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Research paper

RSM based optimization of PEG assisted ionic liquid pretreatment of sugarcane bagasse for enhanced bioethanol production: Effect of process parameters

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ABSTRACT

Production of bioethanol from lignocelluloses is highly dependent on pretreatment process. Therefore, a better understanding of this process is an essential prerequisite to consider the whole bioethanol production from lignocelluloses in a cost and energy efficient way. The first step in performing the pretreatment is to discover the effects of different process parameters on various chemical features of the lignocelluloses. In order to achieve this aim, response surface methodology (RSM) was chosen to assess the exact impact of variables including temperature, polyethylene glycol (PEG) concentration and time on glucan, xylan and acid insoluble lignin contents as responses, also to optimize the pretreatment process to finally achieve higher bioethanol production yields. 1-butyl-3-methylimidazolium chloride (BMIMCl) and PEG in the concentration range of 1–5 (%w/w) were used as pretreatment agents. Temperature and time levels of 100–160 °C and 60–120 min were considered for experimental design, respectively. For further understanding of the effects of pretreatment on lignocelluloses, structural features examined by FT-IR, SEM and XRD analysis, in addition, enzymatic hydrolysis and fermentation were implemented on the samples pretreated in optimum conditions. The optimum pretreatment condition is 154.6 °C, 60 min and 5 (%w/w) of PEG concentration which resulted to the high enzymatic conversion and bioethanol production.

1. Introduction

Lignocelluloses are renewable energy resource that can be used for the production of value-added chemicals and biofuels [1]. However, the recalcitrance of lignocelluloses because of the three-dimensional cell-wall structure of lignocelluloses composed of aggregates of cellulose microfibrils connected with a lignin and hemicellulose matrix strongly hinders the effective conversion of lignocelluloses into value-added products [2]. For this reason, the major issue in the conversion of lignocelluloses into bioethanol is to overcome biomass recalcitrance through pretreatment while retaining green and energy-efficient processing [3]. Pretreatment affects both pre- and post-operation steps (i.e. milling and enzyme requirement). Therefore, effective strategies for pretreatment are highly desirable not only to achieve high yields of biofuel following fermentation, but also to have a reasonable mass and energy balance from an economic and environmental perspective [4].

Recently, ionic liquids (ILs) have attracted a great attention for application in biomass pretreatment and lignocelluloses component extraction due to their potential application as "green solvents" [5–7]. ILs have shown to be able to dissolve a vast range of cellulose and lignocellulosic materials. In addition, it has been proved that ILs are suitable agents for biomass pretreatment, as they act highly effective at reducing lignocelluloses recalcitrance because of their dual ionic and organic nature [8–11]. By employing ILs for pretreatment of the biomass, saccharification time can decrease considerably and the yields of nearly 100% can be achieved [6]. However, the success of any pretreatment is dependent on physico-chemical properties of the lignocelluloses as well as the process conditions. Optimal process conditions during lignocelluloses pretreatment can increase the accessibility of the biopolymers of sugars, thus enhance the viability and the yield of the downstream steps [4]. Therefore, optimization is an efficient way to improve a pretreatment process.

The optimum conditions of pretreatment by 1-ethyl-3-methylimidazolium acetate ([EMIM]oAc) ionic liquid have been identified through RSM. Time, temperature and solid loading have been considered as influencing factors and glucose yield of enzymatic conversion step has been evaluated as the response [12]. A study by Papa et al. optimized the 1-ethyl-3-methylimidazolium acetate and cholinium lysinate pretreatment of corn stover, by considering two levels for process parameters, they provided a comparative material balance and process

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yields in order to establish the upper and lower limits for IL pretreatment [13].

Several studies have proved the effectiveness of surfactant pretreatment of lignocelluloses [14–16]. Also, we have demonstrated the enhanced saccharification rate of SCB pretreated by a novel surfactant assisted ionic liquid method [17]. Nevertheless, the literature lacks the optimization of this novel process as well as a comprehensive understanding of the impact of different process variables on lignocelluloses components in an ionic liquid involved pretreatment. However, the effects of time or temperature have been considered in some studies in a narrow range, we suggested a response surface methodology approach to not only study the effects of parameters in a wide interval, but also to optimize this process. To the best of our knowledge, this is for the first time bioethanol production from a lignocelluloses sample pretreated mainly by IL is evaluated. Other studies on ionic liquid pretreatment only assessed the enzymatic hydrolysis step of the whole process and neglected the fermentation step.

In the present study a response surface methodology approach was chosen to develop correlations for glucan, xylan and acid insoluble lignin content of SCB pretreated by PEG and BMIMCL, also to evaluate the exact impact of various process variables on chemical features of lignocelluloses, and finally to optimize the suggested pretreatment procedure. Effects of pretreatment temperature, time and PEG concentration were assessed and parameter values were optimized to maximize simultaneously glucan and xylan while minimize the lignin content of the pretreated samples to obtain a biomass prone to enzymatic hydrolysis. Structural features of the SCB sample pretreated in optimum conditions was evaluated as well as the enzymatic hydrolysis, and fermentation processes were carried out to complete a biomass to biofuel process steps.

2. Materials and methods

2.1. Feedstock and materials

SCB was used as the model lignocellulosic biomass, and was supplied by the Iranian Research Organization for Science and Technology (IROST). SCB was ground in a cutter mill (Moulinex, AR1044). Sieves of size 70 and 30 were used to obtain particles which are in size between 0.21 and 0.59 mm. Milled and sieved SCB was stored at room temperature in sealed containers. Ionic liquid of [BMIM] Cl (HPLC grade), with the purity of 99% and water content of less than 0.2% was purchased from Sigma-Aldrich. Sulfuric acid (98%), glacial acetic acid, xylose, glucose and phloroglucinol were purchased from Merck. Commercial enzymes of Celluclast 1.5 L (cellulase from *Trichoderma reesei*), and Novozyme 188 (cellubiase from *Aspergillus niger*) purchased from Sigma-Aldrich.

2.2. Experimental and analytical procedures

2.2.1. Characterization of SCB (chemical composition of SCB)

All untreated and pretreated SCB samples were analyzed for total solids, glucan, xylan, acid soluble, insoluble lignin and ash. The SCB was hydrolyzed with H_2SO_4 of 72% (w/w) for 2 h at 30 °C, ratio of acid to solid content was 10:1 ml g^{-1}. Acid was diluted to 4% (w/w) by addition of deionized water. Mixture was further hydrolyzed at 120 °C for 1 h in an autoclave. The suspension was filtered through ashless filter papers; the remaining solid biomass was used to measure acid insoluble lignin (AIL) and ash content of lignocelluloses, while filtrate was used to determine glucan, xylan and acid soluble lignin (ASL) content. The AIL percentage was determined by drying the residue at 105 °C and accounting for ash by incinerating the hydrolyzed samples at 575 °C in a muffle furnace [18]. For glucan content determination, glucose concentration in filtrate was measured via glucose oxidase method [19]. Xylan content was determined by measuring xylose concentration in filtrate via phloroglucinol method [20]. The ASL

Table 1
Actual and coded value of independent variable levels.

Variables	Coding	Unit	Levels				
			-α	−1	0	+1	+α
Temperature	A	°C	100	112	130	148	160
PEG Concentration	B	% (w/w)	1	1.8	3	4.2	5
Time	C	min	60	72	90	108	120

Table 2
Experimental design and the values of responses.

Run	Experimental variables			Responses		
	A:Temperature (°C)	B:PEG (% w/w)	C:Time (min)	%Glucan	%Xylan	%AIL
1	130	3.0	60	50.45	30.85	8.6
2	130	3.0	90	61.4	26.11	5.7
3	130	3.0	90	64.16	22.09	7.3
4	112	4.2	108	50.07	21.18	10.6
5	148	4.2	108	58.74	33.78	2.1
6	130	1.0	90	65.97	16.48	6.1
7	112	1.8	108	67.05	14.73	8.1
8	160	3.0	90	70.5	25.6	1.5
9	148	4.2	72	62.9	29.66	4.8
10	148	1.8	108	73.58	17.22	4.1
11	148	1.8	72	57.24	28.66	4.4
12	100	3.0	90	50.13	22.5	20.2
13	130	5.0	90	55.35	32.84	4.1
14	130	3.0	90	57.35	24.33	8.5
15	112	4.2	72	57.9	23.4	13.6
16	130	3.0	90	62.17	24.29	7.9
17	130	3.0	120	59.87	21.78	5.3
18	112	1.8	72	55.05	23.19	14

Table 3
Analysis of variance (ANOVA) for the models obtained from experimental design.

%Glucan	df	F Value	Prob > F
Model	4	16.19	< 0.0001
A-Temperature	1	23.84	0.0003
B-PEG Conc.	1	12.59	0.0036
C-Time	1	7.70	0.0158
BC	1	20.63	0.0006
Residual	13		
Lack of Fit	10	1.27	0.4734
Pure Error	3		
Cor Total[1]	17		
%Xylan			
Model	5	16.75	< 0.0001
A-Temperature	1	14.76	0.0023
B-PEG Conc.	1	38.50	< 0.0001
C-Time	1	15.91	0.0018
AB	1	2.92	0.1134
BC	1	11.67	0.0051
Residual	12		
Lack of Fit	9	2.17	0.2831
Pure Error	3		
Cor Total[2]	17		
%Acid insoluble lignin			
Model	6	29.35	< 0.0001
A-Temperature	1	144.65	< 0.0001
B-PEG Conc.	1	0.31	0.5917
C-Time	1	11.33	0.0063
AC	1	2.21	0.1651
A^2	1	10.97	0.0069
B^2	1	3.83	0.0760
Residual	11		
Lack of Fit	8	1.49	0.4064
Pure Error	3		
Cor Total[3]	17		

[1,2,3] Degrees of freedom total corrected for the mean.