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Fermentation characteristics of acid hydrolysates by different neutralizing agents

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ABSTRACT

Impact of cations in a fermentation broth by calcium, potassium, or sodium hydroxide was investigated. Acid hydrolysate from lignocellulosics is generally neutralized with calcium hydroxide, which is an insoluble salt (known as gypsum) produced in the process. Also, adsorption of monosaccharides on gypsum surface caused the loss of saccharide. To replace calcium hydroxide, potassium or sodium hydroxide which have high water solubility are used. More glucose was obtained by potassium hydroxide neutralization (glucose yield, 29.6 g) or sodium hydroxide neutralization (glucose yield, 38.9 g) than calcium hydroxide neutralization (glucose yield, 18.1 g) which shows less adsorption on the insoluble salt surface. In fermentation with three yeasts (*Saccharomyces cerevisiae*, *Kluyveromyces marxianus*, and *Pichia stipitis*), the sodium ion acts as an inhibitor and does not ferment the acid hydrolysate. However, acid hydroxide neutralized with potassium hydroxide was well fermented within 24 h with more ethanol production than that neutralized with calcium hydroxide.

Introduction

Due to continuous industrial development, the energy demand has been increasing tremendously, resulting in depletion of fossil fuels, increasing greenhouse gas from carbon dioxide, limited resource location in specific countries [1,2]. Moreover, finite reserves of fossil fuels have made the continuous energy supply uncertain and have also led to the fluctuating prices of crude oil. Additionally, the problem of global warming and climate change has occurred owing to the increasing concentration of carbon dioxide in the atmosphere from fossil fuel uses. Therefore, as an alternative to fossil fuels, the concept of renewable energy has gained increased importance in recent years [3]. Bioenergy, which is considered as one of the renewable energy resources, is produced in liquid form unlike other renewable energy resources such as solar, wind, geothermal, hydrogen, and fuel cells. In addition, it is advantageous to use a carbon-neutral energy source so that carbon dioxide in the air can be re-consumed through photosynthesis. Renewable Fuel Standard (RFS) was announced to promote the use of biofuels and reduce the dependency on fossil fuels under the Energy Policy Act of 2005. Bioethanol, a biofuel, is produced by using sugar, starch, and lignocellulosics as raw materials [4]. Sugar- and starch-based materials are easily hydrolysed to monosaccharides,

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resulting in high ethanol production. However, the use of sugar- or starch-based raw materials leads to completion with food crops and deforestation of land [5]. Because of the structural complexity, lignocellulosic materials, including woody biomass are more difficult to hydrolyse than sugar- and starch-based materials [6].

Woody biomass is intricately linked with three main components: cellulose, hemicelluloses, and lignin. In general, wood is made of cellulose (40%–50%), hemicelluloses (15%–20%), lignin (20%–25%), and extractives (5%–10%). Cellulose and hemicelluloses are polymers which can be obtaining monosaccharides and used for bioethanol fermentation [7]. Cellulose is a linear homopolysaccharide made of D-glucose units which are connected by β-(1,4)-glycosidic bonds. Hemicelluloses are hetropolysaccharides made of hexose and pentose units such as D-glucose, D-mannose, D-galactose, D-xylose, and L-arabinose. Galactoglucomannan is composed of D-galactose, D-glucose, and D-mannose, and it is the principal hemicellulose in softwood (about 20%). The hydroxyl groups at C-2, 3 positions in the galactoglucomannan chain are partially substituted by O-acetyl groups on the average on group per 3–4 hexose unit. These acetyl groups are easily cleaved by alkali. Arabinoglucuronoxylan is composed of L-arabinose, D-glucose, and D-xylose and is also present in softwood (5%–10%), whereas hardwood does not contain L-arabinose and has 15%–30% of glucuronoxylan. Glucuronoxylan is the major hemicellulose in hardwood. Glucuronoxylan has O-acetyl groups (about seven acetyl residues per ten xylose units) and 4-O-methyl-glucuronic acid residue (about one uronic acid per ten xylose residues). Besides xylan, hardwood contains 2%–5% of glucomannan, a minor hemicellulose. These differences in the hemicellulose composition led to different hydrolysate composition.

Monosaccharides can be obtained through enzymatic hydrolysis [8] or acid hydrolysis [9,10] from woody biomass. In enzymatic hydrolysis, various enzymes such as endo-glucanase, exo-glucanase, and cellobiase cleave the bonds of cellulose and hemicelluloses by absorption. The main advantage of enzymatic hydrolysis is that it produces a clean reaction product, which does not form any parallel reaction or side extraction without the formation of any fermentation inhibitors. To improve the enzymatic hydrolysis of lignocellulosic biomass, a pre-treatment process is required [11–14]. Higher prices of the cellulases are another bottleneck.

Acid hydrolysis process can convert polysaccharides to the corresponding monosaccharides under appropriate acids and reaction conditions. Acid hydrolysis processes are of two types: dilute acid hydrolysis [15–17] and concentrated acid hydrolysis [18,19]. Dilute acid hydrolysis is generally performed under acid concentration of less than 1% at 160–240 °C for several minutes. Moreover, acid recovery does not require extensive efforts. However, the process has the drawback of forming undesirable by-products (fermentation inhibitors) at high temperatures [20]. Concentrated acid hydrolysis generally obtains more monosaccharides and consequently higher ethanol yield than that obtained under dilute acid hydrolysis. Concentrated acid hydrolysis is carried out under 30%–70% acid concentration and does not produce any fermentation inhibitors because it is carried out at lower temperatures. However, concentrated acid hydrolysis also has a drawback that in this process, it is required to ferment acid hydrolysate for acid recovery because of the use of a large amount of acids.

In acid hydrolysis, it is essential to remove the acid from the solution prior to enzymatic hydrolysis. Acid in acid hydrolysate is typically removed by two techniques: ion exchange [21] and neutralization [22]. Since the discovery of the ion exchange phenomenon in the early 19th century, this technique has been used for various applications such as desalination of sea water [23], water purification [24], and amino acid purification [25] to develop a variety of stationary phases. In Japan, the Hokkaido process has been applied to acid recovery technique which depended on diffusion dialysis with an anion exchange membrane. Sulphate anion present in acid hydrolysate was removed by exchanging the sulphate anion with a stationary anion in the ion exchange resin membrane. It was then recovered and concentrated for re-use. After ion exchange chromatography was developed, more than 90% of sulphuric acid could be recovered within a short period. However, ion exchange chromatography is not without its drawback: it is difficult to apply it to a continuous process. Therefore, a simulated moving bed (SMB) was developed in the 1960s, which allows the recovery of sulphuric acid by periodically changing the flowing mobile phase and the position of the fixed stationary phase.

In neutralization technique, sulphuric acid from acid hydrolysate is generally neutralized with neutralizing chemicals such as calcium hydroxide or calcium carbonate [22]. Insoluble calcium sulphate forms in the neutralization process, which is referred to as gypsum. Gypsum has been used in board manufacturing, cement, and medicine industries. Gypsum produced by neutralization includes impurities such as sugar, ash, and lignin from biomass, which are discarded. However, this increases the disposal cost in industrial processing. An additional problem occurs if filtering is used to neutralize acid hydrolysate: a large amount of monosaccharides is lost by absorption to gypsum.

In this study, monosaccharide yields and fermentation properties were compared by using different neutralizing chemicals (sodium hydroxide or potassium hydroxide) to solve the disposal problem of gypsum and monosaccharide loss occurring owing to the use of calcium hydroxide and calcium carbonate. When sodium hydroxide or potassium hydroxide are used, some of the resulting salt is present in a cationic form in the aqueous solution owing to its high solubility. The present paper investigates the effect on cations in acid hydrolysates by using the following yeasts: *Saccharomyces cerevisiae*, *Kluyveromyces marxianus*, and *Pichia stipitis*.

Materials and methods

Materials

A 30-year-old tulip tree (*Liriodendron tulipifera* L.) was obtained from Chungbuk National University's experiment forest located in Cheongju-si, Chungcheongbuk-do, Korea. Tulip tree chips were cut by hand and then milled to less than 0.2 mm by using the IKA MF 10B grinder. The milled tulip tree was kept in the air-dried state. Sulphuric acid (purity above 95.0%) and calcium hydroxide (purity above 95.0%) were purchased from

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