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Process of lignin oxidation in an ionic liquid coupled with separation[†]

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A novel approach has been developed in order to use lignin as a renewable resource for the production of a high added-value aromatic aldehyde. The concept is based on the use of an ionic liquid as a reversible medium coupled with the separation process, which prevents the aromatic aldehyde products from oxidizing and increases their yields. The conversion of lignin reached 100%, and the total yield of the aromatic aldehydes (vanillin, syringaldehyde and *p*-hydroxybenzaldehyde) was 29.7% in the coupled process. In addition, the mixture of product and IL phase was easily separated, and the IL phase demonstrated good reusability. Hence, a clean and environmentally friendly strategy for overall utilization of lignin and preparation of an aromatic aldehyde is developed.

1. Introduction

With the gradual diminishing of fossil fuel reserves and growing concerns about global warming, finding ways of exploiting feasible pathways for the replacement of the petroleum-based chemicals are highly desirable.¹ To meet the growing demand for this, biomass can serve as a sustainable source of renewable fuels and chemicals.² Lignin, one of the main components of biomass in the biorefining process, is usually discarded as non-cellulosic waste in industry. It is an extremely complex three-dimensional macromolecule with an irregular structure, which results from random dehydrogenative polymerization of phenylpropane building units, including coniferyl, sinapyl and *p*-coumaryl alcohols. Therefore, lignin can be converted into aromatic aldehydes such as *p*-hydroxybenzaldehyde, vanillin and syringaldehyde by the catalytic oxidation degradation process. These aromatic aldehydes are widely used in flavoring as chemical intermediates for

pharmaceutical drugs and agricultural pesticides.^{3,4} The catalytic wet air oxidation process using air (or oxygen) and supported catalysts has been indicated as one of the most promising processes to convert lignin into aromatic aldehydes.⁵⁻⁷ However, this process still has some shortcomings including a complicated technique, the non-recyclability of the catalyst and serious environmental pollution. Especially, the selectivity and final yield of the products are poor because aromatic aldehydes cannot be separated from the reaction mixture during the process of the reaction, which leads them to over-oxidize to form carboxylic acidic derivatives, such as vanillic acid, syringic acid and minor quantities of carboxylic acidic derivatives etc.8 Otherwise, the dissolution of lignin is critically important for its efficient valorization, but remains a challenge because of the particular property of the structure of lignin which resists chemical or enzymatic degradation.9,10 When lignin is dissolved or swollen in the solvent, the connecting points of the phenylpropane building units are exposed and the reagents are easily in contact with them; as a result the degradation continues smoothly.⁹ Therefore, finding a solvent which can efficiently dissolve lignin and has good reusability is also a prerequisite for its oxidative degradation.

Recently, the effectiveness of ionic liquids (ILs) as solvents for the dissolution of wood and lignocellulosic biomass has been demonstrated.¹⁰⁻¹⁵ Because of their good thermal stability and negligible vapor pressure, they have been regarded as "green solvents" that could potentially replace volatile organic solvents.^{16,17} In a pioneering study by Rogers et al., it was reported that 1-butyl-3-methylimidazolium chloride [C4mim]Cl was capable of dissolving up to 10 wt% cellulose,18 due to the disruption of intramolecular H-bonding by nonhydrated Cl-ions.19,20 Since this study, more researchers have used ILs to investigate the dissolution of biomass including lignin,^{21,22} and based on these initial investigations, the use of ILs as solvents for the oxidative degradation of lignin or lignin-related model compounds with molecular oxygen has also been achieved.^{12,23-26} However, the yields of the desired aromatic aldehydes are poor. One main reason is that they are prone to over oxidation, as they are not separated from the reaction mixture. Herein, several ILs were synthesized, characterized and used to constitute a coupled

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process of reaction-separation for the oxidative degradation of lignin to produce aromatic aldehydes.

2. Experimental

2.1 Chemicals and instruments

Lignin (organosolv lignin from Sigma Aldrich, product No. 371017. It is extracted from mixed hardwoods (maple, birch, and poplar) by an organosolv process using aqueous ethanol), trimethyl phosphite (Albright & Wilson), 1-methylimidazole (99.8 wt%, Sigma Aldrich), 1,3-propane sultone (1,2-oxathiolane-2,2-dioxide, 99.7 wt%), and other chemicals (analytic purity) were commercially available and used without further purification.

IR spectra were recorded by a Nicolet 510P FT-IR spectrometer in the range 4500–400 cm⁻¹. NMR spectra were taken by a Bruker AV500 Fourier Transform spectrometer with reference to SiMe₄, using solvent D₂O containing 5 wt% of the sample. Qualitative analysis of the product sample was recorded by a Shimadzu LC-MS 8040 equipped with a column of an Agilent C18 (1.8 μ m, 2.1 mm × 100 mm) and a UV detector set at 280 nm. The mobile phase was a mixture of ammonium acetate (5 mmol l⁻¹) and acetonitrile (100%). Quantitative analysis of the product sample was recorded by an Agilent HP-LC1100 equipped with a column of Dikma ODSC18 (5.0 μ m, 4.6 mm × 250 mm), and an Agilent1200 detector set at 280 nm. The mobile phase was a mixture of acetonitrile (8.5%), deionized water (90%) and acetic acid (1.5%).²⁷

2.2 IL preparation

Trimethyl phosphite (84.5 g, 0.6 mol) was added dropwise in 1-methylimidazole (41.1 g, 0.5 mol) at 150 °C within 2 h and then reacted for 10 h at 115 °C. The resultant mixture was washed with ether three times, and the residual ether was removed under vacuum, then the IL, 1,3-dimethylimidazolium dimethyl phosphate [mmim][Me₂PO₄], was dried under high vacuum at 70 °C for 4 h (106.8 g, yield 95.8%). Other ILs, [mPy][Me₂PO₄], [mtetn][Me₂PO₄] and [mmo][Me₂PO₄], were synthesized according to the same process (Fig. 1). [mmim][Me₂PO₄]: IR (KBr disc): ν 2954.05, 2849.13, 1650.90, 1578.01, 1462.75, 1229.58, 1181.03, 1048.28, 805.90, 751.42, 621.82; ¹H NMR (500 MHz, D₂O): δ 8.47(s, 1H), 7.23(d, 2H, J = 1 Hz), 3.70–3.68(d, 6H, J = 12.5 Hz), 3.31–3.29(t, 6H, J = 11 Hz); ¹³C NMR(125 MHz, D₂O): δ 136.43, 123.28, 52.45, 35.50; ³¹P NMR (202 MHz, D₂O): δ –9.85. [mPy][Me₂PO₄]: IR(KBr



Fig. 1 The structure of the synthesized ILs.

disc): v 2953.55, 2849.40, 1639.82, 1495.84, 1227.21, 1047.90, 808.09, 676.39; ¹H NMR (500 MHz, D₂O): δ 8.61–8.60(d, 2H, *J* = 6.5 Hz), 8.36–8.33(t, 2H, *J* = 7.5 Hz), 7.88–7.85(t, 2H, *J* = 7 Hz), 4.67(s, 3H), 3.39–3.34(m, 6H, *J* = 5.5 Hz); ¹³C NMR (125 MHz, D₂O): δ 145.14, 144.94, 127.82, 52.60, 47.98; ³¹P NMR (202 MHz, D₂O): δ 3.10. [mmo][Me₂PO₄]: IR (KBr disc): v 3008.35, 2954.97, 1653.34, 1472.52, 1229.10, 1048.76, 925.93, 809.76, 538.97; ¹H NMR (500 MHz, D₂O): δ 3.83(t, 4H, *J* = 2.5 Hz), 3.37–3.35(s, 6H, *J* = 11 Hz), 3.30–3.28(t, 4H, *J* = 10 Hz), 3.04(s, 6H); ¹³C NMR (125 MHz, D₂O): δ 3.12. [mtetn][Me₂PO₄]: IR (KBr disc): v 2991.71, 2953.56, 1649.85, 1460.69, 1228.89, 1047.47, 807.75, 538.89; ¹H NMR (500 MHz, D₂O): δ 3.30–3.29(d, 6H, *J* = 10.5 Hz), 3.08–3.06(q, 6H, *J* = 7.5 Hz), 2.67(s, 9H), 1.06–1.03(q, 6H, *J* = 7 Hz); ¹³C NMR (125 MHz, D₂O): δ 5.68, 52.64, 46.31, 7.10, 7.05; ³¹P NMR (202 MHz, D₂O): δ –3.29.

2.3 Catalytic experiments

The reaction phase (white) contains IL, liginin, and the catalyst $CuSO_4$ and is represented in the bottom half of the batch reactor in . The extraction phase (gray) contains methylisobutylketone and is represented in the top half of the batch reactor. Oxidant O_2 , through its distributor (total volume 6 ml, including pipeline), passes directly into the reaction layer (Fig. 2).

The heterogeneous catalytic oxidation degradation process of lignin was carried out in a 100 ml high pressure reactor equipped with an oxygen distributor, a stirrer and a thermometer. 50 g of an IL solution of lignin dissolved at a concentration of 5 wt% and a certain quantity of catalyst $CuSO_4$ were introduced into the reactor. The heating program was started under a slight N_2 pressure. When the solution in the reactor reached the desired temperature, N_2 was added through its catheter until a total pressure of 2.36 MPa was attained (in order to prevent O_2 touching with the extraction phase, N_2 pressure was determined according to the Clapeyron–Clausius equation), and then O_2 was added through its catheter linking the distributor until its pressure balanced with the N_2 pressure and reached 2.5 MPa. O_2 pressure in the reactor was kept at 2.5 MPa by continuous flushing of O_2 as



Fig. 2 Batch process for the production of aromatic aldehydes from lignin with simulated countercurrent extraction.

a supplement because of its consumption during the reaction. When the reaction was finished, the mixture was separated and the IL layer was extracted with methylisobutylketone three times. The extraction solution and the extraction phase were mixed, and the contents of p-hydroxybenzaldehyde (PHB), vanillin (VAN) and syringaldehyde (SYR) were analyzed by high performance liquid chromatography. The residual lignin was obtained from the extracted phase by centrifugation. 30 ml water was added to the extracted phase, and then the precipitated lignin was centrifuged, washed and dried to determine its conversion. The residual lignin was dissolved in the sodium hydroxide solution and a UV spectrophotometer was used to determine lignin content at a wavelength of 280 nm.²⁸ The filtrate was distilled under vacuum to remove the water and to obtain the IL phase which contained the catalyst and was reused in the recycle experimental. Reactant conversion and product yield were calculated as follows: $X_{\text{reactant}}(\%) = \frac{F_{\text{reactant, in}} - F_{\text{reactant, out}}}{F_{\text{reactant, in}}} \times 100\%$, $Y_{\text{product}}(\%) = \frac{F_{\text{product, out}}}{F_{\text{reactant, in}}} \times 100\%$, $F_{i,\text{in}}$ and $F_{i,\text{out}}$ are the weight of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for receptor to a data of the *i* species for the *i* species for the *i* species for the *i* species for receptor to a data of the *i* species for the *i* sp

the *i* species for reactant and product at the inlet and outlet of the reactor, respectively.

3. Results and discussion

3.1 Effects of different ILs on the reaction results

For the reaction-separation coupled process for the oxidative degradation of lignin, solvents with good solubility to aromatic aldehydes, such as acetone, methylisobutylketone, toluene, benzyl chloride, trichloroethane and n-butanol, were investigated. Their solubility in IL [mmim][Me2PO4] and their effect on IL solubility to lignin at room temperature was monitored. The results showed that n-butanol and trichloroethane had good solubilities in ILs, which made the phase separation become infeasible. Toluene and benzyl chloride decreased the lignin solubility in ILs and made the lignin separate out from the IL phase. Acetone and methylisobutylketone did not have the above phenomena and had good performances to build the coupled process of reaction-separation with IL. However, acetone is easy to lose in the processes of separation and reuse, because its saturated vapor pressure is higher than that of methylisobutylketone under atmospheric pressure. Therefore, methylisobutylketone was selected and used for the coupled process of reaction-separation.

As shown in Table 1, compared with the traditional solvent of NaOH aqueous solution (Entry 1), the investigated ILs were better solvents for the oxidative degradation reaction. Especially, ILs [mmim][Me₂PO₄] and [mPy][Me₂PO₄] exhibited outstanding properties with 100% conversion and nearly 30% total yield of aromatic aldehydes (Entries 2 and 3). Furthermore, the amount of byproducts produced was obviously smaller in the coupled process than that of NaOH (Entry 1). For example, among the determined compounds, the yield of syringate decreased from 8.3% to 1.1%, 3,5-dimethoxybenzoic acid from 4.9% to 0.4%, and p-hydroxybenzoic acid was not detected in the coupled process (see ESI[†] S-Fig. 12 and 13). This good reaction result may be explained by the following three points. Firstly, the properties of the IL greatly affect the catalytic activity of the transition metal salt both by stabilizing the reactive intermediate and by favoring the coordination of the substrate to the metal over the direct oxidation of the

Table 1 Effects of different ILs on the reaction results^a

Entry		$X_{ m reactant}$ (%)	Y_{product} (%)		
	ILs		VAN	SYR	PHB
1^b	_	100	10.2	5.6	3.5
2	[mmim][Me ₂ PO ₄]	100	14.7	8.8	6.2
3	[mPy][Me ₂ PO ₄]	100	14.5	8.7	5.9
4	[mtetn][Me ₂ PO ₄]	92.6	12.3	7.1	5.4
5	[mmo][Me ₂ PO ₄]	86.0	11.2	6.5	4.4
6 ^{<i>c</i>}	[mmim][Me ₂ PO ₄]	100	10.5	5.4	3.3

 a Lignin 2.5 g, solvent IL 47.5 g, catalyst CuSO₄ 0.025 g, O₂ pressure 2.5 MPa, *T* = 175 °C, *t* = 1.5 h. b The solvent was 47.5 g, 2.0 mol l^{-1} NaOH aqueous solution, methylisobutylketone was unused, and the other conditions were the same as a. c Methylisobutylketone was not used, and the other conditions were the same as a.

metal without a substrate.²³ An O₂-[mmin] intermediate (Fig. 3, (4)) may be generated from the IL, which enhances the oxygen contact of lignin and accelerates the generation of the intermediate of the quinone methide radical (Fig. 3, (3)) and quinone methide hydroperoxide (Fig. 3, (5)).²⁹ With the combined effects of the above mentioned factors, the proposed mechanism of oxidation of lignin catalyzed by CuSO₄ in IL is depicted in Fig. 3. Secondly, the used IL is a weak alkali and its basicity is lower than that of NaOH. The weaker alkali environment usually increases the oxidative ability of the active oxygen,³⁰ as a result the degradation in IL is easier than that in NaOH.³¹ Otherwise, the degradation of lignin and the extraction of aromatic aldehydes simultaneously happened in the coupled process. Once lignin is oxidized to form aromatic aldehydes, they are extracted by methylisobutylketone and separated from the IL layer, which avoids their deep oxidation reaction and increases their yields. The result from the experimental without using methylisobutylketone as an extractant was also determined to show the effect of the coupled system (Entry 6). Among all the ILs which were investigated, ILs with an aromatic ring in the cation showed better properties for the oxidative degradation of lignin. This is due to the fact that these ILs have a better solubility to lignin, which makes the connecting points of the phenylpropane building units exposed, and then accelerates the process of degradation.

3.2 Effects of reaction conditions on the reaction results

Table 2 shows the effects of reaction conditions on the oxidative degradation reaction. It was obviously seen that the yields of products became higher with increasing the IL dosage from 2.0 g to 3.0 g. However, when lignin dosage was more than 2.5 g (Entry 3), the yields of products did not obviously increase, but the conversion of lignin decreased to 94.2%, which meant that the degradation reaction did not complete at the given time. O_2 pressure was very important for the oxidative degradation reaction. When O₂ pressure was 2.0 MPa, the conversion of lignin was less than 85% under the given conditions (Entry 4). When the O_2 pressure was more than 2.5 MPa, the conversion of lignin reached 100% (Entry 5), but the yields of products obviously decreased. The above results may be due to the fact that, the higher the O_2 pressure, the stronger the oxidative ability of the active oxygen, which leads to aromatic aldehydes oxidizing thus decreasing their



Fig. 3 Proposed mechanism of lignin oxidation in IL [mmim][Me₂PO₄].

yields. The effects of reaction temperature and time on the oxidative degradation reaction are also shown in Table 2 (Entries 2 and 6–9). It was found that both were very important for the degradation reaction. With an increase of reaction temperature from 155 $^{\circ}$ C to 195 $^{\circ}$ C, the conversion of lignin significantly

Table 2 Effects of reaction conditions on the reaction results ^a								
						$Y_{product}$ (%)		
Entry	Lignin (g)	P (MPa)	$T(^{\circ}C)$	<i>t</i> (h)	$X_{reactant}$ (%)	VAN	SYR	PHB
1	2.0	2.5	175	1.5	100	14.3	8.5	6.9
2	2.5	2.5	175	1.5	100	14.7	8.8	6.2
3	3.0	2.5	175	1.5	94.2	14.8	8.6	6.5
4	2.5	2.0	175	1.5	82.3	9.9	3.7	2.0
5	2.5	3.0	175	1.5	100	10.2	4.3	5.4
6	2.5	2.5	155	1.5	86.0	10.5	4.9	2.5
7	2.5	2.5	195	1.5	100	11.7	5.0	5.4
8	2.5	2.5	175	1.0	88.3	11.4	4.8	2.1
9	2.5	2.5	175	2.0	100	12.5	5.3	5.2

^{*a*} Solvent: IL [mmim][Me₂PO₄] 47.5 g. Catalyst: CuSO₄. Extractant: Methylisobutylketone.

increased. However, when the reaction temperature reached 195 °C (Entry 7), the yields of products decreased. With increasing reaction time (Entries 2, 8 and 9), similar reaction results were obtained. Therefore, it was indicated that a higher reaction temperature and longer reaction time were favorable to the deep oxidation of aromatic aldehydes, which made the yields of products decrease obviously. Otherwise, under harsh reaction conditions, such as increasing reaction temperature and O₂ pressure, or prolonging the reaction time, the results showed that the yields of vanillin and syringaldehyde decreased even more sharply than that of *p*-hydroxybenzaldehyde, which indicated that vanillin and syringaldehyde were more easily oxidized than p-hydroxybenzaldehyde. This is because of the electronic effect. Compared with p-hydroxybenzaldehyde, the methoxy group of vanillin or syringaldehyde, as an electron donor, increases the electron cloud density of the benzene ring, which makes its oxidation easier. Based on the above results, the optimum conditions were obtained: IL [mmim] [Me₂PO₄] 47.5 g, lignin 2.5 g, O₂ pressure 2.5 MPa, reaction temperature 175 °C, and reaction time 1.5 h. Under these conditions, the conversion of lignin reached 100%, and the total yield of products was nearly 30%.

Table 3 Reusability of the IL phase

<i>t</i> (h)	X_{reactant} (%)	Y_{product} (%)			
		VAN	SYR	PHB	
1	100	14.7	8.8	7.2	
2	100	14.8	8.7	7.3	
3	100	14.5	8.5	7.0	
4	100	14.7	8.9	7.4	
5	100	14.6	8.6	7.3	
6	100	14.6	8.5	7.2	

3.3 Reusability of the IL phase

In order to investigate the possibility of recycling the IL $[mmim][Me_2PO_4]$, a recycling experiment was conducted under optimum conditions. The reusability of the IL phase including catalyst CuSO₄ is shown in Table 3. The IL phase could be reused six times without an obvious decrease in its performance. This indicated that the IL phase had good reusable performance in the reaction. The good reusability of the IL is attributed to its good thermal stability and good solubility for the catalyst, which can help to avoid the loss of the IL and catalyst during the reaction and separation processes.

In order to investigate the integrity of the repeatedly utilized IL, the obtained low phase during oxidation degradation of lignin was extracted three times with methylisobutylketone and then distilled to remove the residual methylisobutylketone. The residue which was mainly composed of IL [mmim][Me₂PO₄] was obtained and characterized by IR and NMR. The spectra are given in the ESI† (S-Fig. 1–5). The results showed that IR and NMR spectra of the six time-reused IL [mmim][Me₂PO₄] were identical to that of the unused IL. It was demonstrated that the structure of the reused IL was unspoiled.

4. Conclusions

A coupled process of reaction-separation composed IL and methylisobutylketone exhibited good performance in the oxidative degradation reaction of lignin. Compared with the traditional solvent of NaOH aqueous solution, the coupled process avoided the deep oxidation of the products and significantly improved the lignin conversion and the yield of aromatic aldehydes. Otherwise, the mixture of product and IL phase was easily separated, and the IL phase containing the catalyst CuSO₄ had a good reusability. Hence, a clean and environmentally friendly strategy for overall utilization of lignin and preparation of aromatic aldehyde is developed.

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