

New Synthesis of Vanillin by Degradation of Lignin in Presence of Functional Basic Ionic Liquid

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Received: 12 February 2014;

Accepted: 21 May 2014;

Published online: 19 January 2015;

AJC-16690

The degradation of lignin catalyzed by functional basic ionic liquid was investigated. Higher conversion of lignin and simpler degradation product composition were obtained in the presence of basic ionic liquid, comparing with that under traditional NaOH solution. The reaction conditions were optimized. Ultrasound-assisted test proved that the ultrasound pretreatment favored the degradation process.

Keywords: Basic ionic liquid, Degradation, Lignin, Vanillin, Conversion, Selectivity.

INTRODUCTION

With the shortage of petroleum resources, it has become a hot topic to use the renewable biomass to prepare fuels as well as chemicals. Lignin is the second largest renewable resource, which primarily exist in waste water of the paper industry and agricultural wastes and can cause serious pollution to the ecological environment¹⁻³. The conversion of lignin biomass waste into high value-added chemical products is an economic and environmentally friendly way to improve the utilization of biomass. The structure of lignin contains a large number of phenyl propane units, consisting of guaiacyl propanol, syringyl-propanol and *p*-hydroxy-phenyl propanol^{1,4}. Therefore, lignin can be degraded to obtain vanillin, syringaldehyde and *p*-hydroxybenzaldehyde under alkaline conditions. The degradation products are widely used as spices, pharmaceutical and pesticide intermediates^{5,6}. Vanillin are widely present in plants (such as vanilla, vanilla bean, benzoin, balsam and Peru balsam properly Lu, *etc.*) in free form or as glucoside form naturally⁷. Vanillin can be used as fixative agents and flavoring agents in food and cosmetics^{8,9}, but also as plant growth promoters and ripening agent¹⁰⁻¹¹. However, due to the tedious produce process, the shortage of vanillin limited its uses. On the other hand, the synthetic vanillin contained some toxic substances during the production, which hindering the application^{12,13}. Therefore, it is a very significant method to prepare vanillin by degradation of lignin.

In the traditional catalytic wet air oxidation of lignin, sodium hydroxide is used to provide basic system. However, the condition suffers from some drawbacks, such as corrosion, low conversion and difficulty of product separation. The ionic liquids, green catalyst and solvent, has attracted much attention

for the wide application in organic synthesis, electrochemistry, dealing with environmental pollution problems, rational use of resources problems, *etc.*¹⁴⁻¹⁹. Therefore, it is expected that the functional basic ionic liquids could replace the traditional inorganic alkaline solution to promote the lignin oxidation. Moreover, there is no literature about the research of lignin degradation catalyzed by ionic liquids. In this paper, we report the results of production of vanillin by lignin degradation in the presence of basic ionic liquids. This method provide an efficient way to provide high conversion of lignin and selectivity of vanillin.

EXPERIMENTAL

Chemicals were obtained from commercial suppliers and used without further purification. Degradation reactions were carried out as the following typical procedure. A mixture of lignin (3 g), copper catalyst (0.2 g), ferric chloride (0.02 g), ionic liquids [Bmim]OH (0.7 g) and water (40 mL) was heated for the appropriate time in the three-necked flask. During the reaction, the color of solution changed from black to brown red. Degradation macromolecules were obtained by filtration with the semi-permeable membrane. Then, they were dried for 48 h at 50 °C in oven, then characterized by IR spectrograph. The filtrate was extracted with CHCl₃, then evaporated solvent to give the small molecules, which were subjected to gas chromatography-mass spectrometry (GC-MS). The crude product of reaction was measured by UV-visible spectrograph at 297 nm. Finally, vanillin was purified by flash column chromatography. The ¹H NMR spectra were recorded on a BRUKER Avance III (500 MHz for ¹H) in deuterio-chloroform (CDCl₃) at room temperature. ¹H NMR (CDCl₃, 500MHz)

δ : 3.96 (s, 3H), 6.46 (s, 1H), 7.04 (d, $J = 5$ Hz, 1H), 7.42 (s, 2H), 9.83 (s, 1H).

RESULTS AND DISCUSSION

Firstly, the products of degradation with and without basic ionic liquid were characterized by IR spectra. After reaction, the red-brown crude products were filtered through a semi permeable membrane (0.45 μm aperture) and the IR spectra of macromolecules on the semi permeable membrane were carried out. As shown in Fig. 1, for the reaction in the presence of [Bmim]OH²⁰, the characteristic absorptions of functional groups were mainly in the range of 1800-800 cm^{-1} , including frame vibrations of aromatic ring at 1600 and 1500 cm^{-1} , C-C bond stretching vibrations of aromatic ring at 1500-1600 cm^{-1} , C-H bond bending vibrations of aromatic ring at 680-880 cm^{-1} and C-O bond vibrations of alcohols, phenols and ether at 1000-1300 cm^{-1} . Comparing B with C, it was observed that the absorption decrease at 1300-1000 cm^{-1} indicated the break of C-O bond. The strong absorption at the 1750-1650 cm^{-1} , the characteristic peak of C=O double bond, suggested that the formation of the carbonyl group of the degradation macromolecules product. The IR results comparison between before and after reaction (line B and C) proved the decomposition of lignin structure. The line A was similar with line C, which indicating that the lignin could not be degraded when no ionic liquid added.

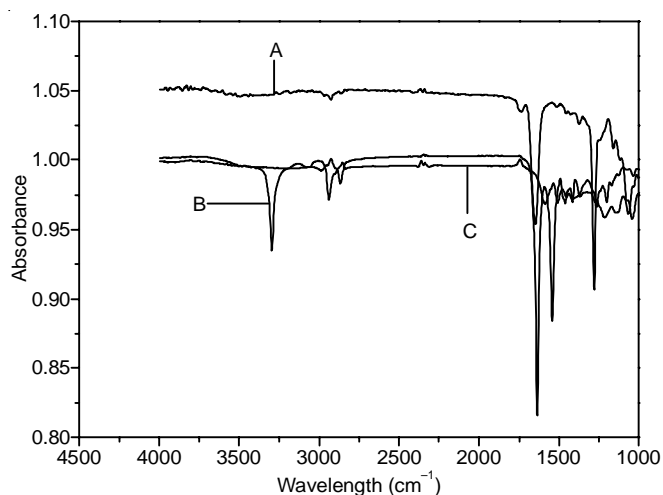


Fig. 1. IR of macromolecules after decomposition, A: no ionic liquid added; B: in presence of ionic liquid [Bmim]OH; C: lignin

Also, the filtrate of the degradation crude product filtering by semi permeable membrane was analyzed by GC. Figs. 2 and 3 showed the GC results of lignin degradation catalyzed by [Bmim]OH and NaOH, respectively. The peak at retention time 16.1 min in Fig. 2 was assigned to vanillin, a major degradation product, with content of 36.2%. Other most of the main products were listed in Table-1. The content of vanillin in Fig. 3 was obviously smaller than that in Fig. 2, which revealing the higher selectivity of vanillin. Furthermore, the simpler composition of products obtained in the presence of ionic liquid resulted in easy separation of decomposition products.

The reaction conditions were optimized by UV-visible spectrophotometer method. Two basic ionic liquids [Bmim]OH

and [Bmim]OAc²¹ and one inorganic catalyst NaOH were examined. As shown in Fig. 4, the absorbance decreased with the reaction processing, except for the reaction with no base added. When the degradation was catalyzed by the ionic liquid [Bmim]OH, the absorbance did not decrease significantly after 2 h any more. The reaction completed. While, for the base of [Bmim]OAc and NaOH, the decomposition finished after 3 and 4 h, respectively. The results suggested that the catalyst [Bmim]OH exhibited an outstanding performance and was an excellent catalyst for decomposition of lignin in this work. The effect of reaction temperature on the degradation of lignin was investigated and the results were shown in Fig. 5.

TABLE-1
GC-MS ANALYSIS OF MAIN PRODUCTS,
DEGRADATION CATALYZED BY BASIC IONIC LIQUIDS

Compound	Structure
N-butylformamide	<chem>CCCCNC=O</chem>
Guaiacol	<chem>COc1ccc(O)cc1</chem>
4-Methyloctanoic acid	<chem>CCCC(C)CCCC(=O)O</chem>
Vanillin	<chem>COc1ccc(C=O)cc1O</chem>
3-Methoxy-4-hydroxyphenyl propane	<chem>COc1ccc(O)cc1CCC</chem>
3-Methoxy-4-hydroxybenzoic acid	<chem>COc1ccc(O)cc1C(=O)O</chem>
4-Hydroxy-3-methoxyphenyl acetic acid	<chem>COc1cc(O)ccc1CC(=O)O</chem>
4-Hydroxy-3,5-dimethoxybenzaldehyde	<chem>COc1cc(O)c(OC)cc1C=O</chem>

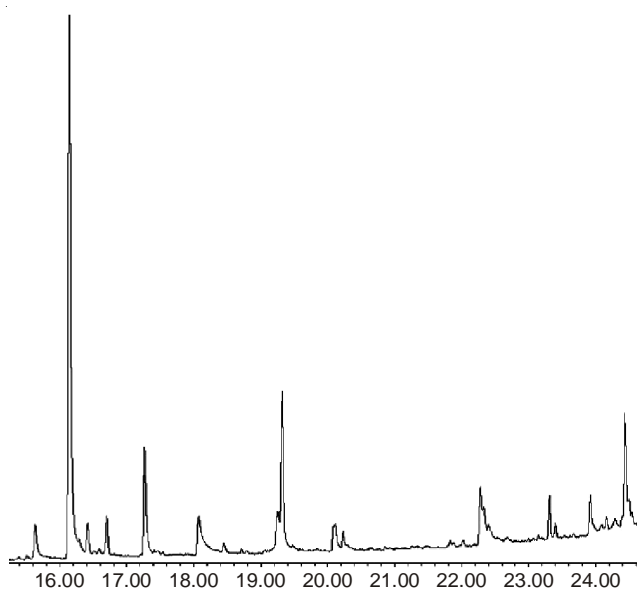


Fig. 2. GC-MS of decomposition product (using ionic liquid as catalyst)

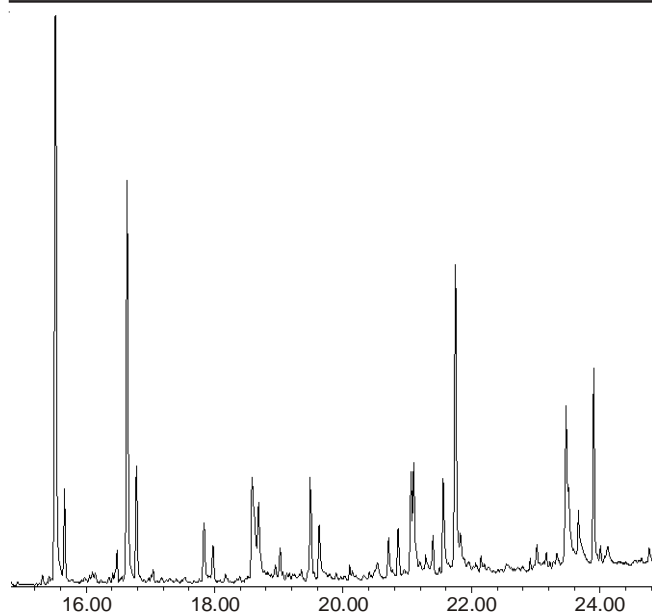


Fig. 3. GC-MS of decomposition product (using NaOH as catalyst)

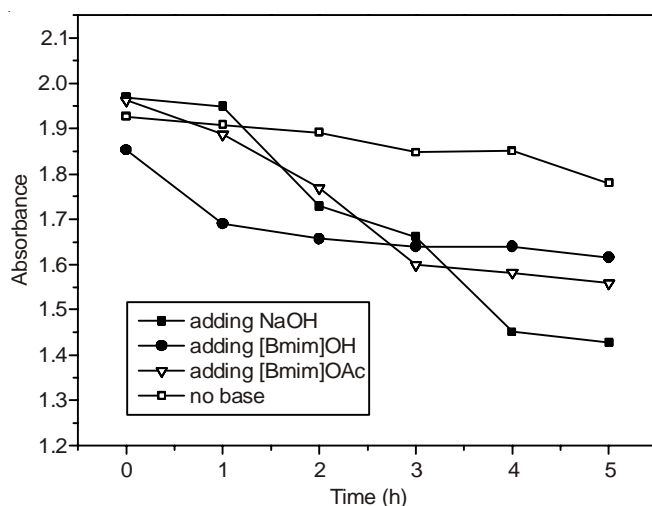


Fig. 4. Relationship of reaction time and absorbance

A great decrease in the crude product absorbance with increasing reaction temperature was observed. Thus, the high temperature was beneficial to the formation of degradation products. When reaction temperature raised to 130 °C, no obvious absorbance decrease was observed. The best degradation temperature that we choose for the optimum condition was 130 °C. The concentration of catalyst is also a very important parameter for the degradation. The effect of catalyst concentration was evaluated and summarized in Fig. 6. The results showed the dependence of degradation conversion on catalyst concentration. The conversion of lignin was improved with the dosage increase of the catalyst. When the concentration of catalyst was higher than 0.15 mol/L, no significant absorbance change occurred. At last, the effect of ultrasound pretreatment to the degradation conversion was also examined. Before heating, the reaction mixture was pretreated by ultrasound equipment and the degradation conversion results were summarized in Table-2. The vanillin content was highest after treating for 0.5 h. The product vanillin was separated by column chromatography and the structure was confirmed by ^1H NMR and purity reached 99 %.

TABLE-2
EFFECT OF PRETREATMENT TIME TO THE DEGRADATION

Entry	Ultrasonic time (min)	Vanillin content ^a (%)
1	0	34.65
2	20	28.59
3	30	39.68
4	60	25.74

^aDetermined by GC-MS; catalyst: [Bmim]OH (0.15 mol/L), reaction time: 2 h, reaction temperature: 130 °C

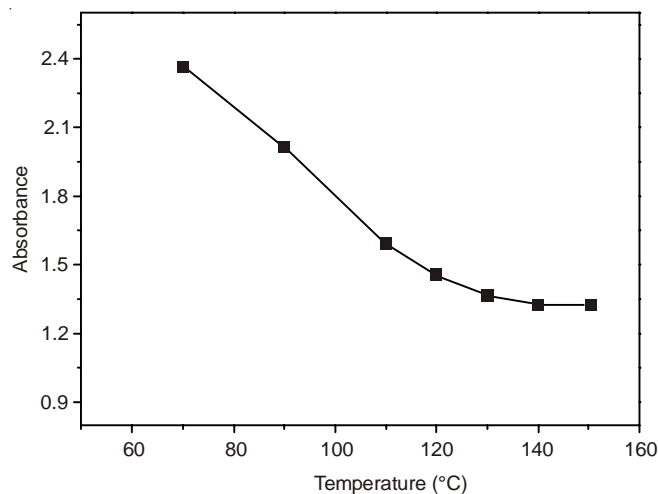


Fig. 5. Relationship of reaction temperature and absorbance (catalyst: [Bmim]OH, reaction time: 2 h)

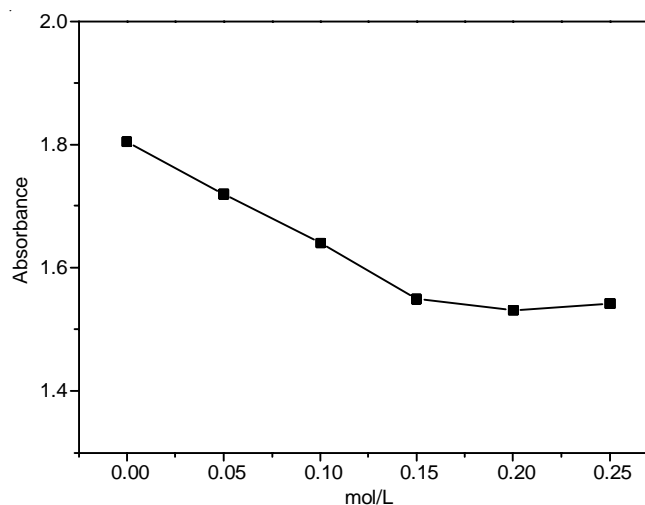


Fig. 6. Relationship of ionic liquid dosage and absorbance (catalyst: [Bmim]OH, reaction time: 2 h, reaction temperature: 130 °C)

Conclusion

In conclusion, functional basic ionic liquid [Bmim]OH was used to promote the degradation of lignin to produce vanillin. The optimized reaction conditions were obtained. Comparing with the reaction under traditional conditions, NaOH solution, the degradation in the presence of the ionic liquid showed high conversion of lignin and selectivity of vanillin.

ACKNOWLEDGEMENTS

The authors thank the financial support from Program of Local Colleges Ability Building of Science and Technology Commission of Shanghai Municipality No. 11520502600 and Alliance Program Project of Shanghai No. LM201247.

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