets (Gregoire and Becker, 2012). There are also successful reports of promoted power generation by a cellulolytic enzyme mixed with, otherwise unable to digest cellulose, consortium of bacteria (Rezaei et al., 2008) or pure cultures (Hassan et al., 2012), but they do not seem to follow the CBP principle.

The second approach is the combination of physical and/or chemical and/or enzymatic hydrolysis with MFC. (A note: In the fermentation technologies for production of the second generation fuels from lignocellulosic sources a term 'hydrolysis' refers to enzymatic digestion of the biomass pretreated by any physico-chemical method. Throughout this report, by hydrolysis we mean any 'wet' treatment imposed on the lignocellulosic material, which, regardless of efficiency, leads to its saccharification.)

Enzymatic hydrolysis is a common biological approach to hydrolysis and offers the benefits of mild reaction conditions and selective hydrolysis (Sun and Cheng, 2002). Enzymatic hydrolysis leads to high yields of reducing sugars, because cellulase enzymes catalyze only hydrolysis reactions and not sugar degradation processes (Palmqvist and Hahn-Hagerdal, 2000). Prior to hydrolysis, the cellulose structure usually is made available to the enzymes by physical or chemical modification methods.

A hydrothermal hydrolysis technology does not require addition of chemicals. The technology utilizes pressure to cook biomass in water at temperatures above 100 °C. During the process, water penetrates into the biomass cell structure, hydrating cellulose, solubilizing hemicellulose, and slightly removing lignin. The procedure is also highly effective for enlarging the accessible and susceptible surface area of cellulose and improving cellulose degradability to enzymes (Thomsen et al., 2008). The challenge of the hydrothermal treatment is the difficulty in concise control of thermochemical reactions. When hemicellulose is degraded, xylose, mannose, acetic acid, galactose, and glucose are liberated. Cellulose is hydrolysed to glucose. At high temperature and pressure xylose is further degraded to furfural. Similarly, 5-hydroxymethyl furfural is formed from hexose degradation. Formic acid is formed when furfural and HMF are broken down. Levulinic acid is formed by HMF degradation. Phenolic compounds are generated from partial breakdown of lignin, and have also been reported to be formed during carbohydrate degradation (Palmqvist and Hahn-Hagerdal, 2000). These reaction byproducts, including furan derivatives and phenolic compounds, seem not to deteriorate electricity generation by MFCs (Borole et al., 2013). Few reports on the hydrothermal treatment of cultivation residues (for example. wheat straw) prior its use as the sole fuel in MFC have been so far published (Thygesen et al., 2011).

A microwave treatment has a high heating efficiency and is easy to implement. Studies have shown that microwave irradiation changes the ultrastructure of cellulose, degrades lignin and hemicellulose in lignocellulosic materials, and increases the enzymatic susceptibility of lignocellulosic materials (Azuma et al., 1985). The microwave treatment seems to be similar to steam treatment. Angelidaki et al. (2011), used microwave pretreatment of rapeseed straw for bioethanol production (2011).

The objectives of this study were to (1) investigate the hydrothermal, microwave, enzymatic, hydrothermal followed by enzymatic, and microwave followed by enzymatic hydrolysis efficiency of rapeseed straw and (2) test the rapeseed straw hydrolysates as a potential fuel in the MFC for electricity production.

2. Methods

2.1. Rapeseed straw and hydrolysis

Rapeseed straw was collected from a farm in northern Poland. It was dried for three weeks at 70 °C, ball-milled and screened through 10–18 mesh sieves. The content of cellulose (38.1%) and hemicellulose (22.6%) was determined as described by Lewandowska et al. (2014). Before further treatment the straw was soaked in a phosphate buffer (1.74 g/dm^3 KH_2PO_4, 1.38 g/dm^3 K_2HPO_4) at 80 °C until it softend and turned into a homogenous pulp. The hydrolysis of the pre-soaked biomass were conducted at a solid concentration of 10.0% (w/w) using the phosphate buffer for dilution.

2.1.1. Hydrothermal treatment

The straw pulp was liquefied in a sealed reactor under high temperature (120 °C) and raised pressure (1.2 bar) for 2 h. After the desired reaction time had elapsed, the reaction mixture was cooled, neutralized with 0.1 M NaOH solution and centrifuged at 10.000 rpm for 10 min. The processes resulted in a predominately cellulose-containing solid fraction and a liquid fraction, called the hydrolysate. The aqueous fraction was separated and subjected to the analysis of reducing sugars (Fig. 1). Before use, the hydrolysate was diluted to the desired concentration using a buffered nutrient medium (hydrolysate T).

2.1.2. Microwave treatment

The straw pulp was transfered to a conical flask, and placed in a microwave oven (2.45 GHz, 600 W) for 2 h. During the reaction process, the distilled water was successively added to the reactor to compensate for water consumed (hydrolysate M, further steps as in 2.1.1). The solid fraction obtained by the process was highly hydrolysable with cellulolytic enzymes and therefore useful as fuel material for MFC. The drawback of this process was that the hemicellulose recovery was moderate due to sugar degradation.

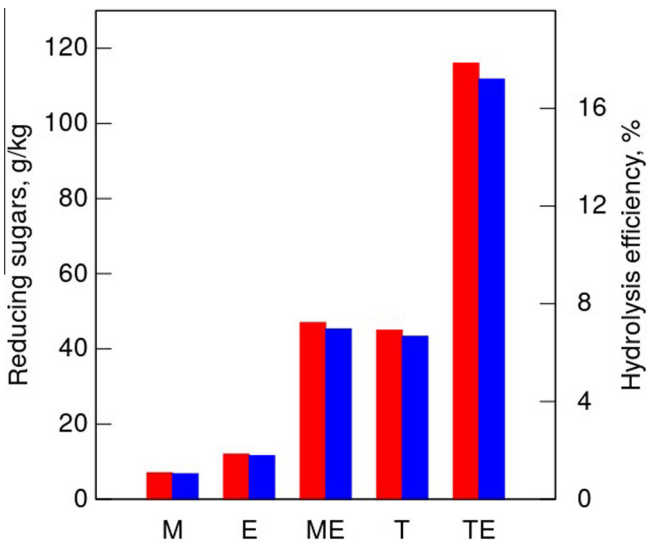

Fig. 1. Release of sugars (left) and efficiency of hydrolysis (right) as a function the saccharification method at 10% (w/w) biomass.