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Enzymatic hydrolysis enhancement of corn lignocellulose by supercritical CO₂ combined with ultrasound pretreatment

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ABSTRACT

Supercritical carbon dioxide (scCO₂) combined with an ultrasound method using 15–25 MPa and the temperature range of 120–170 °C for 0.5–4 h was proposed as a pretreatment for corn cob and corn stalk with moisture contents of 50%. The results showed that both scCO₂ pretreatment and scCO₂ combined with ultrasound pretreatment could improve the total reducing sugar yields of the two materials. Enzymatic hydrolysis of both corn cob and corn stalk sugar using scCO₂ pretreatment was increased by 50% and 29.8% compared with the control samples, respectively, while they were increased by 75% and 13.4%, respectively, using the scCO₂ combined with ultrasound pretreatment under our experimental conditions. Following treatment from the two pretreatment processes, X-ray diffraction results indicated no significant change in crystallinity of the two materials. However, scanning electron microscopy images demonstrated that the microscopic structure of lignocellulose changed considerably and the surface area of lignocellulose increased significantly.

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1. Introduction

Bioethanol is a renewable fuel and can be a partial substitute for gasoline. It can be derived from fermentation of the total reducing sugars after lignocellulosic biomass hydrolysis. Lignocellulosic biomass contains hemicellulose, cellulose, and lignin, and the former two components can be hydrolyzed to total reducing sugars that can be fermented to ethanol. The vast amounts of corn produced every year in China provides an abundant source of lignocellulose. Both corn stalk and corn cob contain about 20%–36% hemicellulose, 34%–38% cellulose, and 3%–10% lignin. It is well known that enzymatic hydrolysis of lignocellulose can only be performed efficiently following pretreatment of the corn. The process of pretreatment is thought to reduce the degree of crystallinity, increase the contact surface area with cellulase, and remove lignin and hemicellulose.

Therefore, pretreatment technology is essential for the production of bioethanol.

The technology that uses supercritical carbon dioxide (scCO₂) as a pretreatment is a new method developed in recent years. The advantages of scCO₂, such as zero surface tension, low viscosity, high diffusivity, and tunable solvent power, favor the pretreatment of biomass [1–7]. The main principle of scCO₂ pretreatment is similar to that of the steam explosion pretreatment [4]. The high operating temperature of steam explosion (190–240 °C) will cause the loss of hydrolyzed hemicellulose sugar, whereas in the process of scCO₂ pretreatment, a large amount of CO₂ molecules penetrate into the interior of the biomass and destroy the structure of the biomass by releasing CO₂ so rapidly that the effect of a physical explosion is produced, but without causing chemical hydrolysis. Puri et al. [8] was the first to propose the use of high pressure CO₂ as an ad-

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ditive together with 200 °C steam as the main solvent to result in steam explosion. Its action was through the formation of carbonic acid depressurized rapidly through a special nozzle to destroy the structural integrity of the biomass. Zheng et al. [9,10] were the first to pretreat cellulose using scCO_2 at low operating temperatures (35–80 °C). They did not however investigate the influence of moisture content of the biomass on the efficiency of the treatment. This was probably because they used microcrystalline cellulose instead of lignocellulose. Kim et al. [2] found that moisture content (0–73%) was critical for the scCO_2 pretreatment of lignocellulose, and that higher operating temperatures (112–165 °C) enhanced the efficiency even further. Srinivasan et al. [4] and Stamenic et al. [11] demonstrated that the main role of scCO_2 pretreatment was physical release. Narayanaswamy et al. [12] reported that the effect of using a scCO_2 pretreatment on corn stalk was remarkable but not quite so significant for switchgrass. They reasoned that the effect of scCO_2 pretreatment towards different lignocelluloses was due to differences in the structure and composition of the biomass. Santos et al. [6] and Srinivasan et al. [4] studied the hydrolysis of bagasse using an scCO_2 pretreatment. They obtained reducing sugar yields of 72% and 86%, respectively. Gao et al. [13] studied scCO_2 pretreatment on rice straw at 30 MPa and 110 °C for 0.5 h giving a glucose yield of $33.42\% \pm 2.1\%$. The authors did not discuss the influence of moisture content and in addition a low operating temperature (40–110 °C) was used, which resulted in very different results compared with other reports in the literature. Alinia et al. [5] investigated scCO_2 pretreatment of wheat straw, and obtained an optimum reducing sugar yield of 20.84%. These literature findings suggest that the effects of scCO_2 pretreatment on hardwood (aspen, bagasse) were better than that of softwood (rice straw, wheat straw, and southern yellow pine) under their experimental conditions. The pretreatment time in these reports, however, was limited to 1 h, which may be too short for softwood. For this reason, a longer pretreatment time for softwood was worth investigating. Matsushita et al. [14] studied the scCO_2 pretreatment of eucalyptus bark and found that the primary plant cell wall swelled and a large number of nanoscale cracks appeared on the secondary wall. The presence of water in the process of scCO_2 pretreatment resulted in the uptake of a small amount of water (moisture content 30%–75%) resulting in swelling of the biomass and promoted the penetration of scCO_2 molecules into the interior of biomass fiber. It is thought that the small amounts of carbonic acid formed by water and scCO_2 may have only a small impact on acid hydrolysis [4,12,15].

Compared with scCO_2 pretreatment, there are fewer reports that use ultrasound pretreatment. Despite this, it has been proven that ultrasound has a positive effect on the enzymatic hydrolysis of biomass [16–19]. The purpose of this paper is to investigate the amplification that scCO_2 combined with ultrasound has on the effect of pretreatment processes on both corn cobs and stalks. We aimed to discover what influence the operating conditions had on the effect of the pretreatment and to obtain the optimized conditions necessary to get the maximum sugar yield from enzymatic hydrolysis. Furthermore, it was hoped that our experimental design and analysis would help us

to understand the main mechanism of the pretreatment method.

2. Experimental

2.1. Materials

Corn stalk and corn cob were collected from a farm in Wafangdian, Dalian, Liaoning Province, China. The raw materials were air-dried and milled into particles, then sieved using Standard Taylor Sieve (0.39–0.83 mm). The raw materials were then dried at 50 °C to a constant weight and stored in jars for further use. Industrial grade carbon dioxide was purchased from Dalian Guangming Gas Co. Ltd. Cellulase (activity 4000 U/g) was purchased from Shanghai Bolan Biotechnology Co. Ltd.

2.2. Reactor and scCO_2 pretreatment

The reactor was made of 316L stainless steel with a volume of 30 ml and a rated working pressure of 30 MPa. In a typical experiment, 1.2 g raw biomass material (with known moisture content) was placed in the reactor, which was placed under vacuum to remove the air inside. Next, the reactor was heated to the fixed temperature using an oil bath following charging of the reactor with carbon dioxide using an HPLC pump. Finally, the reactor was pressurized again to the experimental value. Generally, several rounds of charging CO_2 into the reactor are needed because of temperature and pressure changes following heating by the oil bath. In our experiment, we estimated the amount of CO_2 charged into the reactor for the first time using an equation of state (ignoring the volume occupied by biomass and water) to pressurize the system following heating to be close to the final experimental pressure. Thus, the amount of the supplementary CO_2 for the second time was small enough to make the operation process stable and accurate. In the process of heating, the reactor was shaken slightly to promote mixing of the biomass and CO_2 . As soon as the temperature and pressure were stable inside the reactor the experiment was started. After 0.5 to 4 h in the supercritical state, the ball valve was opened and depressurized rapidly. In this paper, the pretreatment temperatures were 120, 140, and 170 °C; pretreatment pressures used were 15, 20, and 25 MPa, respectively. The pretreated biomass was taken out of the reactor and dried at 45 °C in an oven for 24 h prior to enzymatic hydrolysis.

2.3. Ultrasound- scCO_2 pretreatment

Three grams of the raw biomass material was placed into a beaker and soaked for 24 h using 100 ml deionized water. Following this, the beaker was placed in an ultrasonic bath with a power output of 600 W, 20 kHz at 80 °C for 2–8 h. Following filtration, the residue was dried. A 1.2 g residue with a moisture content of 50% was pretreated using scCO_2 at 170 °C, 20 MPa for 0.5 h. For the final stage, the pretreated biomass was taken out of the reactor and dried at 45 °C in an oven for 24 h and then used for enzymatic hydrolysis.

2.4. Enzymatic hydrolysis

The pretreated biomass was hydrolyzed using cellulase. The pretreated material (1 g, dry basis) and 50 ml acetic acid/sodium acetate buffer solution with a pH = 4.8 (4.92 g anhydrous sodium acetate, 2.31 ml glacial acetic acid, mixed uniformly in a beaker and diluted to 1000 ml) were used in each experiment. The reaction mixtures were put into a 100 ml conical flask reactor and incubated in a shaking water bath at 50 °C, 100 r/min for 72 h. Samples were taken at regular time intervals to analyze the total reducing sugar and glucose yield.

2.5. Total reducing sugar test

The DNS (dinitrosalicylic acid) method was used to determine the total reducing sugar from enzymatic hydrolysis of pretreated biomass [20]. The hydrolysate was placed in a boiling water bath for 10 min to inactivate it. The hydrolysate was then centrifuged and separated and diluted with deionized water prior to using it with DNS reagents. The absorbance of the hydrolysate was measured at 540 nm using a UV-Vis spectrophotometer (UV-1800, Shimadzu Scientific Instruments, Suzhou, China). The glucose contents of the hydrolysate were determined using a glucose analyzer (SBA-50B, Shandong Academy of Sciences, Jinan, China).

2.6. XRD and SEM measurements

An X-ray diffractometer was used to measure the crystallinity of treated and untreated biomass samples. The length of biomass particles contained within the samples was less than 0.42 mm. The analysis was conducted by using a continuous mode from 10° to 90° of 2 θ at a scanning speed of 5°/min on a PW3040/60 X' Pert PRO (PANalytical) diffractometer using a Cu K α radiation source (λ = 0.15432 nm) operated at 40 kV and 40 mA. Scanning electron microscope (SEM, KYKY-2800B, KYKY Technology Co. Ltd, Beijing, China) was used to observe the surface morphology of treated and untreated biomass samples. The samples were cut into small pieces carefully to avoid damage to the outer surface of the sample. Samples were

placed in the sample holders and deposited with platinum to conduct electricity using the sputtering method.

3. Results and discussion

3.1. Supercritical carbon dioxide pretreatment

3.1.1. Effect of CO₂ pressure on sugar yield

The scCO₂ treatment was performed on corn cob and corn stalk with moisture contents of 50% at 170 °C for 1 h at pressures of 15, 20, and 25 MPa. The results are shown in Fig. 1. A significant effect was observed (Fig. 1(a)) from scCO₂ pretreatment of corn cob. The best result was obtained at 20 MPa; the total reducing sugar yield had increased from 12.0% (untreated sample) to 62.0%. For corn stalk, however, there was no obvious effect under identical scCO₂ treatment conditions. After 72 h of enzymatic hydrolysis, the total reducing sugar yield for the untreated corn stalk was 16.6%, whereas for the samples treated with scCO₂ at 20 MPa for 1 h, the yield of reducing sugar was 25.5%. In consideration of the tough structure of the corn stalk, pretreatment time was prolonged from 1 h to 2.5 h. As can be seen in Fig. 1(b), the total reducing sugar yield after enzymatic hydrolysis for the untreated corn stalk was 16.6% and increased to 46.4% for the pretreated (scCO₂ at 20 MPa) samples. Pretreatment with scCO₂ appears therefore to have a significant positive effect on the total reducing sugar yield from corn stalk. Pressure however was found to have only a minimal effect on the total reducing sugars. This, however, is perhaps because of the tough structure of the corn stalk. During control experiments, higher conversion of corn stalk was observed. This could be due to corn stalk containing the more easily hydrolyzed cellulose than does the corn cob.

3.1.2. Effect of pretreatment temperature

To investigate the effects of operating temperature on total reducing sugar yield, scCO₂ treatment was performed on the corn cob and corn stalk with moisture contents of 50% at 20 MPa for 1 h (corn cob) or 2.5 h (corn stalk) at temperatures of 120, 140, and 170 °C. The effect (Fig. 2) was that the total re-

Fig. 1. Effect of CO₂ pressure on total reducing sugar yield. (a) Corn cob; (b) Corn stalk. Control experiment stands for the sample without pretreatment.

Fig. 2. Effect of pretreatment temperature on total reducing sugar yield (enzymatic hydrolysis time: 72 h).

ducing sugar yield for corn cob significantly increased with increasing temperature. Compared with the total reducing sugar yield from the untreated samples (12.0% at 170 °C), the total reducing sugar yield of the pretreated biomass was 62.0% at 170 °C, making this a 50.0% (in absolute terms) increase. For corn stalk, the effect of pretreatment at low temperatures was also not obvious. However, the total reducing sugar yield of the pretreated corn stalk was 46.4% at 170 °C, a 29.8% increase compared with the untreated samples. A possible reason is that higher pretreatment temperatures are required to break down the resilient corn stalk structure.

3.1.3. Effect of pretreatment time

To investigate the effects of pretreatment time on total reducing sugar yield, scCO₂ pretreatments were performed on corn cobs and stalks at 20 MPa, 170 °C, moisture content of 50%, and treatment times of 0.5 to 4 h. The results are shown in Fig. 3. The influence of reaction time differed for the cobs and stalks; the maximum total reducing sugar yield for cobs

Fig. 3. Effect of pretreatment time on total reducing sugar yield (enzymatic hydrolysis time: 72 h).

reached 62.0% following pretreatment for 0.5 h, which was an increase of 50.0% over untreated samples. The reducing sugar yield dropped by 16% for cobs following longer pretreatment. This may be due to the decomposition of hemicellulose and cellulose at the high temperatures used in the experiment. For stalks, 0.5–1 h of pretreatment time was insufficient to result in an obvious effect. However, the total reducing sugar yield increased significantly to 46.4% when the time was prolonged to 2.5 h, an increase of 29.8% over untreated samples. Owing to the resilient structure of the corn stalk, the best scCO₂ pretreatment time was 2.5 h, which was higher than that for corn cob (0.5 h).

3.2. Pretreatment of ultrasound combined with supercritical carbon dioxide

To further enhance the scCO₂ pretreatment process, ultrasound was coupled with scCO₂ to pretreat the corn cobs and stalks. Ultrasound pretreatment was performed at 20 kHz, 600 W, 80 °C for 2–8 h, and scCO₂ pretreatment was performed at 170 °C, 20 MPa, moisture content 50% for 0.5 h. The results of enzymatic hydrolysis for the three samples including untreated, scCO₂ pretreated, and ultrasound combined with scCO₂ are shown in Fig. 4. It can be seen that for corn cob, the effect of ultrasound combined with scCO₂ significantly improves the enzymatic hydrolysis. The glucose yield and total reducing sugar yield obtained from the hydrolysate of the biomass pretreated using ultrasound for 6 h and scCO₂ at 170 °C, 20 MPa was 42.0% and 87.0%, respectively, which was a dramatic increase compared with the results of the biomass treated with only scCO₂ (31.0% and 62.0%, respectively) and the untreated biomass (10.0% and 12.5%, respectively). For corn stalk (Fig. 4(c) and (d)), the maximum glucose yield and total reducing sugar yield obtained using the method of ultrasound for 8 h coupled with scCO₂ pretreatment was 16.0% and 30.0%, respectively, which was slightly higher than using scCO₂ pretreatment alone (14.0% and 25.5%, pretreated for 1 h) and untreated (13.5% and 16.6%). As can be seen in Fig. 4(a) and (c), the total reducing sugar yield for corn cob increased as the ultrasound treatment time increased up to 6 h but decreased after 6 h. For corn stalk (Fig. 4(c) and (d)), changes in the total reducing sugar yield was not apparent under different ultrasound when different treatment times were used. This may be because the ultrasound power rating was not high enough to break down the tough structure of the corn stalk. Despite this we concluded that too long under ultrasonic conditions is not beneficial. For this reason both the treatment time as well as the product cost should be taken into consideration for practical applications.

3.3. XRD analysis

Figure 5 shows the XRD patterns of untreated corn cobs and stalks as well as for the samples pretreated with ultrasound, scCO₂, and ultrasound/scCO₂ combination. The figure shows that none of these pretreatment methods influence the crystalline structure of the two kinds of lignocellulose. Similar results

Fig. 4. Effect of ultrasound time on the yield of total reducing sugars in the combined pretreatment process of corn cob (a, b) and corn stalk (c, d).

Fig. 5. XRD patterns of corn cob and corn stalk before and after pretreatment. (a) Corn cob; (b) Corn stalk; (1) Control; (2) scCO₂; (3) Ultrasound; (4) scCO₂+ultrasound.

from the scCO₂ treatment on corn stalk have been reported by Narayanaswamy et al. [12]. Zheng et al. [9] however used scCO₂ to pretreat Avicel and found that the amount of crystals observed decreased by 50% following scCO₂ pretreatment when compared with the untreated Avicel. This is most likely a result of Avicel being pure cellulose, and therefore containing no other polymer cell walls. This of course is different for corn, which is wrapped in hemicellulose and lignin. It is therefore important to note that the change in crystallinity is not the only factor that influences the enzymatic hydrolysis of biomass.

3.4. SEM analysis

To investigate the underlying reason for the enhanced effi-

ciency of the enzymatic hydrolysis that pretreatment provides, microstructure changes to corn cob after scCO₂ (20 MPa, 170 °C, 1 h), ultrasound (600 W, 20 kHz, 80 °C, 2 h), and ultrasound combined with scCO₂ treatment were analyzed using SEM, and the results of which are presented in Fig. 6. The results showed that the structure of lignocellulosic samples under each pretreatment condition changed; micropores and ruptures of different numbers and sizes were found to appear on the surface. Compared with scCO₂ pretreatment (Fig. 6(a) and (b)) and ultrasound treatment (Fig. 6(c) and (d)), it can be seen that the ultrasound/scCO₂ combined treatment (Fig. 6(e) and (f)) resulted in greater disruption of the biomass structure, which could further enhance the efficiency of enzymatic hydrolysis. Moreover, it was found that the water content was very im-

Fig. 6. SEM images of corn cob after different pretreatment processes. (a, b) scCO_2 pretreatment; (c, d) Ultrasound pretreatment; (e, f) Combined pretreatment.

portant during scCO_2 treatment of biomass. The water permeates the biomass causing it to swell, thereby promoting even greater penetration by CO_2 molecules into the micropores of

the biomass fiber. This process is favorable to the rupture of the cellular structure by the quick release of CO_2 (Fig. 6(a) and (b)). Thus, water can be considered as the initiator in the process of scCO_2 biomass treatment. In addition, carbonic acid would be formed when an appropriate amount of water is dissolved in the carbon dioxide, which in turn might contribute favorably to hydrolysis of the biomass.

4. Conclusions

For corn cob and corn stalk, the process of enzymatic hydrolysis was significantly improved by pretreatment with scCO_2 and a scCO_2 /ultrasound combination. Compared with the untreated sample, the maximum total reducing sugar yield of corn cob using these two methods increased by 50% and 75%, respectively. For corn stalk, longer pretreatment time, about 2.5 h, was needed compared with corn cob. The maximum total reducing sugar yield using these two methods increased by 29.8% and 13.4%, for corn stalk and corn cob respectively. XRD analysis showed that the crystalline structure of the corn did not differ between the treatments and is therefore not one of the main factors that influence enzymatic hydrolysis of biomass.

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Graphical Abstract

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The figure shows the significant effects of both supercritical CO_2 (scCO_2) and scCO_2 /ultrasound combined pretreatments for enhancement of enzymatic hydrolysis to increase the yield of reducing sugars in corn cob.

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超临界二氧化碳耦合超声预处理强化玉米秸秆酶水解

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摘要: 提出了一个木质纤维素生物质预处理的全绿色加工过程. 以玉米秸秆和玉米芯为原料, 以超临界CO₂和超声耦合法对木质纤维素进行预处理. 超临界CO₂预处理条件为: 压力15–25 MPa, 温度120–170 °C, 含水量50%, 反应时间0.5–4 h. 超声场功率600 W, 温度80 °C, 作用时间2–8 h. 用纤维素酶水解反应获得的还原糖总量来评价预处理效果. 结果表明, 单纯超临界CO₂和超临界CO₂耦合超声预处理都能够提高生物质水解反应还原糖产量. 对于玉米芯, 超临界CO₂预处理(170 °C, 20 MPa, 30 min)后, 还原糖产率为62% (未预处理的为12%). 对于玉米秸秆(170 °C, 20 MPa, 2.5 h), 还原糖产率为46.4%. 对于玉米芯, 超临界CO₂耦合超声预处理(600 W, 80 °C下超声处理6 h, 然后用170 °C, 20 MPa超临界CO₂预处理30 min)后, 还原糖产率为87%. 对于玉米秸秆, 超临界CO₂耦合超声预处理(600 W, 80 °C下超声处理8 h, 然后用170 °C, 20 MPa超临界CO₂预处理1 h)后, 还原糖产率为25.5%. 与未处理生物质相比, X射线衍射结果表明玉米秸秆和玉米芯在超临界CO₂和超声预处理后其结晶度没有明显变化. 扫描电镜分析则发现木质纤维素的表面积显著增加.

关键词: 木质纤维素; 预处理; 超临界CO₂; 超声场; 酶水解

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