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Isolation of cellulose from steam-exploded rice straw with aniline catalyzing dimethyl formamide aqueous solution

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ABSTRACT

An efficient and clean procedure was put forward for isolation of cellulose from rice straw, which included delignification of steam-exploded rice straw with recyclable mixed solvent system and bleaching with alkaline hydrogen peroxide. The condition of steam explosion was optimized through a series of experiments using statistical software (SPSS). The optimized conditions of steam explosion pretreatment was to keep the rice straw under 2.5 MPa for 25 min and then explode. A series of mixed solvent systems were designed and their delignification capabilities were analyzed. The most efficient mixed solvent consists of water, dimethyl formamide (DMF) and aniline in volume ratio of 20:10:1, and the delignified sample was analyzed to contain 0.87% lignin. After bleached with alkaline hydrogen peroxide, the bleached cellulose was analyzed to contain 95.58% cellulose, and the ratio of α-cellulose is 84.05%. The bleached cellulose possesses moderate degree of polymerization (549), and contains no detectable acid-insoluble lignin. The as-obtained cellulose was further characterized by FT-IR and ^{13}C CP/MAS NMR spectroscopy. The recycled lignin and hemicelluloses were analyzed by FT-IR spectra.

1. Introduction

Agricultural residue is one of the most important and renewable biomass as well as a promising alternative for cellulose materials. But usually, the cellulose accompanies with other structural components of biopolymers in straws, primarily hemicelluloses and lignin [1]. Efficient separation of constitutive biomass components has long been the major obstacle to the efficient utilization of such renewable resource. Under such circumstances, novel environmentally friendly processes have been developed continuously to isolate cellulose from biomass. Chlorine-free method [2], combined with chemical and enzymatic extraction [3], ionic liquids [4,5] have also been applied for isolation of cellulose from cellulosic materials. Except those methods, steam explosion [6–8] has become a well-known method for separating lignocellulosic material into its main components. During steam explosion, most of the hemicelluloses are partially hydrolyzed and a small amount of lignin is depolymerized, which resulted in loosening fiber with micro-pores of different sizes. Organosolv process, as a promising pretreatment strategy, has attracted much attention and demonstrated the potential utilization in isolation of lignocellulosic biomass [9,10]. Organosolv process is considered to be an environmentally friendly way because it can be recycled conveniently, and the structure of the dissolved component will be protected from degrading under such moderate conditions, which is benefit for further utilization. Efficient solvent for delignification combined with steam-explosion pretreatment would realize the separation of the three components. However, little organosolv process has been proved attractive as regards efficiency and selectivity, even though intensive researches have been done [11–13]. Ethanol, methanol and acetic acid were the main solvents adopted in organosolv process always catalyzed by hydrogen chloride [14,15]. During the process, hemicellulose and lignin components hydrolyzed and degraded in different degree, while both the physical properties and the cellulose chains were damaged [16,17]. Glycerol was also applied in treatment of lignocellulosic biomass under high temperature and pressured conditions to decrease the hemicelluloses and lignin to make the cellulose susceptible to enzymatic attack [10,13], but the treatment conditions met the efficiency-high and cost-effective issues.

In this paper, we focused on a sequential procedure for cellulose isolation from rice straw, including steam-explosion pretreatment, delignification with mixed solvent under ambient pressure, and bleaching the crude cellulose with alkaline hydrogen peroxide, especially a new convenient delignification process was put forward. To explore the optimal conditions (pressure and steaming

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time) to degrade hemicelluloses component as completely as it can, and to protect the cellulose from being depolymerized in this procedure, a series of experiments have been designed, and regression is carried out using the nonlinear method in the SPSS statistical software. After delignification, the obtained crude cellulose was further bleached with H_2O_2-TAED (tetraacetylethylenediamine) aqueous solution [2]. FT-IR and ^{13}C CP/MAS solid state NMR spectra were used to analyze the products and recycled lignin as well as hemicelluloses produced during the whole isolation procedure.

2. Material and methods

2.1. Main materials

Air-dried rice straw was collected in Sichuan Province, China. It was cut into pieces for about 2 mm in length and then shedded in a high speed pulverizing mill. The chemical composition of the rice straw was determined as: 35.06% cellulose, 17.98% pentose, 15.24% acid-insoluble lignin, 14.90% ash, and 9.55% moisture content. In this research, distilled water was used and all kinds of protonic or aprotonic organic solvents and additives were analytically pure agents.

2.2. The procedures for isolation of cellulose from rice straw

A flow chart of the procedure for isolation of cellulose was shown in Fig. 1. The shedded rice straw was pretreated with steam explosion in a pilot-scale equipment with 10,000 ml reactor (with a maximum operating pressure of 4.0 MPa) fitted with a quick-opening butterfly valve (the operating pressure releases to atmosphere in 5 s). Experiments were performed according to a two-variable design (pressure and steaming time) the steaming temperature was from 235 to 265 °C, which is in correspondence with the operating pressure. When the desired pressure was reached, kept it steaming for a while, then the valve was opened to explode, and the material was collected. The depolymerised hemicelluloses and related sugars as well as the small amount of degraded lignin were recovered from the exploded straw by extracting with hot water and ethanol subsequently in a Soxhlet's apparatus. The residues were then dried at 105 °C for 6 h in an oven. It should be pointed out that the yield could not be calculated accurately because the materials could not be collected completely for each sample after steam explosion, and it was not included in the response variables.

Table 1
Values of the independent variables and the properties of the steam-exploded rice straw.[a]

Number	P X1/MPa	t X2/min	lgR_0	γ C	α C	[η]
1	1(3.0)	1(30)	6.19	%	%	229.5
2	−1(2.0)	1	5.60	3.01	70.43	303.3
3	1	−1(20)	6.01	8.66	69.85	198.4
4	−1	−1	5.42	3.84	65.03	272.7
5	0(2.5)	1.414(32)	5.92	3.25	67.58	360.2
6	0	−1.414(18)	5.67	6.29	72.96	276.2
7	1.414(3.2)	0(25)	6.25	6.68	70.51	246.0
8	−1.414(1.8)	0	5.37	2.72	61.77	418.6
9	0(2.5)	0(25)	5.81	8.46	70.49	268.3
10	0	0	5.81	1.45	64.80	266.0
11	0	0	5.81	1.38	64.72	270.9

[a] X1: normalized pressure; X2: normalized steaming time; lgR_0: treatment severity, $R_0 = t\exp\,(T - 100)/14.75$; γ C: γ-cellulose and α C: α-cellulose (% dry matter after treatment); [η] values were determined according to the CED method.

The steam explosion treatment conditions and the properties, such as: contents of γ-cellulose (γ C), contents of α-cellulose (α C) and [η] values of the steam-exploded rice straw were summarized in Table 1. According to the main propose of steam explosion treatment, which is to loosen the texture of the straw though its mechanical function and to degrade hemicelluloses component as completely as it can, and for convenient optimization of the treatment conditions, only the three properties were characterized. It can be clearly seen that the central point (2.5 MPa and 25 min) is the most proper condition, because the lowest γ-cellulose content

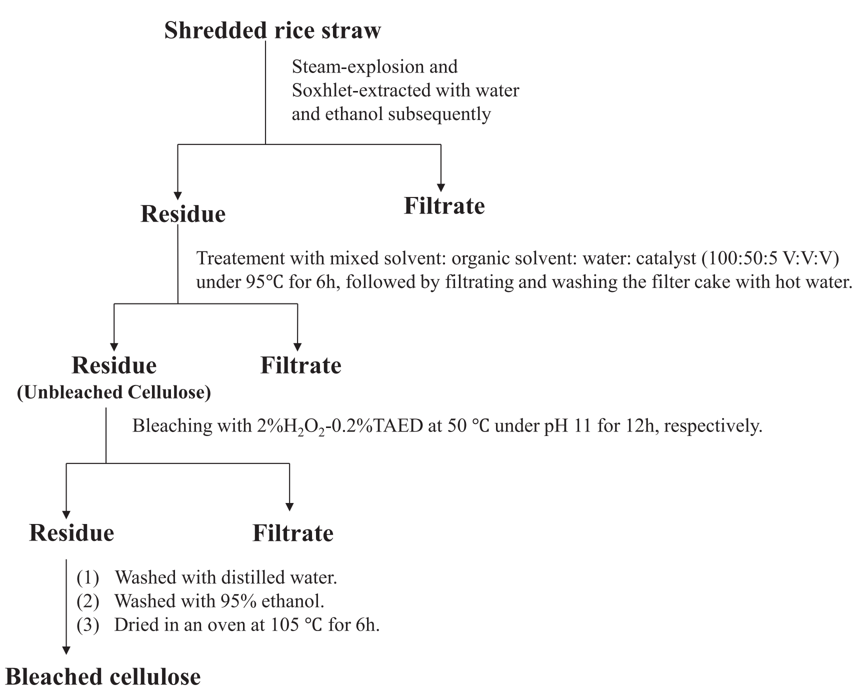

Fig. 1. Scheme for isolation of cellulose from rice straw.