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The freezing pre-treatment of lignocellulosic material: A cheap alternative for Nordic countries

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ABSTRACT

Using lignocellulosic biomass as an alternative resource for transportation fuel is an attractive prospect due to its abundance and low cost. Conventional pre-treatment methods such as steam explosion or ammonia fibre expansion need technologically complex equipment and high energy input, and they use toxic chemicals in order to achieve high glucose and ethanol yields. In this paper, the freezing pre-treatment of barley straw is investigated as a low energy input and cost-effective alternative pre-treatment method for second generation bioethanol production.

In the freezing pre-treatment method, milled biomass mixed with water was frozen in temperatures as low as −18 °C for a certain period of time and was then thawed to room temperature (around 22 °C). The freezing cycles were repeated several times so that the effect of repeated freezing could be studied. In addition, field experiments were carried out by taking samples of barley straw which had been stored outside, both in bales and swathes during a period of time between September and March in two consecutive years (in winter 2014–2015 and 2015–2016). Freezing pre-treatment was followed by enzymatic hydrolysis and fermentation. Glucose and ethanol yields and, additionally, hydrolysis and fermentation efficiencies were used as indicators of pre-treatment efficiency.

The highest hydrolysis efficiency figure was 19.42%, which was achieved in laboratory tests where the biomass was frozen and thawed a total of four times. The best result from a field test was 10.28% from straw which had been stored in a swathe and which has been gathered in March. Fermentation yields ranged up to 88.80 g per kilogramme of biomass. Field tests showed that in the bale the temperature never fell below freezing and therefore the pre-treatment was not effective. When in the swathe the straw does freeze through, but the winter in Estonia was too changeable for this method to work effectively.

1. Introduction

Lignocellulosic biomass has been widely used for a long time as an energy source. It is most commonly used for heating and electricity production by burning it directly. Despite this, most of the primary energy (up to 80%) which is consumed worldwide today is produced from fossil fuels. From this, a total of 58% is used for the transportation sector alone [1]. As the demand for energy rises, new, cheap, and sustainable alternatives for liquid fuel production are needed. One alternative is to use bioethanol as engine fuel.

Global bioethanol production in 2015 was 98.3 billion litres, the majority of which was first generation bioethanol which had been produced from food crops such as sugar cane, maize, etc [2]. Given the fact that the world's population is increasing every year and, in some areas, food is somewhat lacking, using food crops as fuel feedstock is considered immoral. In order to decrease the food-versus-fuel competition which is associated with first generation bioethanol, an alternative has to be found in order to prevent food crops being used as fuel production feedstock [3,4]. At the moment lignocellulosic biomass is considered to be the most favourable alternative for biofuel production due to its abundance, its biodegradability, its ability to be renewed, and its cost-effectiveness [5–8]. Lignocellulosic biomass is made up either from the non-edible residue of food crop production or the non-edible whole plant biomass [9], and makes up the majority of the cheap and abundant non-food materials which are available from plants [10,11]. By using lignocellulosic biomass for biofuel production, we

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can solve two problems at the same time. We can valorise different residues (agricultural residues, urban wastes, etc) [12], and can also eliminate food-versus-fuel competition [13].

Plants consist primarily of plant cell walls of which about 70% are made up of various polysaccharides (mainly cellulose 40–50% and hemicellulose 20–30%) [14,15], which can be used for ethanol production with the right conversion treatment [16]. Therefore, lignocellulosic biomass as a potential ethanol production feedstock has attracted the attention of many researchers worldwide.

Ethanol production from lignocellulosic biomass using the traditional biochemical route consists of four main steps: pre-treatment, hydrolysis, fermentation, and distillation [6]. The pre-treatment is used to break down the structure of the lignocellulosic material to enable better access to cellulose for enzymes in the next process step. The purpose of the pre-treatment is to increase the porosity of the biomass, reduce the degree of polymerisation, and ensure the removal of the lignin [17,18]. The conversion of pre-treated material to ethanol includes two processes: the hydrolysis of cellulose into monomeric sugars, and the fermentation of the sugars into ethanol [9,19]. The hydrolysis is usually catalysed by cellulase enzymes or chemically using acids [14,20], and the fermentation is carried out by yeasts or bacteria [21]. At the moment, the weakest link in the bioethanol production process is the pre-treatment step. While a wide selection of different pre-treatment methods have been proposed, an optimum and cost-effective pre-treatment process is yet to be found.

Although several commercial lignocellulosic ethanol production plants have started work worldwide, second generation bioethanol is still not preferred due to its high cost. The high cost is caused by the complexity of the pre-treatment process [22]. Today, the most commonly used methods for opening the biomass cellular structure for enzymes are chemical pre-treatment, steam explosion, ammonia fibre explosion (AFEX), SO_2, CO_2, N_2, and air explosion [13,23–26]. These methods result in high sugar and ethanol yields; however, these methods are very energy-intensive or they use chemicals which are expensive and offer a potential threat to the environment [27,28]. Due to these expensive pre-treatment options, the price of the lignocellulosic ethanol is high and is therefore not competitive against the use of fossil fuels.

In this paper a new pre-treatment method - the freezing pre-treatment - is being studied. The method is based on the change in the volume of water due to the change in state from liquid to solid. The change in state is caused by a decrease in temperature, which causes the water to freeze. The biomass, which is mixed with small amount of water, is placed in a freezer until the water freezes. During this process, the water diffuses into the biomass and when the volume of water increases during freezing the structure of the cell walls is broken. This method enables the cellulosic structure of biomass to be opened up and increases the accessible surface area of the biomass for enzymatic hydrolysis. The freezing pre-treatment uses no chemicals or catalysts, which makes it environmentally-friendly and an economically cheap method. In Nordic areas, this pre-treatment method can be used in accordance with the natural change of the seasons when the slightly moistened biomass is left in an open field so that the moisture in the biomass freezes and thaws due to changes in the outside temperature. In this case, there is no energy input into the pre-treatment process.

In this paper, the freezing pre-treatment method was investigated on barley straw as a cheap pre-treatment method for Nordic countries. Laboratory and field experiments were carried out to investigate the effects of freezing on glucose and ethanol yields in a standard three-step bioethanol production process. In addition, investigations were carried out in regard to the Estonian winter. Would it be suitable for implementing such a pre-treatment method?

2. Materials and methods

2.1. Biomass

The barley straw was used as feedstock because it is one of the most common crops grown in Estonia with a relatively high cellulose content. Since straw production per hectare is between 1.6 and 2.0 tons [29] and the sown area was 132,600 hectares [30], the feedstock potential in 2016 for lignocellulosic bioethanol production was between 212,160–265,200 tons.

Samples were gathered once a month from both swathes and bales that were being stored outside. The experiments with bales were conducted during the winter of 2014–2015, and with swathes during the autumn and winter period between September 2015 and March 2016. Biomass collected in September was used in laboratory freezing pre-treatment experiments.

2.2. Pre-treatment

The cellular structure of the biomass was broken down using two different approaches. For the laboratory tests, milled and moistened biomass was frozen in a freezer. For the field tests, barley straw was left in swathes and bales on the field to freeze.

In the laboratory tests, 100 g of milled dry biomass was moistened with 800 g of distilled water and was then inserted into a closed thermo-box. The thermo-box with its moistened biomass was then placed into a freezer at a temperature of −18 °C so that it could freeze. As changing the freezing temperature did not significantly change the pre-treatment efficiency, only the number of repetitive 24-hour freezing cycles was changed during the experiments. One freezing cycle included leaving the sample in a freezer for 20–24 h following a thawing of the frozen sample to room temperature. Five different experiments in total were conducted. One for the determination of the reference point with the initial unfrozen biomass and four experiments with a different number of 24-hour freezing cycles - freezing the moistened biomass between one to four times. All of the experiments were carried out in triplicate at the very least.

The field experiments took place during the winters of 2014–2015 (with barley straw stored in bales) and 2015–2016 (with barley straw stored in swathes).

During the winter of 2014–2015, several straw bales were left out in the field. For the reference point, the first sample was taken right after baling the straw in August 2014. The following samples were taken at 30, 60, and 90 days after baling the straw.

During the winter of 2015–2016, the barley straw was left outside in swathes. In order to obtain a reference point for the swathes, the first samples were taken in September 2015, immediately after harvesting. During October and November, no samples were taken due to the warm weather. The average temperatures were 13.3 °C in September, 5.8 °C in October, and 4.9 °C in December. In these three months there were only a few night frosts (the minimum temperature measured during these three months was $T_{min} = -8.8$ °C) [31]. Furthermore, averaged samples from bales and swathes were taken after first night frosts, where the temperature fell below −8 °C in December, and from there averages were taken once a month until March.

The samples were thawed and dried at room temperature to a moisture content which was less than 10%, and were milled using a Retch SM 100 mill (Retch GmbH) to a particle size of 1 mm or less. At least three parallel experiments were carried out using all of the samples.