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Research paper

Persulfate oxidizing system for biomass pretreatment and process optimization

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ABSTRACT

The functions of radicals in the pretreatment of lignocellulose remain a fascinating topic about which there are more questions than answers. The effect of persulfate-based radical species on lignin degradation and carbohydrate yield was investigated. Wheat straw was pretreated with three persulfate activation systems which generated $OH^{\bullet}$, $SO_4^{2-\bullet}$, and $O_2^{\bullet-}$. Radical species were monitored using nitrobenzene, anisole, and hexachloroethane, respectively. Pretreatment variables affecting sugar yield were optimized by using the response surface method based on central composite design. Enzymatic hydrolysis and compositional analysis were performed to quantify changes in biomass composition, lignin removal, and glucan yield. Fourier transmission infrared spectroscopic and scanning electron microscopy were used to characterize the effect of pretreatment on biomass structure. The maximum sugar yields were 66.8%, 49.4%, and 41.7% in base, heat, and hydrogen peroxide activated persulfate, separately, while untreated material showed only 3.7% glucan yield. The radical analysis confirmed the existence of radicals in these three systems. The results from compositional analysis and Fourier transmission infrared spectroscopic provided proof that parts of lignin and hemicellulose were degraded after the treatment. Scanning electron microscopy indicted that radical pretreatment converted the smooth surface of wheat straw to that of scattered, uneven morphology. Base-activated persulfate, capable of producing sulfate radical, hydroxyl radical, and superoxide anion radical was demonstrated as an efficient radical system to treat biomass.

1. Introduction

One of the main sources of renewable feedstock to produce green fuels is lignocellulosic biomass which exists in abundance, composed mainly of agricultural and forestry residues, and can be degraded by enzymatic hydrolysis to become fermentable sugars. Fermentable sugars then can be converted to value-added products and fuels [1]. Howsoever, the most important challenge in this process is the complex biomass structure which makes its decomposition difficult for enzymatic hydrolysis [2]. Lignin as one of the constituents of plant's cell walls has critical structural that make lignocellulose a complex network of cellulose and hemicellulose resistant to degradation. The breakdown of the lignocellulosic structure into specific chemicals is difficult because of the recalcitrance of lignin and the intricate structure of the plant cell wall. Therefore, the removal or modification of lignin is prerequisite for enhancing the conversion of cellulose to fermentable sugars by enzymes [3]; this removal is made feasible by pretreatment. An ideal pretreatment protocol removes or modifies lignin, reduces biomass recalcitrance, prevents cellulose degradation and limits the formation of microbial inhibitory compounds [3,4]. Most existing pretreatment techniques are expensive as they are operated under harsh reaction conditions that require the intensive input of energy and with the assistance of chemicals. On the other hand, biological systems such as fungi and termites can modify lignocellulosic biomass under natural conditions. White rot fungi, *Phanerochaete chrysosporium,* generates reactive oxygen species which catalyze the oxidation of lignocellulosic materials. Lignin peroxidases (LiP) and manganese peroxidases (MnP) in white rot fungi generate free radicals that are responsible for biomass deconstruction. Most of the white rot fungi contain MnP rather than LiP, MnP can enhance the enzymatic degradation of lignocellulose by utilizing H_2O_2 to oxidize Mn^{2+} to Mn^{3+} [1]. These systems can inspire the development of industrial processes that are more sustainable. Through closer inspections of biological processes, it is recognized that the mechanisms of lignocellulosic degradation are oxidative and hydrolytic. In the oxidative mechanism, reactive oxygen species (ROS) cause lignin degradation [5]. In the hydrolytic mechanism, monomeric sugars are released when hydrolytic enzymes break glycosidic linkages in cellulose and hemicellulose [6].

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ROS are a group of ions and free radicals with oxygen atoms that normally have a short lifetime and are unstable and highly reactive. Superoxide radical anion ($O_2^{\bullet -}$), peroxide radical anion ($O_2^{\bullet 2-}$), peroxyl radical ($ROO^{\bullet}$), alkoxyl radical ($RO^{\bullet}$), and hydroxyl radical ($HO^{\bullet}$) are common examples of ROS [7].

Hydrogen peroxide is a well-known strong oxidizing agent with a high redox potential. It can be degraded to form reactive oxygen species and hydrogen peroxide anions, so it is commonly utilized for radical and oxidative pretreatment. Hydrogen peroxide is a combination of oxygen and water that naturally decomposes into its components. The oxygen bonds in H_2O_2 can be broken and generate hydroxyl radicals, which are able to degrade lignin [8]. The radical system in combination with other kinds of pretreatment proved to have a notable effect on sugar yield. Chemical pretreatment of rice hulls with H_2O_2 and *Pleurotus ostreatus* as a fungi biological treatment [9] showed high lignin degradation and high sugar yield under optimum conditions of H_2O_2 (0.85 mol/L, 48 h) and 18 days pretreatment with *P. ostreatus*. Lucas et al. [10] also examined two-step method by investigating oxidative delignification of poplar wood at room temperature with manganese acetate and hydrogen peroxide. After pretreatment, optical and Raman microscopy confirmed lignin oxidation, and glucan yield of the treated biomass was 20–40% higher than that of the raw material.

Ozone is also commonly used to disrupt the structure of many different lignocellulosic materials such as wheat straw, bagasse, pine, peanut, cotton straw and poplar sawdust [11–13]. Ozonolysis, well-known as an oxidation method, is capable of producing radicals and has an affinity to attack high electron density areas of the lignin structure [14]. Ozone pretreatment alone is not very effective at degrading lignin and cannot result in high sugar yields. However, a combination of ozonolysis with other pretreatment processes including ozone-dioxane pretreatment [14], ozone-wet disk milling pretreatment [15], alkaline-ozonolysis [16], and acid-ozone pretreatment [17] exhibited promising results [15].

White-rot and brown-rot fungi usually are considered as a model oxidative system in which lignin is degraded via Fenton chemistry. Fenton reaction is a process of hydrogen peroxide decomposition to reactive hydroxyl radicals involving soluble ferrous ions. Fenton reaction refers to Henry John Horstman Fenton who discovered this method in 1894. The reaction mechanism was further investigated by Haber and Weiss in 1934, and this oxidizing process has attracted lots of attention in organic compounds oxidation [18,19]. The degradation of lignocellulose materials by fungi is caused by some enzymes and Fenton's reagent [20]. The production of extracellular H_2O_2 by wood-rotting fungi was demonstrated by Koenigs [21], and he pointed out fungi uses H_2O_2 and Fe^{2+} to degrade biomass structure. In order to mimic this biological system, Fenton reaction was used to treat four different biomass compounds, which led to 212% increase in enzymatic saccharification of the biomass relative to the raw material, although a minimal decrease occurred in acid-insoluble and acid-soluble lignin feedstock [22]. Fenton reaction typically cannot degrade lignin but convert carbohydrate to sugar in considerable amounts [23]; the reaction needs long residence times or second pretreatment techniques. For instance, Fenton reaction was combined with a sonocatalytic reaction to generate more hydroxyl radicals. The resultant lignin degradation was 60% while Fenton alone degraded 49.9% of lignin, and the enzymatic saccharification increased by 25% [24].

The common limitations of radical/oxidative systems include high chemical input, low stability, short lifetimes, poor solubility of the reagents, low rate of radical generation, pH dependence, and insufficient delivery of oxidants to the treatment zone [25]. A novel system that has potential to overcome these limitations is persulfate-based oxidation process. Persulfate, with a standard oxidation-reduction potential of 2.1 V, is a stable oxidation agent that can act as a direct oxidant, or it can decompose to other radical species by activation. Persulfate can produce hydroxyl ($OH^{\bullet}$), sulfate ($SO_4^{2\bullet}$), and superoxide anion ($O_2^{\bullet -}$) radicals with hydroxide anions, heat, ultraviolet, gamma radiation, hydrogen peroxide and transition metals as activators [26]. Sulfate and hydroxyl radicals are both strong oxidants, however, the sulfate radical is a more stable oxidant, is pH independent and has a longer half-life in comparison with the hydroxyl radical [27]. All are factors that support using the persulfate system to take advantage of both sulfate and hydroxyl radicals as well as the superoxide radical anion.

The fact that persulfate decomposition results in a combination of powerful oxidative agents, reductive species, and nucleophilic ones [5,28,29] makes it a desirable system for attacking bond linkages of lignin. It is thus hypothesized that the combination of radicals is promising in providing a treatment matrix with greater reactivity. The early study [30] investigated the usefulness of heat activated persulfate oxidative strategies for biomass pretreatment, where rice straw was pretreated by heat activated persulfate. Rice straw was treated by potassium persulfate at concentrations from 5 to 100 mmol/L and at pH 3. Reaction temperatures were adjusted to 80, 100, 120, and 140 °C, and biomass was treated under these conditions for different residence times (0.5–3 h). Based on enzyme digestibility, the optimum treatment was achieved with 75 mmol/L of potassium persulfate at 120 °C for 2 h where the lignin content changed from 19.6% in raw material to 18.96% after pretreatment, and the glucan and xylan content decreased from 35.30% to 18.50% to 31.90% and 14.28%, respectively. The enzymatic digestibility improvement, biomass physical changes, and an increase in cellulose crystallinity index correlated to persulfate anions and heat. However, the exact radical species and their existence were not measured. The goal of this research is, therefore, to elucidate the physical and chemical processes associated with the function of persulfate-based radicals in biomass pretreatment and describe how each activation method can affect sugar yield based on its capability to produce different kinds of radicals.

2. Materials and methods

2.1. Overview

In this study, sodium persulfate was activated by hydroxide anions (SPB), heat (SPH), and hydrogen peroxide (SPHP). Optimization of SPB, SPH, and SPHP was carried out to convert wheat straw to sugars using a central composite design (CCD) for response surface method (RSM). Design Expert software 7 was used to identify and optimize key independent factors in the pretreatment process (persulfate concentration, the amount of activator, and time of reaction) and their effect on the dependent variable (glucan yield). Pretreated samples were analyzed by compositional analysis, enzymatic hydrolysis, Fourier transmission infrared (FTIR), and scanning electron microscopy (SEM). Hydroxyl, sulfate, and superoxide radicals were tracked and measured by using nitrobenzene, anisole, and hexachloroethane, respectively to determine which activated methods generate a diverse mixture of radicals with higher concentration.

2.2. Reagents

Sodium persulfate, anisole, and hexachloroethane were purchased from Sigma Aldrich. Sodium hydroxide and nitrobenzene were obtained from J.T. Baker. Hydrogen peroxide and n-hexane were purchased from Fisher Scientific. E pure water used in this process was purified to $> 18\ M\Omega\ cm$.

2.3. Milling of wheat straw and particle size separation

Wheat straw (*Triticum aestivum*) was obtained from the Grange Supply Co. in Pullman, WA. It was collected from the remaining stalks during the grain harvesting process from local Whitman County's farms and stored in dry sheets in the air at ambient conditions. The stored wheat straw which has not been degraded or decayed was hammer milled at the Washington State University's Wood Materials and