Aromatic Aldehydes Production by Oxidative Degradation of Solid Residue Derived from Pine Waste Hydrolysis Coupling Acetylation

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Abstract. Xylose and cellulose acetate were prepared by hydrolysis and acetylation of hemicellulose and cellulose in landscaping biomass waste (pine) by dilute acid hydrolysis and acetylation, respectively. The obtained solid residue was rich in lignin that mainly contains three phenylpropane structural units and can be used to prepare aromatic chemicals under hydrothermal conditions. In this work, the synthesis of high value-added aromatic aldehydes (vanillin, syringaldehyde, and p-hydroxybenzaldehyde) from the solid residue (rich in lignin) by mild catalytic oxidation was studied. The oxidation degradation of the solid residue in NaOH solution to produce aromatic aldehydes was investigated by single factor experiment. The optimum reaction conditions were obtained as follows: 175 °C, 90 min, 3.0 g solid residue, 100.0 ml NaOH solution (concentration of 2.0 mol/L), and oxygen pressure of 1.5 MPa. Under these conditions, the total yield of aromatic aldehydes from pine branch residue was 23.8 wt%.

1 Background

Greening waste refers to the falling branches, fallen leaves, flower decay, grass debris, tree and shrub cutting and other plant residues produced by human pruning or natural withering, which is also called green waste garbage or garden waste by some researchers [1,2]. Wet oxidation refers to the process in which organic or inorganic substances in aqueous solution or suspension are oxidized by oxidants at higher temperature and pressure [3]. The operating temperature and pressure range are 100 °C ~ 320 °C and 0.5MPa ~ 20MPa [4]. Although some studies on wet oxidation of lignin have been applied to wastewater treatment [5-7], others have focused on the production of organic acids through lignin oxidation. It has been reported that alkali lignin and organic solvent lignin can produce 0.45g/g and 0.20g/g organic acids at different temperatures [8,9]. However, most of the wet oxidative degradation of lignin is used to produce aromatic aldehydes, such as vanillin (VLA), syringaldehyde (SA) and p-hydroxybenzaldehyde (PHBA). These compounds have many applications, especially vanillin is widely used in food, cosmetics and pharmaceutical industries as condiments and spices. However, among these products, only vanillin has been industrialized. In this work, the synthesis of high value-added aromatic aldehydes (vanillin, syringaldehyde, and p-hydroxybenzaldehyde) from the solid residue (rich in lignin) by mild catalytic oxidation was studied.

2 Experimental

2.1 Pretreatment of greening waste

The discarded pine branches were collected from Handan Road Campus of Fudan University in Shanghai, China. At that time, the collection time was just the time when the green pruning workers pruned the branches and leaves in spring, and all the branches and leaves were just trimmed by the workers. After the raw materials are collected, they are dried in an oven at 105 °C for 8 hours, and then mechanically crushed through a 40 mesh sieve, and the screened samples are kept for standby.

2.2 Basic operation steps for preparation of aromatic aldehydes by catalytic oxidation of cellulose acetate solid residue

3.0 g of cellulose acetate solid residue was used and 100 ml sodium hydroxide solution with concentration of 2.0 mol/L and the addition of 0.02g CuSO₄ under oxygen pressure of 1.5 MPa at 175 °C for 90min. After reaction, the reaction liquid was cooled and acidified with 1mol/L hydrochloric acid to pH = 3.5. After filtration, the filter cake is washed, dried, and weighed, and the content of filter cake is determined according to the NREL standard method. Then the conversion rate of lignin (lignin conversion rate = 1 - m/M) was calculated according to the lignin mass (m) in the original cellulose acetate solid

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residue. The filtrate and washing solution were combined and extracted by 300 mL chloroform in three times. The content of aromatic aldehydes in the extraction solution was determined by GC-MS external standard method (e.g., Fig. 1 and 2), and the yield of aromatic aldehyde was finally calculated based on M.

Fig. 1. TIC spectrum of cellulose acetate solid residue catalytic oxidation products (conditions: 2.0mol/l NaOH solution 100.0ml, 1.5MPa, 175 °C, 90min).

Fig. 2. Mass spectrum of cellulose acetate solid residue catalytic oxidation products (conditions: 2.0mol/l NaOH solution 100.0ml, 1.5MPa, 175 °C, 90min).

3 Results and Discussion

3.1 Effect of catalyst types

The effects of different catalysts on the preparation of aromatic aldehydes from cellulose acetate solid residue under the conditions of 3.0 g (cellulose acetate rsm16-ca), 2.0 mol/L NaOH solution 100.0 ml, 1.5 MPa, 175 °C and 90min were investigated. The results are shown in Table 1.

Table 1. Effect of catalyst types on catalytic oxidation of cellulose acetate solid residue.

Catalyst	VLA (g)	SA (g)	PHB A (g)	Lignin Conversion rate (%)	Total Yield (%)
ZnCl ₂	0.026	0.017	0.010	77.1	10.6
FeCl ₃	0.042	0.034	0.016	85.2	18.4

CuNO ₃	0.065	0.029	0.020	98.7	22.8
CuSO ₄	0.065	0.032	0.022	100	23.8

It can be seen from the above Table that different catalysts have different effects on the yield of aromatic aldehydes. CuSO₄ is the best catalyst, and the total yield of aromatic aldehydes is as high as 24.4%, and the effect of iron salt is also good. This may be due to the promotion of oxidative degradation of wood in the process of electron gain and loss of transition metal salt ions [10].

3.2 Effect of NaOH solution concentration on reaction

Without changing other conditions, CuSO₄ was selected as catalyst to investigate the effect of NaOH solution concentration on the yield of aromatic aldehydes. The experimental results are listed in Table 2.

Table 2. Effect of NaOH concentration.

NaOH (mol/L)	VLA (g)	SA (g)	PHB A (g)	Lignin Conversion rate (%)	Total Yield (%)
1.6	0.041	0.021	0.017	86.3	15.8
2.0	0.065	0.032	0.022	100	23.8
2.4	0.062	0.030	0.019	100	22.2
2.8	0.045	0.024	0.018	100	17.4

It can be seen from the above table that too high or too low alkali concentration is not conducive to the formation of aromatic aldehydes. Properly increasing the alkali concentration is conducive to the degradation of lignin, and its conversion and product yield increase correspondingly. However, when the concentration of NaOH is too high, the side effects will increase correspondingly, leading to the decrease of aromatic aldehyde yield [11,12]. Therefore, 2.0 mol / L is the optimal concentration of NaOH solution.

3.3 Effect of catalyst dosage

Without changing other reaction conditions, the yield of aromatic aldehydes was investigated with different amount of CuSO₄. The experimental results are shown in Table 3.

Table 3. Effect of catalyst dosage.

CuSO ₄ (g)	VLA (g)	SA (g)	PHBA (g)	Lignin Conversion rate (%)	Total Yield (%)
0	0.022	0.011	0.005	33.2	7.6

0.01	0.034	0.014	0.010	66.7	11.6
0.02	0.065	0.032	0.022	100	23.8
0.03	0.039	0.021	0.013	100	14.6

As shown in the above table, when CuSO₄ dosage is 0.02 g (4wt%), the yield of aromatic aldehydes is the highest. Excessive Cu²⁺ can cause excessive oxidation of phenylpropane structure in lignin to form acid compounds [13]. Therefore, the optimal dosage of CuSO₄ is 0.02 g.

3.4 Effect of the amount of cellulose acetate solid residue

The influence of the amount of cellulose acetate solid residue on the preparation of aromatic aldehydes by catalytic oxidation degradation of cellulose acetate solid residue was investigated under the condition of other fixed conditions unchanged. The experimental results are shown in Table 4.

Table 4. Effect of solid residue amount on catalytic oxidation of cellulose acetate solid residue.

Solid residue (g)	VLA (g)	SA (g)	PHBA (g)	Lignin Conversion rate (%)	Total Yield (%)
1.0	0.021	0.010	0.006	100	7.4
2.0	0.033	0.018	0.015	100	13.2
3.0	0.065	0.032	0.022	100	23.8
4.0	0.058	0.029	0.021	96.2	21.6

It can be seen from the above table that the yields of aromatic aldehydes are significantly different under different solid residues. When the amount of cellulose acetate solid residue is small, all lignin can be reacted, but the yield of aromatic aldehyde is obviously low. When the solid residue amount is 3.0 g, the yield reaches the maximum value of 23.8%. If the amount of cellulose acetate is increased continuously, the lignin can not be completely transformed, and the yield is slightly reduced. Therefore, the optimal amount of cellulose acetate solid residue is 3.0 g.

3.5 Effect of oxygen pressure

It can be seen from table 5 that under low oxygen pressure (no more than 1.2 MPa), the lignin in solid residue can not be completely converted, and the yield of aromatic aldehyde is also low; when the oxygen pressure reaches 1.5 MPa, the conversion rate of lignin reaches 100%, and the yield of aromatic aldehydes reaches the maximum value; if the pressure continues to increase,

the aromatic aldehydes will decrease, which may be due to the deep oxidation of aromatic aldehydes into acids by excessive oxygen [14,15].

Table 5. Effect of oxygen pressure on catalytic oxidation of cellulose acetate solid residue.

O ₂ (MPa)	VLA (g)	SA (g)	PHBA (g)	Lignin Conversion rate (%)	Total Yield (%)
0.9	0.028	0.015	0.011	88.2	10.8
1.2	0.044	0.023	0.016	93.5	16.6
1.5	0.065	0.032	0.022	100	23.8
1.8	0.059	0.034	0.020	100	22.6

4 Conclusion

The oxidation degradation of cellulose acetate solid residue in NaOH solution to produce aromatic aldehydes was investigated by single factor test. The optimum reaction conditions were obtained as follows: cellulose acetate solid residue 3.0 g, concentration of 2.0 mol/l NaOH solution 100.0 ml, oxygen pressure 1.5 MPa, reaction temperature 175 °C, reaction time 90 min. Under this condition, the total yield of aromatic aldehydes (vanillin, syringaldehyde, p-hydroxybenzaldehyde) of pine branch was 23.8 wt%.

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