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·研究报告——生物质能源·

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:研究了不同浓度酸/碱预处理下芒草预处理上清液中副产物的生成和预处理上清液发酵产乙醇的规律,并对预处理副产物与乙醇发酵的关系进行了相关性分析。结果表明:酸/碱预处理上清液中预处理副产物浓度差异较为明显,酸处理产生的糠醛、5-羟甲基糠醛浓度明显高于碱处理,而碱处理上清液中丁香酸、香草醛、对香豆酸、阿魏酸浓度明显大于酸处理;预处理上清液补糖发酵中,1% H_2SO_4 预处理上清液糖醇转化效率高于 10 g/L NaOH 预处理,半纤维素含量高和木质素含量低的材料具有较高的糖醇转化效率;糖醇转化效率与相应预处理上清液中副产物浓度相关性分析显示,糖醇转化效率与 5-羟甲基糠醛呈极显著正相关,相关系数达 0.795,与香草醛和丁香酸分别表现为极显著和显著负相关,相关系数分别为-0.811 和-0.671。

:芒草;预处理副产物;化学预处理;乙醇发酵;糖醇转化效率

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Effects of Byproducts Obtained from Alkali or Acid Pretreatment of *Miscanthus* Biomass on Yeast Fermentation

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Abstract: Total supernatants were obtained from various alkali or acid pretreatments of *Miscanthus* biomass in order to detect the released byproducts and the ethanol production by yeast fermentation. And the correlations of byproducts and ethanol fermentation were analyzed. The results showed that concentrations of byproducts in supernatant obtained by different pretreatments were different. The contents of furfural and 5-hydroxymethylfurfural of acid pretreatment were higher than those of alkali pretreatment. And the contents of vanillin, p-coumaric acid, ferulic acid of alkali preteratment were higher. In the feeding glucose fermentaion of supernatant, the sugar-alcohol conversion efficiency of 1 % H_2SO_4 pretreatment was higher than that of 10 g/L NaOH. The hemicelluloses and lignin contents in raw *Miscanthus* biomass materials respectively exhibited positive and negative effects on sugar-ethanol conversion rate. Correlative analysis indicated that vanillin and syringic acid exhibited negative effects on ethanol production, while 5-HMF was a positive factor.

Key words: *Miscanthus*; byproduct; chemical pretreatment; yeast fermentation; sugar-ethanol conversion rate

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, [1-2]。 、
, *β-D-* ,
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、 3 ; 、
, [3-4]。
、 3 , ,
, , [5-6]。 ,
、 , [5,7]。
(*Miscanthus*) , , 、 、
、 , [8-9]。 /
, ,
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1

1.1

200 (*Miscanthus*) ,
, 0.25 mm, 60 ℃ , 。
200 6 , 3 (I、II III),
、 、 。 I : 1# (*M. floridulus*) 2#
(*M. sinensis*); II :3# (*M. purpurascens*) 4# (*M. sacchariflorus*); III :5# (*M. sinensis*)
6# (*M. lutarioriparius*)。 (*Saccharomyces cerevisiae*),
。

1.2

Peng [10] , Xu [11]
。

1.3 /

0.500 0 g 15 mL , NaOH H_2SO_4
10.00 mL, 。 120 ℃ 20 min, , 50 ℃,
150 r/min 2 h; 50 ℃ 150 r/min 2 h。 ,
, , 。 3 ,
。

1.4 /

0.500 0 g 15 mL , 10.00 mL 10 g/L NaOH
1 % H_2SO_4 , **1.3** 。 5.00 mL 2 , 2
。 H_2SO_4 NaOH pH 4.8,
20.00 mL。 4.00 g。 20.00 mL
, 200 g/L。 ,
1.00 mL, 2 g/L, 37 ℃ 48 h,
, 3 , 。

1.5

、 , [5] 。

[12] , (HPLC) , ,
0.05% (pH 2.2~2.3), 90% (
0.05%), 8%,5 min 65 min 25%,73 min
100%,74 min 8%, 10 min ; 0.80 mL/min,
30℃, Universal C18 (Kromat,4.6 mm×250 mm,5 μm), (210 nm)。

1.6

1.6.1 糖醇转化效率及其差异 ,
。
,
。

1.6.2 相关性分析 ,
SPSS Spearman 。

2

2.1

6 3 , 1 。I、II、III 、
、 , 58.86%、33.28%、31.98%, 。

1

Table 1 Cell wall composition of *Miscanthus* samples **%**

group	No.	cellulose	differences	hemicelluloses	differences	lignin	differences
I	1#	21.93±0.50	58.86	16.81	0.55	23.20±0.36	0.71
	2#	34.84±1.35		16.90		23.03±0.88	
II	3#	31.70±0.33	1.67	15.58	33.28	28.31±0.19	1.14
	4#	31.18±0.97		20.76		27.99±0.54	
III	5#	34.57±0.41	0.09	20.89	1.16	23.57±0.24	31.98
	6#	34.54±1.00		21.14		31.10±0.98	

2.2 /

6 0.25%、1%、4% H_2SO_4 5、10、40 g/L NaOH
, HPLC , 2。
10 g/L NaOH 1% H_2SO_4 3。

2 NaOH H_2SO_4

Table 2 Range of byproducts concentration from pretreatment supernatants of *Miscanthus* with alkali and acid in various concentration

byproducts	content of different pretreatment/(μmol·L^{-1})	
	H_2SO_4 pretreatment	NaOH pretreatment
formic acid(FoA)	778.52~6263.83	1280.30~6143.11
acetic acid(AA)	1357.44~7485.49	2469.22~6707.32
5- 5-hydroxymethylfurfural(HMF)	17.63~4679.78	0~90.65
furfural(Fur)	0.08~996.55	10.86~176.46
4- 4-hydroxybenzoic acid(HA)	3.28~38.04	13.65~37.66
vanillic acid(VA)	10.48~69.37	21.98~51.21
syringic acid(SA)	7.58~15.81	23.23~64.97
4- 4-hydroxybenzaldehyde(H)	10.49~73.60	18.46~94.70
vanillin(G)	12.45~52.05	23.27~96.31
syringaldazine(S)	4.04~28.64	5.97~66.51
p-coumaric acid(*p*CA)	42.99~738.15	555.00~2815.56
ferulic acid(FeA)	25.70~202.87	224.54~906.11
sinapic acid(SiA)	1.76~18.91	1.41~18.97

3 10 g/L NaOH 1 % H_2SO_4

Table 3 Concentration of byproducts in pretreatment supernatant with 10 g/L NaOH and 1 % H_2SO_4 μmol/L

pretreatment	group	No.	FoA	AA	HMF	Fur	HA	VA	SA	H	G	S	*p*CA	FeA	SiA
10g/L NaOH	I	1#	3372.78	6707.32	80.25	27.79	30.09	46.73	36.49	32.54	25.15	7.47	1494.52	780.24	8.77
		2#	1855.39	3919.03	15.51	10.86	37.66	32.50	47.18	32.50	32.20	9.03	1704.99	574.45	16.92
	II	3#	6143.11	3921.32	—	46.93	31.85	36.07	37.90	26.74	59.33	20.08	1669.56	570.84	18.97
		4#	1280.30	2753.02	5.98	38.34	21.34	29.92	32.25	39.01	40.22	18.65	1219.67	484.61	8.04
	III	5#	2054.00	4131.67	33.38	34.94	24.68	29.87	30.62	19.50	34.22	9.41	1556.42	583.37	11.31
		6#	2889.70	2924.73	—	156.62	28.18	51.21	64.97	94.70	84.26	66.51	2130.77	906.11	17.30
1% H_2SO_4	I	1#	3224.80	2674.46	4679.78	143.18	21.76	49.39	9.53	32.11	22.53	12.11	384.96	202.87	3.00
		2#	2268.65	2644.55	1959.31	96.37	15.98	29.01	9.38	24.26	16.96	10.13	345.74	134.93	4.51
	II	3#	1070.88	2367.39	46.10	68.26	16.64	22.00	10.95	18.26	31.33	17.12	377.00	174.12	2.86
		4#	876.46	2164.98	61.24	52.44	9.36	16.18	9.14	17.18	24.93	12.58	283.20	130.74	2.11
	III	5#	1477.19	2179.79	882.51	11.18	10.04	20.65	8.21	19.87	23.83	11.59	337.17	153.23	1.88
		6#	1509.42	2154.45	62.69	115.92	10.66	33.33	11.16	35.76	35.47	20.12	441.45	201.97	4.73

2 3 : / , : 、 、 5- , 、 ; 、 、 , , / 。 、 , 5- 、 , 、 、 、 。 , , , Xu [12] 、 。 ,5- 、 , , 5- ; , 、5- 、 , 5- , 、 。

2.3

3 / , 4。

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Table 4 Sugar-ethanol conversion rate of fermentation by the supernatant of pretreatment

group	No.	sugar-ethanol conversion rate/%		/%
		10 g/L NaOH alkali pretreatment	1 % H_2SO_4 acid pretreatment	differences of sugar-ethanol conversion
I	1#	58.98±1.91	67.10±0.00	13.76
	2#	57.71±0.84	65.42±1.84	13.37
II	3#	50.09±1.49	53.07±1.81	5.95
	4#	53.12±0.48	60.08±0.96	13.11
III	5#	59.61±2.88	71.08±0.65	19.23
	6#	54.38±1.27	54.95±1.27	1.06

3 ,1 % H_2SO_4 10 g/L NaOH , , 。 1 ,I , 1# 2# , , , ; II , 3# 4#, ;III

, 5# 6#,
; II III ,
,
, ○

2.4

6
, 12 ,
○ R_{FoA}-0.035、R_{AA}-0.245、R_{HMF} 0.795、R_{Fur}-0.105、R_{HA}-0.329、R_{VA}-0.811、R_{SA}-0.552、R_{H}-0.427、R_{G}-0.280、R_{S}-0.671、R_{pCA}-0.545、R_{FeA}-0.385 R_{SiA}-0.573。 , 5-
, 、 ; 、 、 ,
; 、 、 ,
0.50, ○

3

3.1 / , , /
, 、5- ,
、 、 , /
○

3.2 , ,
, ,
○

3.3 5-
, 0.795; 、 ,
-0.811、-0.671。

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