Effects of Steam Explosion on Bagasse Specific Surface Area and Grafting Degree of Acrylamide-Grafted Bagasse

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The effect of steam explosion pretreatment conditions, such as steam explosion pressure, maintained pressure time, and bagasse water content, on bagasse specific surface area were investigated through single-factor experiments. After determining the optimal pretreatment conditions, bagasse graft acrylamide was prepared by grafting polymerization reaction of the acrylamide monomer onto the pretreated bagasse. The effects of surface area on the grafting degree were analyzed. Results showed that the grafting degree increased with increasing specific surface area. The optimized steam explosion pretreatment conditions were as follows: steam explosion pressure, 2.0 MPa; pressure maintaining time, 60 s; and bagasse water content, 25%.

Keywords: Bagasse; Steam explosion; Specific surface area; Graft copolymerization

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INTRODUCTION

Bagasse is a complex material that contains lignin and cellulose as its major constituents, and it has several advantages, including low cost, non-toxicity, renewability, and biodegradability. It contains large amounts of hydroxyl groups and can easily be modified (Wang *et al*. 2010). Chemical derivatizations, based on reactions with hydroxyl groups at the biomass surface, have the potential to improve its performance in a wide range of applications. However, the extensive interactions among hydroxyl groups at the bagasse surface can limit the reactivity of the material due to the extensive formation of intermolecular and intramolecular hydrogen bonds (Ma *et al*. 2014; Fernandes *et al*. 2015). Therefore, in applications where a high degree of surface derivatization is needed, it may be necessary to process the bagasse surface before modification. Hydroxyl groups in the biomass also may be inaccessible to chemical reagents or enzymes due to the presence of lignin or due to a dense physical structure.

The pretreatment method plays an important part in the lignocellulose modification process. It can damage the cellulosic fiber structure through hydrolysis of hemicelluloses and partial removal of lignin. There are a variety of existing pretreatment methods. These include chemical methods, such as strong/weak acid and alkali treatments. Also there are physical and mechanical combination methods, such as ball milling, as well as physical and chemical combination methods, such as steam explosion (Elliston *et al*. 2015; Su *et al*. 2015). Among them, steam explosion is one of the most effective pretreatment methods for improving the accessibility and the specific area of the bagasse surface. Although the method requires only water and high pressure steam, which are both physical reactions, chemical reactions occur during this process as well. The steam explosion breaks down the bagasse *via* the instant release of pressure, which leads to the degradation of hemicellulose and lignin reticular structure, a decrease in bagasse cellulose crystallinity, and an increase of the porosity of bagasse and specific surface area. These outcomes improve the accessibility of the surface (Qin and Chen 2015; Sui and Chen 2015; Wang *et al*. 2015).

Acrylamide is a cheap and easily purchased chemical compound that possesses strong affinity toward heavy metal ions (Pulat and Nuralin 2014). Graft copolymerization is a commonly used approach for cellulose modification and bagasse fiber modification, because it not only retains the excellent inherent properties of the fibers but also presents an enhanced performance of the branched polymer (Pulat and Isakoca 2006; Ma *et al*. 2012). In principle, the grafting of acrylamide onto suitably pretreated bagasse fibers can be considered as a way to prepare an adsorbent material for use in removing heavy metal ions from aqueous systems. The grafting degree is an important indicator for evaluating the functionality of modified bagasse during this process, and the grafting degree is related to the specific surface area. In the present investigation, the effects of steam explosion pretreatment conditions on the bagasse specific surface area were investigated. The relationship between the specific surface area of bagasse and the grafting degree was also studied by the grafting polymerization reaction of acrylamide monomer onto the pretreated bagasse.

EXPERIMENTAL

Materials and Reagents

All the reagents used in this experiment were of analytical grade (if not specified), and all solutions were prepared with deionized water. Bagasse was obtained from a local sugar factory. The bagasse was ground, sifted, and then dried in a vacuum oven for 24 h at 60 °C. Acrylamide (AM, Sigma-Aldrich Co.), acetic acid, ammonium iron (II) sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2.6H_2O$), hydrogen peroxide (H_2O_2), and ethanol were used as received.

Steam Explosion Pretreatment of Sugarcane Bagasse

The bagasse was first washed by stirring with deionized water at 80 °C for 2 h and then dried at 105 °C for 10 h. Deionized water was sprayed on the material to obtain bagasse with varying water contents. The resulting bagasse was pretreated with steam-explosion at a certain pressure for some time. Finally, the bagasse was washed with distilled water and 0.5% acetic acid, and then dried at 60 °C for 24 h.

Preparation of Bagasse Grafting Acrylamide

The following steps were performed according to the optimized graft conditions presented in previously published work (Ma *et al*. 2014). First, 2.0 g of pretreated bagasse and 10.0 g of acrylamide were dissolved in 100 mL of deionized water in a 250-mL flask. Then, 0.06 g of the catalyst, $(NH_4)_2Fe(SO_4)_2.6H_2O$, and 0.5 mL of H_2O_2 were added sequentially. The grafting reaction was carried out at 50 °C for 3 h in the absence of air. After reaction, the grafted fibers were boiled in water, and then changed for fresh water with continued boiling to remove the residual monomer and homopolymers. The grafted bagasse was washed with distilled water and 95% ethanol, and dried at 50 °C for 48 h. The grafting degree (G%) was obtained according to Eq. 1,

$$G\% = \frac{Wg - Wo}{Wo} \times 100 \quad (1)$$

where W_o and W_g are the weights of the bagasse and grafted bagasse, respectively.

Specific Surface Area Measurements and Morphology Characterization

N_2 adsorption-desorption isotherms were acquired at -196 °C with an automatic gas adsorption instrument (ASAP2020, Micromeritics Corp., USA) at relative pressures ranging from 10^{-6} to 1. V_{total} was calculated based on the N_2 amount adsorbed at P/P_0 = 0.95. S_{BET} was calculated using the Brunauer-Emmett-Teller (BET) method.

Scanning electron microscope (SEM, PRO X, Phenom, Netherlands) was used to observe the morphology and microstructure of the bagasse samples.

RESULTS AND DISCUSSION

Effects of Steam-Explosion Conditions on Specific Surface Area

Effect of pressure

The effect of the steam explosion pressure on the specific surface area was investigated by varying the setting of the steam explosion pressure. The valves used in this study were 1.0, 1.5, 2.0, and 2.5 to 2.8 MPa, and the results are shown in Fig. 1. The specific surface area first increased with increasing steam explosion pressure, and it decreased rapidly when the pressure exceeded 2.0 MPa. This may be due to a large extent of hemicellulose saccharification and degradation in the bagasse under high steam pressure. The maximum specific surface area that bagasse reached was 5.84 m^2/g, which occurred when the pressure was 2.0 MPa (Fig. 1).

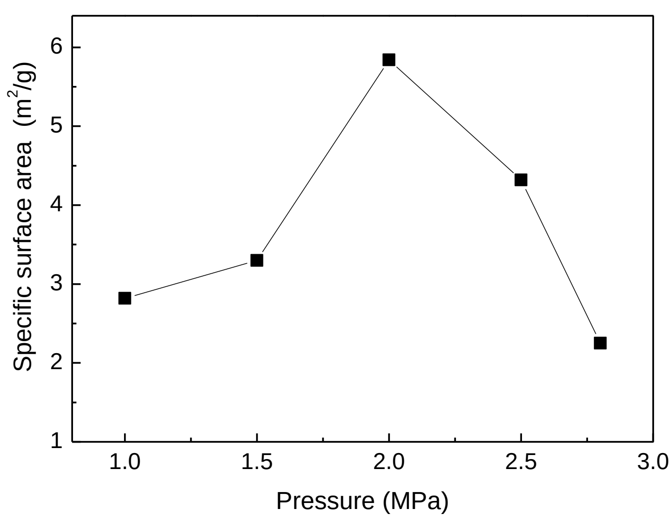

Fig. 1. Effect of steam-explosion pressure on specific surface area

Effect of maintained pressure time

The effect of pressure maintaining time on specific surface area was investigated by maintaining steam pressure for different amounts of time. The maintaining times used in this study were 30, 60, 90, or 180 s, and the results are shown in Fig. 2. The proper maintaining time to obtain the maximum specific surface area was determined to be 30 to 60 s. When the pressure maintaining time was longer than 60 s, the specific surface area decreased rapidly with increasing maintaining time. Steam explosion can lead to the cleavage of some hydrogen bonds and pyrolysis of polymers such as cellulose, hemicellulose, and lignin. The longer the pressure maintaining time, the more water vapor permeates into the intracellular matrix of the bagasse, which promotes the degradation of the lignin and hemicellulose intercellular layer.

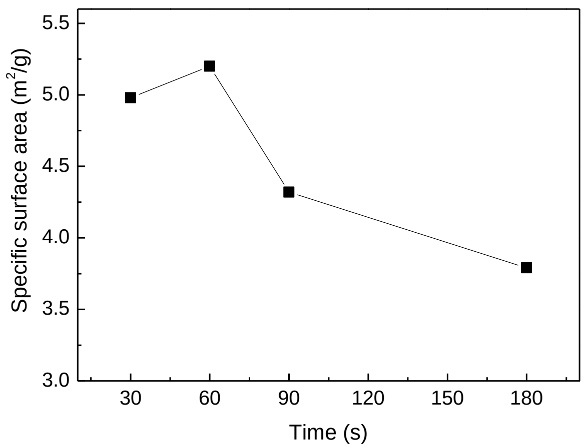

Fig. 2. Effect of maintained pressure time on specific surface area

Effect of water content

The effect of bagasse water content on specific surface area was investigated by varying the water content of the bagasse. This study used water content values of 0%, 25%, 50%, and 75% to carry out the steam explosion experiments, and the results are shown in Fig. 3. Results showed that extremely high or low water contents are not ideal. The 25% water content bagasse reached the maximum surface area of 6.47 m^2/g.

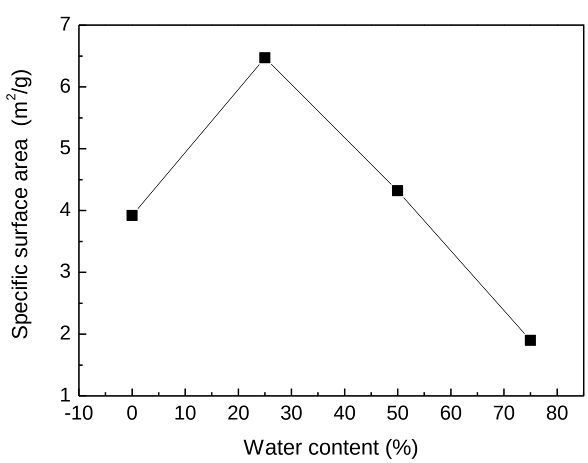

Fig. 3. Effect of water content on specific surface area

When there is too much water in the bagasse, the steam explosion process is separated into two stages: the vapor cooking stage and the steam explosion stage. In the first stage, a large amount of hemicellulose was hydrolyzed into the bagasse as a result of water vapor infiltration, which weakens the adhesion of cellulose and lignin. In the second stage, steam explosion leads to biomass pyrolysis and the dissolution of some insoluble substances. For example, cellulose was transformed into soluble polysaccharides, which promote lignin softening and the degradation of intercellular layers (Su *et al*. 2015).

It can be seen that the specific surface area of bagasse was greatly affected by the three aforementioned factors. In order to increase the specific surface area and porosity of the bagasse and to increase the accessibility of bagasse surface, the optimized steam explosion pretreatment conditions are as follows: steam explosion pressure, 2.0 MPa; pressure maintaining time, 60 s; and bagasse water content, 25%.

Surface Appearance

Figure 4 shows SEM images of different steam explosion pretreated bagasse, and it can be seen that steam explosion pressure has a great influence on the surface of the material.

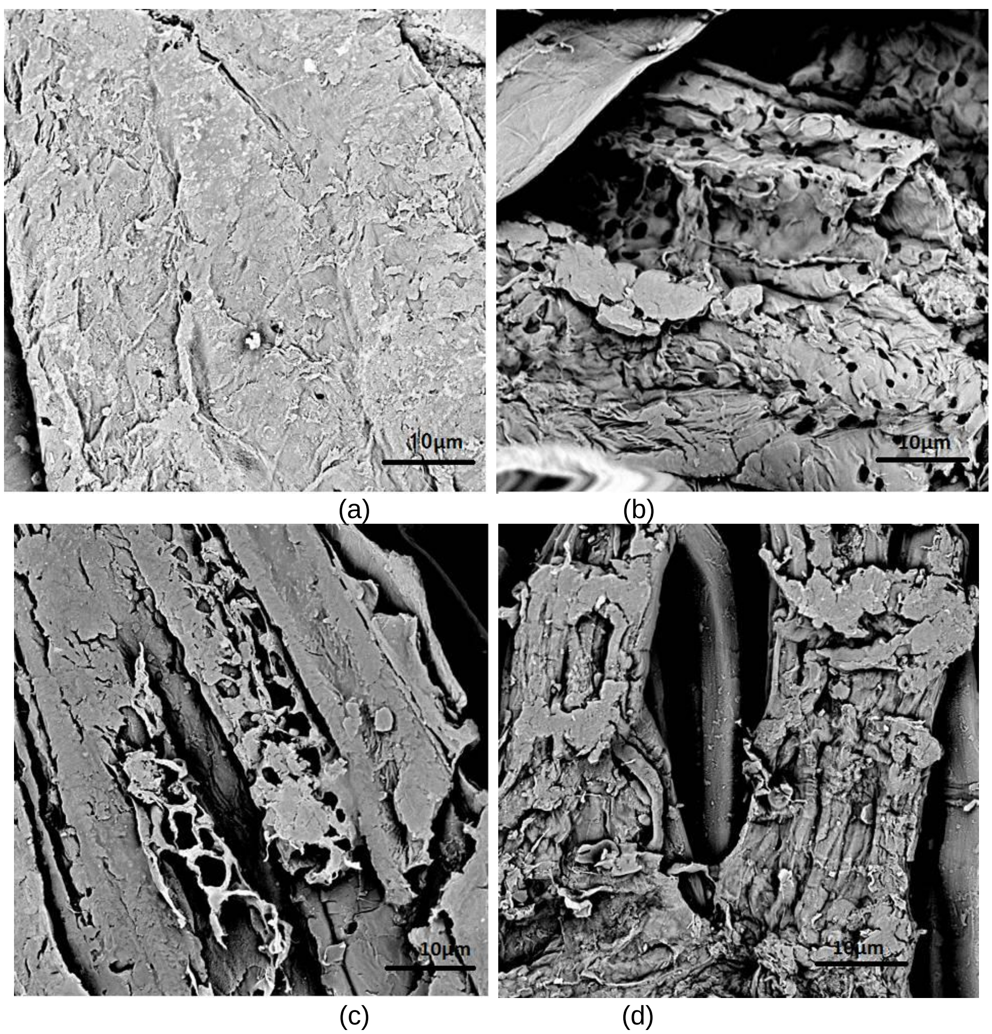

Fig. 4. SEM images of pretreated bagasse: (a) 1.0 MPa, water content 50%, 90 s; (b) 2.0 MPa, water content 50%, 90 s; (c) 2.5 MPa, water content 50%, 90 s; (d) 2.5 MPa, water 75%, 90 s

Higher vapor pressure results in increased damage to the bagasse surface. When the pressure was 1.0 MPa, the damage to the surface was small enough to be neglected. The thin wall of the bagasse epidermis was crushed by the steam explosion as the pressure was increased, and the surface of bagasse showed several cavities.

High pressure combined with high water content (Fig. 4d) led to the degradation and separation of the bagasse surface. The originally neat surface structure was completely destroyed, and the degradation of the bagasse fiber bundle was extruded together, leading to a sharp decrease in the specific surface area.

Effect of Specific Surface Area on the Grafting Degree

The effect of the specific surface area on the grafting degree of bagasse grafting acrylamide was investigated by carrying out the graft copolymerization reaction using four different specific surface areas: 3.12, 4.32, 5.20, and 6.47 m^2/g (Fig. 5). The results show that the grafting degree of bagasse graft acrylamide increased at a nearly linear rate with increasing specific surface, which proves that steam explosion is an effective pretreatment method for increasing grafting degree and the functionality of modified bagasse.

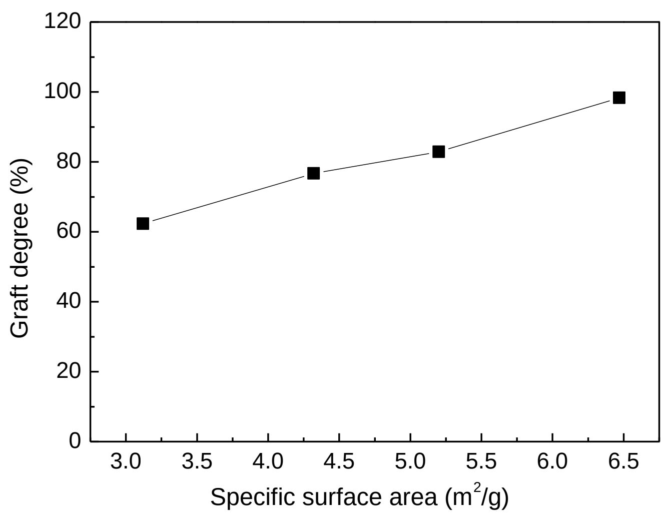

Fig. 5. Effect of specific surface area on the grafting degree of bagasse graft acrylamide

CONCLUSIONS

1. Steam explosion pretreatment conditions, such as steam explosion pressure, pressure maintaining time, and water content in bagasse greatly influence the specific surface area of the material.
2. The best steam explosion conditions were determined to be the following: steam explosion pressure, 2.0 MPa; pressure maintaining time, 60 s; and bagasse moisture content, 25%.
3. The grafting degree increased with increasing specific surface area, which indicates that moderate steam explosions is helpful for preparing bagasse with a high degree of grafting modification.

4. It was also shown that steam explosion is a feasible pretreatment method for bagasse to increase its grafting degree.

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