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Full Length Article

The use of ionic liquid pretreatment of rye straw for bioethanol production

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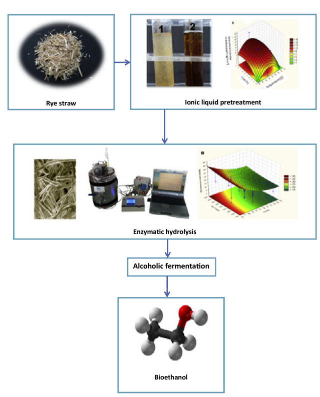
HIGHLIGHTS

- Rye straw is a second-generation substrate that can be used in bioethanol production.
- Pretreatment with EMIM OAc led to a 3x increase in the content of reducing sugars.
- The results of the optimization process are illustrated with response surface models.

GRAPHICAL ABSTRACT



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ABSTRACT

Rye straw was pretreated with ionic liquid and subjected to enzymatic hydrolysis to produce reducing sugars. The experiment had a Box-Behnken design. The aim of the optimization process was to maximize the yield of reducing sugars after enzymatic hydrolysis of rye straw and to determine the optimal conditions for biomass purification with ionic liquid and for enzymatic hydrolysis. The input variables for rye straw pretreatment were temperature, time and quantity of ionic liquid, and the input variables for enzymatic hydrolysis were time, temperature and the quantity of *T. reesei* and *A. niger* enzymes. The yield of reducing sugars was highest when rye straw was pretreated under the following conditions: time – 2 h, temperature – 120 °C, quantity of ionic fluid – 10 ml/10g DM rye straw, and subjected to enzymatic hydrolysis under the following conditions: time – 72 h, temperature – 50 °C, quantity of cellulase from *T. reesei* – 350 µl, quantity of cellobiohydrolase from *A. niger* – 150 µl. Model validation did not reveal significant differences between the approximated and measured values.

1. Introduction

The progress made in the production of new generation liquid fuels relies on the availability and processing suitability of inedible

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biological materials as renewable sources of energy. Biological substrates can be processed to produce ethanol, a second generation biofuel which contributes to greater reduction in CO_2 emissions than petroleum combustion.

In Poland, ethanol is also obtained from molasses, a by-product of sugar production. Ethanol derived from potatoes is used mainly in the food processing industry. Potato tubers are characterized by low energy value, therefore, they are not used in the production of ethanol biofuel.

Raw materials are subjected to various types of preliminary treatments to increase the efficiency of ethanol extraction from starchy vegetables. Such processes include grinding, mashing, steaming, enzymatic hydrolysis and thermal hydrolysis. Similar treatments are applied to obtain ethanol from lignocellulosic biomass [1].

The source of sugars that undergo fermentation is cellulose, a fraction of lignocellulosic biomass. Regardless of the substrate, ethanol production always involves the following stages:

- pretreatment of raw materials – breakdown of complex carbohydrates into simple sugars,
- alcohol fermentation – conversion of simple sugars to alcohol and carbon dioxide,
- distillation, rectification and dehydration.

The profitability of ethanol production could be increased by maximizing the efficiency of lignocellulosic biomass conversion. A standardized method for biomass processing is not easy to develop, and it is influenced by numerous factors, including the type of lignocellulosic material applied in production [2]. Sugars can be extracted from cellulose with the involvement of various physical, physicochemical, chemical and biological methods. Many of them are too costly to be applied on an industrial scale or pose environmental risks by generating toxic waste and by-products. For this reason, the pretreatment of lignocellulosic materials continues to attract the interest of researchers around the globe. The choice of an appropriate method for the pretreatment of lignocellulosic material is a very important consideration because it determines the success of subsequent stages of bioethanol production. Lignocellulosic biomass does not undergo bioconversion easily because it constitutes a densely packed and nearly crystalline complex of three polymers: cellulose, hemicellulose and lignin joined by covalent and hydrogen bonds [1]. The degradation of lignocellulosic matrices and their hydrolysis products has been described by [2,3]. The use of cellulose biomass in ethanol production has also been discussed by Faraco and Hadar [4], Garvey et al. [5], Jessen et al. [6], Miao et al. [7], Sun and Cheng [8].

The aim of pretreatment is to separate lignin from cellulose, increase the proportion of amorphous cellulose which is more susceptible to enzymatic hydrolysis, increase material porosity, eliminate the loss of simple sugars, and create hydrolysis and fermentation inhibitors. In the absence of cellulose pretreatment, hydrolysis yield is estimated at 20% of the theoretical value. Pretreatment increases the effectiveness of cellulose breakdown by 90% and more, subject to the applied method [9]. Lignocellulosic materials can be pretreated with the use of ionic liquids which are not environmentally toxic. Ionic liquids containing the imidazolium cation can replace popular organic solvents because they do not produce toxic fumes [10]. The properties and practical applications of selected ionic liquids have been discussed by Li et al. [11], Jain et al. [12], Liu et al. [13], Stewart et al. [14], and Zhu et al. [15].

Swatlowski et al. [16] demonstrated that high concentrations of chloride ions and the presence of the chloride anion in ionic liquids break intramolecular and intermolecular hydrogen bonds in cellulose chains. The solubility of cellulose in ionic liquids is also determined by the addition of water. The addition of only 1% of water to the ionic liquid promotes the formation of new hydrogen bonds. For this reason, water is used to precipitate cellulose from the ionic liquid.

The acetate anion (OAc^-) is a hydrogen bond acceptor which dissolves cellulose more effectively than the chloride anion (Cl^-) [17]. Zhang et al. [18] dissolved cellulose in 1-ethyl-3-methylimidazolium acetate [(C_2MIM)OAc] and observed that the acetate anion in the ionic liquid promotes the formation of hydrogen bonds between cellobiose molecules.

Wang et al. [17] demonstrated that the type of cation also affects the solvation behavior of cellulose. Liu et al. [19] observed that hydrophobic reactions between the imidazolium cation in the ionic liquid and glucopyranose molecules in the cellulose chain play an important role in cellulose solubility. Despite the above, the role of cations in cellulose solubility has not been fully elucidated and requires further investigations [20,21].

Ionic liquids are widely used as electrolytes, catalyzers, wood preservatives [10], detergent solutions (antifeedants) [19] and herbicides [22–24]. Imidazolium-based ionic liquids are also used as lignocellulose solvents that separate lignin from cellulose and facilitate the breakdown of cellulose to simple sugars.

The objective of this study was to optimize the pretreatment and enzymatic hydrolysis of rye straw and to identify process conditions which maximize the content of reducing sugars. Ethanol yield from lignocellulosic biomass is determined by the composition of the processed material (proportions of cellulose, hemicellulose and lignin) and the availability of fermentable sugars. For this reason, bioethanol production from rye straw requires the determination of optimal pretreatment and enzymatic hydrolysis conditions, which play a key role in the extraction of reducing sugars. The study also attempted to determine whether reducing sugars can be effectively extracted with small amounts of ionic liquid and cellulolytic enzymes which are expensive.

2. Materials and methods

2.1. Materials

The lignocellulosic substrate for the production of bioethanol was rye straw from a conventional production system in the Region of Western Pomerania (Poland). Straw was pretreated with the use of ionic liquid – 1-ethyl-3-methylimidazolium acetate (IoLiTec Ionic Liquids Technologies GmbH) whose structural formula is presented in Fig. 1.

Enzymatic hydrolysis was carried out with two enzymatic preparations: cellulase from *Trichoderma reesei* ATCC 26921 (Sigma Aldrich, 7 FPU$\cdot g^{-1}$ DM substrate) and Novozyme 188 cellobiase (*Aspergillus niger*, 30 CBU$\cdot g^{-1}$ DM substrate).

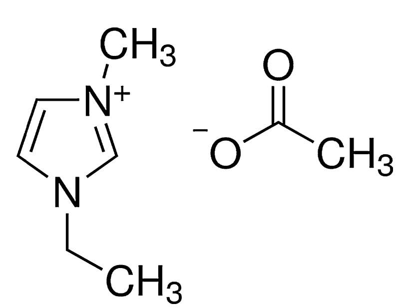

Fig. 1. Structural formula of 1-ethyl-3-methylimidazolium.