



Maderas. Ciencia y Tecnología

ISSN: 0717-3644

anantias@ubiobio.cl

Universidad del Bío Bío

Chile

Gu, Xiaoli; Kanghua, Cheng; Ming, He; Shi, Yijun; Li, Zhongzheng
LA-MODIFIED SBA-15/H₂O₂ SYSTEMS FOR THE MICROWAVE ASSISTED OXIDATION OF
ORGANOSOLV BEECH WOOD LIGNIN

Maderas. Ciencia y Tecnología, vol. 14, núm. 1, 2012, pp. 31-42

Universidad del Bío Bío

Concepción, Chile

Available in: <http://www.redalyc.org/articulo.oa?id=48522716003>

- How to cite
- Complete issue
- More information about this article
- Journal's homepage in redalyc.org

redalyc.org

Scientific Information System

Network of Scientific Journals from Latin America, the Caribbean, Spain and Portugal

Non-profit academic project, developed under the open access initiative

LA-MODIFIED SBA-15/H₂O₂ SYSTEMS FOR THE MICROWAVE ASSISTED OXIDATION OF ORGANOSOLV BEECH WOOD LIGNIN

Xiaoli Gu ¹*, Kanghua Cheng¹, Ming He¹, Yijun Shi¹, Zhongzheng Li¹

ABSTRACT

In this manuscript, the influence of organosolv beech wood lignin (LOB) on its oxidative conversion to high added-value phenolic aldehydes is discussed. Environmental friendly and low-cost H₂O₂ was used as the oxygen atom donor. The catalyst was prepared by immobilizing Lanthanum compounds onto the periodic mesoporous channels of siliceous SBA-15. The activity of the La/SBA-15 was investigated towards oxidation of LOB in the presence of hydrogen peroxide as oxidant with microwave irradiation. Considering the characteristics of LOB, an unexpected low syringaldehyde concentration at 10min of reaction time (1.47 g/L, corresponding to 15.66% yield) was obtained; the other major product was vanillin at 25min (0.78 g/L, i.e., 9.94% yield). The high reactivity of syringyl nuclei may be pointed out as the main reason for the faster production and degradation of syringaldehyde in oxidation. Other low molecular weight phenolic products were found: vanillic acid, syringic acid and minor quantities of aceto-derivatives. The profile of products concentration with the reaction time of catalytic oxidation with microwave irradiation are shown and discussed with reference to the investigated lignin features. The mechanism of the microwave catalytic oxidation for LOB under alkaline conditions was proposed.

Keywords: La/SBA-15, organosolv lignin, heterogeneous catalysis, microwave oxidation

INTRODUCTION

Lignin is an extremely complex three-dimensional macromolecule with irregular structure, which is mainly formed by the polymerization of three phenyl propane monomers, i.e. guaiacyl, syringyl and p-hydroxyphenyl units (Caballero *et al.* 1996a, Caballero *et al.* 1996b, Li *et al.* 2002, Wool and Sun 2005). Generally, lignin from hardwood contains higher methoxyl content due to the presence of both guaiacyl and syringyl units. Because of the difficulty for the separation of lignin from biomass, the organosolv process takes the advantage of high efficiency and overcomes the pollution caused by alkali or sulphur containing inorganic compounds (Willauer *et al.* 2000). Currently, the vast majority of lignin is burned or discarded without any industrial utilization for the complexity of lignin and the difficulty in extraction. Consequently, increasing research efforts have been made over the past few years to develop environmentally friendly processes, for example, by the use of oxygen, hydrogen peroxide (H₂O₂), and ozone as primary oxidants.

Lignin offers perspectives for higher added value applications and could be converted to several profitable commodities (Lora and Glasser 2002, Zakzeski *et al.* 2010). It was worthy to be noticed that aromatic aldehyde such as vanillin, syringaldehyde and p-hydroxybenzaldehyde can be obtained from the oxidation process of lignin. These aldehydes have wide applications such as flavoring, chemical intermediates for pharmaceutical drugs and agricultural defensives (Wu *et al.* 1994, Sridhar *et al.* 2005, Sales *et al.* 2006, Sales *et al.* 2007). The chemical composition of lignin and its content

¹Mobile Station for Post-doctoral in Forestry Engineering, College of Chemical Engineering, Nanjing University of Forestry, Nanjing 210037, China

*Corresponding author: njfuchemistry@gmail.com

Received: 08.07.2011 Accepted: 19.10.2011.

in wood vary greatly within a plant, depending on its species, age, morphological location and growth environment. It is recognized that the lignins from softwoods are predominantly based on structural units derived from guaiacyl units in major quantities, which are the precursors for vanillin yield (Kirk *et al.* 1980, Adachi *et al.* 1992). On the other hand, hardwood lignins present structures with much broader chemical compositions, consisting in varying proportion ratios of guaiacyl and syringyl groups. Lignin from different sources can be oxidized to obtain phenolic compounds and the substrate (lignin) properties has certain effect on the yield of oxidation products such as vanillin and syringaldehyde. For instance, it has been shown that lignin with low molecular weight derived from softwoods are preferred to obtain a better vanillin yield than high-molecular weight lignin (José *et al.* 2010).

Industrially, the routine way to convert lignin into aromatic aldehydes selects softwood including isolated lignosulphonates and Kraft lignins as lignin resources, in alkaline media, by oxygen or air to produce vanillin (Bjorsvik 1999, Mathias and Rodrigues 1995). However, with the formation of radical intermediates, such as hydroxyl radicals during the degradation of lignin, the conventional chemical oxidation of lignin leads to a poor selectivity and final product yield (Tarabanko and Petrukhov 2003). And the chemical oxidation of lignin with oxygen is a reaction in which typical operating conditions involve high pH values (close to 14), high temperatures (up to 150 °C) and high total pressure (e.g., 10 bar) (Mathias and Rodrigues 1995). Microwave assisted reactions can be highly efficient and polluteless, allowing a reduction in reaction time and energy consumption together with an increase in yields and selectivity in some cases (James *et al.* 2006, Conesa *et al.* 2007, Kappe 2008). Therefore, microwave assisted selective catalytic process based on a concerted oxygen atom transferred from H₂O₂ might solve these problems with water as the only by-product. In a word, the use of organosolv lignin as raw material, instead of the conventional application of lignosulphonates or Kraft lignin, is lacking presently. Our aim fits in the organosolv hardwood lignin application, but instead of using softwood lignin, to explore the possibility of LOB catalytic oxidation to manufacture aldehydes with microwave irradiation.

Recently, studies of SBA-15 or SBA-15 modified with some noble metals as catalyst in the lignin oxidation process have received significant attention (Badamali *et al.* 2009, Gu *et al.* 2010a) because of their regular pore array with uniform pore diameter (2.0-8.0 nm), high surface area and pore volume (Kresge 1992). Moreover, SBA-15 and Metal/SBA-15 catalyst are known to show interesting activities in the synthetic transformations, such as selective oxidation of styrene, cyclohexane and total oxidation of toluene (Reddy *et al.* 2009, Bendahou *et al.* 2008, Zhang *et al.* 2007). Our research team has successfully investigated the oxidation of lignin model compounds with microwave catalysis and now we are applying the system to a real lignin sample. In the present work, we report the application of Lanthanum-containing SBA-15 mesoporous molecular sieves into lignin catalytic oxidation with hydrogen peroxide as oxidant. A typical hardwood lignin, organosolv beech wood lignin (LOB), was chosen as target molecule and its oxidation was investigated with a heterogeneous La/SBA-15 catalyst and microwave irradiation. To the best of our knowledge, few studies dealing with the catalytic conversion of organosolv lignin and the use of immobilized La-containing SBA-15 for the oxidation of LOB have been reported.

MATERIALS AND METHODS

Materials

In the lignin structure, each of the monomer gives rise to distinct aromatic nuclei: p-hydroxyphenyl (H), guaiacyl (G) and syringyl nuclei (S), respectively. As a typical hardwood lignin, beech wood lignin was supplied by Yunnan, China. Proximate analysis (moisture, ash, volatile content and fixed carbon of lignin sample) and ultimate analysis of the combustible fraction (in weight-by-weight

percentage) are shown in table 1 and table 2. Lignin was treated with oxygen-acetone (150 °C, 4.5 h) to prepare organosolv beech wood lignin (LOB), according to the procedure described in literature (Evtugvin and Andreolety 1998). After being dried in an oven at 105 °C for 3 h to constant weight, and the sample lignin had a high total lignin content (above 94%). The original materials were crushed and pulverized to a size of <0.2 mm before they were analyzed. The carbohydrates on lignin were quantified by gas chromatography with flame ionization detection (GC-FID) as trimethylsilyl derivatives after hydrolysis (Browning 1967, Coimbra *et al.* 1994).

Table 1. Analysis of moisture, volatile matter, ash content, lignin content and carbohydrate in LOB (% (w/w) on dry matter)

Proximate analysis (wt %, dry basis)	
Moisture	11.26
Ash	0.61
Volatile matter	75.32
Fixed carbon ^a	12.81
Total lignin	94.2
carbohydrate	2.5

a: Estimated by difference

The proximate analysis (Table 1) was developed according to ISO standards for moisture (100 °C in air), volatile matter (900 °C in nitrogen atmosphere) and ash (gravimetrically quantified after incineration at 525 °C for 4 h). Table 2 shows the elementary composition and methoxyl content obtained for LOB. Elemental analysis (carbon, hydrogen and nitrogen contents) was performed in a Perkin Elmer 2400 Series II CHN Elemental Analyzer and the percentage of oxygen was calculated by subtracting the C, H and N contents from 100%. The methoxyl group was determined as follows: lignin (0.15 g) was treated with refluxing concentrated sulfuric acid (10 mL) for 10 min, the reaction mixture was cooled, 70 mL of distilled water was added, and the methanol produced in the reaction was distilled off under vacuum and quantified by gas chromatography (Balogh *et al.* 1992, Vázquez *et al.* 1997, Vázquez *et al.* 1999).

Table 2. Elemental composition, methoxyl contents of LOB (% (w/w) on dry matter)

Ultimate analysis (wt%, ash and moisture free)	
Carbon	63.50
Hydrogen	5.54
Nitrogen	0.04
Oxygen ^a	31.22
Methoxyl	19.30

a: Estimated by difference

The gel permeation chromatography (GPC) analysis was performed in Waters-515 attached Ultrastaygel 10³A chromatographic column with lignin solutions prepared in DMF with LiCl, according to the procedure published elsewhere (Pinto *et al.* 2002). Table 3 shows empirical formula of the investigated lignin and its weighted average molecular weight (Mw) and number average molecular weight (Mn). Empirical formula is one current way to describe the lignin, allowing the

estimation of molar mass of ppu (the phenylpropane units of lignin). The oxygen atom per ppu (in range 2.0-3.1) belongs to aliphatic hydroxyl, carbonyl and carboxyl groups of ppu, as well as ether linkages. For each lignin type (softwood and hardwood), an increase in oxygen is accompanied by an increase of hydrogen content. Methoxyl frequency per ppu expresses the contribution of the two methoxyl groups from S units and one methoxyl group from G units for hardwood lignin. The Mn of LOB lignin reveals some degree of depolymerization, corresponding to the delignification process. The valued obtained (1170 g/mol) is similar to the value (1210 g/mol) reported in literature (Lange and Schweers 1980).

Table 3. C₉ formula and results of Mw, Mn and polydispersity (Ps) of LOB

LOB empirical formula and GPC analysis	
C ₉ formula	C ₉ H _{8.36} O _{2.53} (OCH ₃) _{1.20}
Mw of C ₉ formula (g/mol)	194.24
Mw (weight-average, g/mol)	1732
Mn (number-average, g/mol)	1170
Ps (Mw/Mn)	1.5

The following chemicals were purchased from Merk: (i) HPLC grade: methanol, chloroform, formic acid; and (ii) p.a. grade: sodium sulfate anhydrous, sodium hydroxide, hydrogen peroxide (35 wt%). The standard agents for HPLC analysis were as follows: vanillin (V) >98%, syringaldehyde (Sy) 98%, vanillic acid (VA) >97%, syringic acid (SA) 97%, acetovanillone (VO) 98%, acetosyringone (SO) 97% (Sigma-Aldrich).

La/SBA-15 was prepared and characterized according to documented procedures (Gu *et al.* 2010b). Triblock poly(ethylene oxide)₂₀-poly(propylene oxide)₇₀-poly(ethylene oxide)₂₀ (P123, average molecular mass about 5800, Aldrich) and lanthanum nitrate were dissolved in a mixture (pH≈1) under stirring and added tetraethyl orthosilicate (TEOS) to this solution. The mixture was kept under continuous agitation at 40 °C for 24 h. Then the gel was transferred to autoclave and aged at 100 °C for 24 h. The solid product was recovered by filtration and repeated washing with deionised water, followed by drying at 50 °C overnight. The P123 template was removed by calcining at 550 °C for 8 h in air.

Methods

The low molecular weight phenolic compounds (Figure 1) produced by lignin oxidation with La-SBA-15/H₂O₂ were extracted by solid phase extraction and quantified by HPLC-UV, as described in literature (Pinto *et al.* 2010).

Reversed Phase High Pressure Liquid Chromatography analyses were carried out on Agilent 1100 HPLC system, equipped with a Hypersil ODS column (100 mm × 2.1 mm × 5 μm film thickness) using methanol/NaH₂PO₄ solution (water adjust 5 mmol/L) (70/30, v/v) as mobile phase, flow rate 0.4mL/min, UV-DAD detection wavelength 280 nm, the column temperature 30 °C, the injection volume 5 μL, calculating the reaction products concentration with external standard method (Herrmann and Stockli 1982).

Catalytic activity studies

In a typical reaction, 15 g of LOB (Mn=1170 g/mol) and 35% aqueous H₂O₂ (10 mL) was dissolved in 150 mL of alkaline solution (20 g of NaOH). After complete dissolution, 5 g catalyst was added in the resulting mixture and diluted until a final volume of 250 mL (pH=13-14). Then the reaction mixture were placed in a 300 mL microwave tube and irradiated at 200 W on a CEM discover microwave reactor for the time specified in table 4. The same mixture in a round-bottomed flask was also reacted under conventional heating at 60 °C for 24 h for comparative purposes. Products yield were calculated as follows:

$$Y_{product} (\%) = \frac{F_{product, out}}{F_{reactant, in}} \times 100\%$$

$F_{i, in}$ and $F_{i, out}$ are the molar flow rate of the *i* species for reactant and product at the inlet and at the outlet of the reactor, respectively.

The low molecular weight phenolic compounds (Figure 1) produced by lignin oxidation with La-SBA-15/H₂O₂ were extracted by solid phase extraction and quantified by HPLC-UV, as described in literature (Pinto *et al.* 2010).

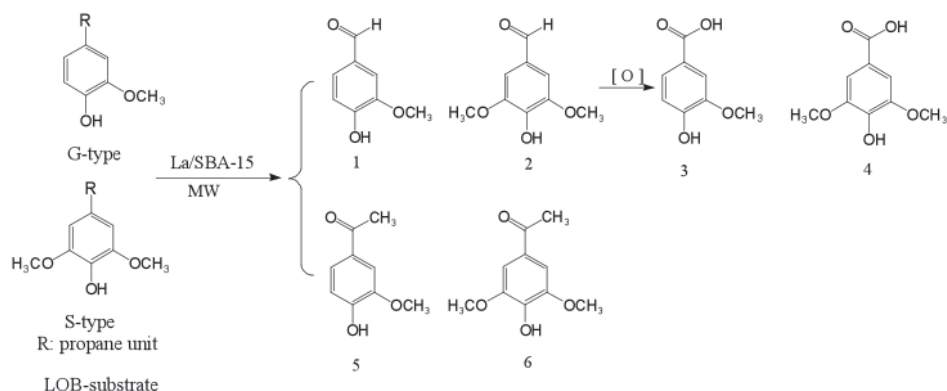
GC analyses were carried out on Agilent 6890 GC system, equipped with a DB-17MS capillary column (30 m × 0.25 mm × 0.25 μm film thickness) using nitrogen as carrier gas. The initial column injector was set to 300 °C with an initial column temperature of 60 °C, raised to 150 °C with a ramp rate of 15 °C /min and then 25 °C /min to 290 °C keeping for 15 min. Substrate conversion and product selectivity were determined using external standard method, with n-decane as external standard

RESULTS AND DISCUSSION

LOB is a hardwood lignin and, accordingly, G and S (Figure 1) products were found. The maximum yield of V was 0.78 g/L (9.94% molar yield) and the yield of Sy was 1.47 g/L (15.66% molar yield) at different reaction times. Secondary products were also found, but below 6% yield based on initial molar amount of lignin (see Table 4).

Oxidation of LOB substrate resulted in formation of major phenolic aldehydes:

Vanillin (4-hydroxy-3-methoxybenzaldehyde) (1),
 syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde) (2), and minor aceto derivatives: acetovanillone (4-hydroxy-3-methoxyacetophenone) (5),
 Acetosyringone (3,5-dimethoxy-4-hydroxyacetophenone) (6)
 Phenolic aldehydes is the first oxidation product, while vanillic acid (4-hydroxy-3-methoxybenzoic acid) (3) and syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid) (4) is formed through oxidation of the phenolic group together with further oxidation.



- 1: Vanillin (4-hydroxy-3-methoxybenzaldehyde)(V)
- 2: Syringaldehyde (4-hydroxy-3,5-dimethoxybenzaldehyde)(Sy)
- 3: Vanillic acid (4-hydroxy-3-methoxybenzoic acid) (VA)
- 4: Syringic acid (4-hydroxy-3,5-dimethoxybenzoic acid) (SA)
- 5: Acetovanillone (4-hydroxy-3-methoxyacetophenone)(VO)
- 6: Acetosyringone (3,5-dimethoxy-4-hydroxyacetophenone)(SO)

Figure 1. Product distribution in the oxidation of LOB substrate under microwave irradiation

Table 4 includes results of the oxidation of LOB using La/SBA-15 at different times with changeable temperature (<423K) under microwave irradiation. The changes of product distribution of LOB oxidation with time are shown in figure 2. The plot shows that the amounts of V and Sy increase significantly during the initial 10 min. In the same period of time, the amount of VA and VO increased slowly. With progressive reaction time, the yield of V reaches a plateau of 9.94% at 25 min; the yield of Sy decreases after it passes a maximum yield of about 17% at 7 min; the yield of VA slightly increase (max at 12 min) and then decreases to a constant yield of 2.5%; and similarly, the yield of VO slightly increases (max at 5 min) and then decreases to zero after 20 min. During the whole reaction time, negligible amounts of SA and SO was detected because the S units have higher reactivity than guaiacyl counterparts in alkaline systems (Tsutsumi *et al.* 1995) and under conditions of O_2 or H_2O_2 oxidation in alkaline medium (Wu *et al.* 1994; Sultanov and Wallis 1991). We suggest the Sy is produced at higher yield, but it is promptly degraded; in the case of S units, this effect is probably more evident due to the above mentioned reactivity of S nuclei. VA and SA were also formed, showing similar trend of the profile of V and Sy, respectively. The total molar yield of products was up to 32% and the selectivity of phenolic aldehydes was about 25% when the reaction time was 10 minutes. Compared with the present report of lignin oxidation with O_2 as oxidant (Pinto *et al.* 2011), our microwave catalytic oxidation with H_2O_2 as oxidant method has advantages of efficient activity with higher aldehydes yield and reduction in reaction time, as well as friendly environmental effects with milder condition and lower environmental compared with conventional chemical oxidation. The aromatic aldehyde, the oxidative products from lignin in the catalytic process, can be further oxidized to aromatic acids, and even to high molecular weight compounds including phenolic dimers and quinines (Crestini *et al.* 2005).

It was also shown that rate of substrate conversion and yield of each oxidative products were significantly higher with the catalyst La/SBA-15 than that without the catalyst. In the absence of a catalyst, the total product yield was only 2% at 24 h (Table 4, entry 7), in comparison with 32% for product molar yield with La/SBA-15 as catalyst at 10 min (Table 4, entry 2). For example, the yield of V and Sy were 9.56% and 15.66% in 10 minutes with the La/SBA-15 catalyst, 9.18% and 15.14%

higher than that of the non-catalytic process, whose maximum yield was only 0.38% and 0.52%. The maximum yield of VA and SA were 5.19% (10 min) and 2.45% (5 min) in the La/SBA-15 catalytic process, 8.95 and 3.45 times those obtained in the non-catalytic process, respectively.

Aceto derivatives (VO and SO) were detected at low concentration because of the competing addition of OH⁻ to α -position (leading to aceto derivatives) and to γ - position (leading to phenolic aldehydes) of quinonemethide (Villar *et al.* 2001, Tarabanko *et al.* 2004). The concentration of aceto derivatives is comparatively low, e.g., VO concentration increased during the reaction and it did not exceed 0.1 g/L while the concentration of SO in LOB oxidation mixture was only residual.

Table 4. Products concentration and yield obtained from LOB oxidation with different reaction time using La/SBA-15 catalysis^a

Entry	Time of reaction (min)	Product concentration (g/L)						Product yield (mol %)					
		1	2	3	4	5	6	1	2	3	4	5	6
1	5	0.47	1.46	0.21	0.25	0.02	- ^b	5.99	15.56	2.42	2.45	0.23	0.00
2	10	0.75	1.47	0.45	0.13	0.03	0.01	9.56	15.66	5.19	1.27	0.35	0.10
3	15	0.76	1.18	0.45	0.05	0.05	-	9.69	12.57	5.19	0.49	0.58	0.00
4	20	0.75	0.81	0.25	0.01	0.05	-	9.56	8.63	2.88	0.10	0.58	0.00
5	25	0.78	0.73	0.23	-	0.06	-	9.94	7.78	2.65	0.00	0.70	0.00
6	30	0.66	0.74	0.21	-	0.06	-	8.41	7.89	2.42	0.00	0.70	0.00
7	1440 ^c	0.03	0.05	0.05	0.07	-	-	0.38	0.52	0.58	0.71	0.00	0.00

^a Microwave reaction conditions: 15 g LOB, 5 g catalyst and 10 mL 35% aqueous H₂O₂ in a final volume of 250 mL alkaline solution (pH=13-14), microwave irradiation 200 W

^b - Not detectable

^c 60 °C for 24 h, without microwave irradiation and without catalyst

As a hardwood lignin for LOB, G and S (Figure 2) products were found. In details, the maximum yield of V was 0.78 g/L (9.94% molar yield) and the yield of Sy was 1.47 g/L (15.66% molar yield) at different reaction times, comparative evaluation with those reported in the literature (Pinto *et al.* 2011). Over-oxidized products were also found, but below 5.2% in product molar yield (Table 4). Taking into consideration of LOB high proportion of S units, a high yield in alkaline catalytic oxidation was expected. However, the yield of products for the S relative yield (about 15%) was even lower than the G yield (18%), which is in agreement with results published by other authors (Pinto *et al.* 2011).

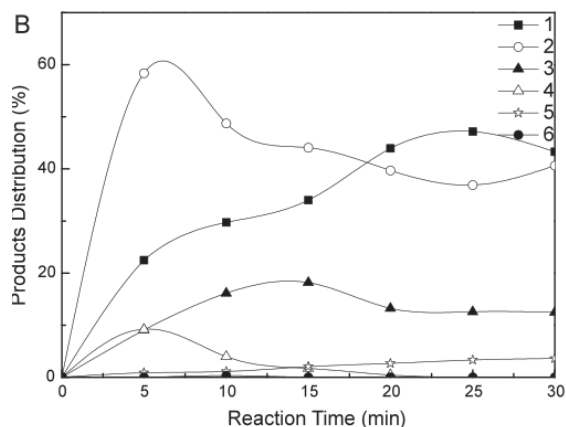


Figure 2. Products yield (a) and distribution (b): 1. Vanillin(■), 2. Syringaldehyde(o), 3. Vanillic acid(Δ), 4. Syringic acid(Δ), 5. Acetovanillone(★), 6. Acetosyringone(●) at different reaction time. The microwave reaction conditions: 15 g LOB, 5 g catalyst and 10 mL 35% aqueous H_2O_2 in a final volume of 250 mL alkaline solution (pH=13-14).

Based on the results of this work and previous studies concerning the reaction between hydrogen peroxide and lignin compounds (Kempf 1975, Xiang and Lee 2000), we propose a possible reaction mechanism for oxidation of LOB by hydrogen peroxide under alkaline conditions with microwave catalysis (Figure 3). Under alkaline conditions, hydrogen peroxide is quickly decomposed to molecular oxygen and other radical species. An extremely strong nucleophile (HOO^-), produced by hydrogen peroxide, is considered to be the active species for alkaline hydrogen peroxide oxidation (Eq. 1). Some perhydroxyl anions (HOO^-) and hydroxyl anions ($\cdot OH$) produced by HOO^- (Eq. 2) attack the aryl ether bonds and other linkages under these conditions (Eq. 3), and others decomposed to O_2 and H_2O (Eq. 4-5), which influence oxidation efficiency for hydrogen peroxide. Lignin-derived products of commercial interest such as vanillin and syringaldehyde are produced by side-chain reaction through this pathway.

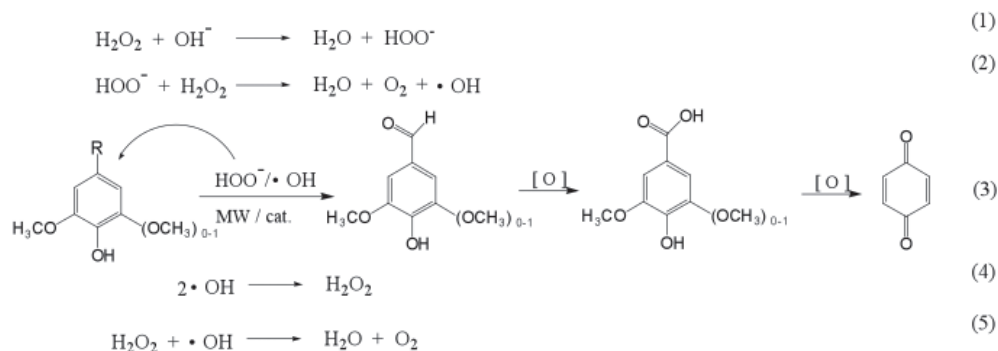


Figure 3. Proposed reaction sequence for catalytic oxidation of LOB by hydrogen peroxide with microwave irradiation under alkaline condition

CONCLUSION

In this work, microwave assisted catalytic oxidation of a typical organosolv lignin over Lanthanum modified SBA-15/H₂O₂ system was investigated. The following conclusions were reached from this systematic study.

A typical hardwood organosolv beech wood lignin (LOB) was prepared and characterized by GPC and the empirical formula was assessed, which was selected to proceed for catalytic oxidation with hydrogen peroxide under microwave irradiation.

For the first time we have demonstrated that mesoporous La/SBA-15 acts as an efficient catalyst for oxidation of LOB. The active La species seemed to be stabilized within the mesoporous host, rendering unusual oxidative ability and excellent selectivity for aldehydes.

The catalytic oxidation with hydrogen peroxide had lead to different yields of aldehydes, and the respective acids and aceto derivatives. The highest yield on V was 0.78 g/L (9.94% yield) and the yield of Sy was 1.47 g/L (15.66% yield). The balance of the reactions leading to aldehydes production, aldehydes degradation and competing reactions determines the maximum yield and selectivity to be attained.

9.56% yield of vanillin and 15.66% yield of syringaldehyde were obtained after 10 min of reaction under 200W microwave irradiation, compared to a poor 0.38% and 0.52% yield of corresponding aldehydes. The result is attributed to the presence of isolated hydroxyl groups and the meso-micro pore architecture, which provides an ideal environment for the reaction. Microwave assisted reactions were found to be efficient and selective as compared to the thermal reactions.

The mechanism of the microwave catalytic oxidation for LOB under alkaline conditions was proposed. The reaction patterns of the oxidation involve the cleavage of lignin ring, aryl ether bond, or other linkages within lignin. By using the findings of this investigation and those of previous work, we have illustrated the reaction pathway for oxidation of LOB.

ACKNOWLEDGEMENTS

A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions. The authors are grateful to the financial support from China Postdoctoral Science Foundation funded project (No. 20110491435), Jiangsu Planned Projects for Postdoctoral Research Funds (No. 1101028C), Forestry industry research special funds for public welfare project (201104032), National Natural Science Foundation of China (50903043, 51005123) and '863' National High Technology Research and Development Key Program of China (2010AA101602).

REFERENCES

- Adachi, S.; Tanimoto, M.; Tanaka, M.; Matsuno, R. 1992.** Kinetics of the alkaline nitrobenzene oxidation of lignin in rice straw. *Journal of Chemical Engineering* 49(2): 17-21.
- Badamali, S.K.; Luque, R.; Clark, J.H.; Breeden, S.W. 2009.** Microwave assisted oxidation of a lignin model phenolic monomer using Co(salen)/SBA-15. *Catalysis Communication* 10(10):1010-1013.

Balogh, D.T.; Curvelo, A.A.S.; De Groote, R.A. 1992. Solvent effect on organosolv lignin from *Pinus Caribaea Hondurensis*. *Holzforschung* 46(4): 343-348.

Bendahou, K.; Cherif, L.; Siffert, S.; Tidahy, H. L.; Benaïssa, H.; Aboukaïs, A. 2008. The effect of the use of lanthanum-doped mesoporous SBA-15 on the performance of Pt/SBA-15 and Pd/SBA-15 catalysts for total oxidation of toluene. *Applied Catalysis A: General*. 351(1): 82-87.

Bjorsvik, H.R. 1999. Fine chemicals from lignosulfonates. I. Synthesis of vanillin by oxidation of lignosulfonates. *Organic Process Research & Development* 3(5): 330-340.

Browning, B.L. 1967. *Methods in Wood Chemistry*. Interscience Publishers: New York, USA. Vol. 2. pp. 387.

Caballero, J.A.; Font, R.; Marcilla, A. 1996a. Study of the primary pyrolysis of Kraft lignin at high heating rates: yields and kinetics. *Journal of Analytical and Applied Pyrolysis* 36(2):159-178.

Caballero, J.A.; Font, R.; Marcilla, A. 1996b. Kinetic study of the secondary thermal decomposition of Kraft lignin *Journal of Analytical and Applied Pyrolysis* 38(1):131-152.

Coimbra, M.A.; Waldron, K.W.; Selvendran, R.R. 1994. Isolation and characterisation of cell wall polymers from olive pulp (*Olea europaea* L.). *Carbohydrate Research* 252(3):245-262.

Conesa, T.D.; Campelo, J.M.; Clark, J.H.; Luque, R.; Macquarrie, D.J.; Romero, A.A. 2007. A microwave approach to the selective synthesis of ω -laurolactam. *Green Chemistry* 9(10): 1109-1113.

Crestini, C.; Pro, P.; Neri, V.; Saladino, R. 2005. Methyltrioxorhenium: a new catalyst for the activation of hydrogen peroxide to the oxidation of lignin and lignin model compounds. *Bioorganic & Medicinal Chemistry* 13(7): 2569-2578.

Evtugvin, D.V.; Andreolety, J.P. 1998. Polyurethanes based on oxygen-organosolv lignin. *European Polymer Journal* 34(8): 1163-1169.

Gu, X.L.; He, M.; Shi, Y.J.; Li, Z.Z. 2010a. Production of aromatic aldehyde by microwave catalytic oxidation of a lignin model compound with La-containing SBA-15/H₂O₂ systems. *Bioresources* 5(4):2029-2039.

Gu, X.L.; He, M.; Shi, Y.J.; Li, Z.Z. 2010b. La-containing SBA-15/H₂O₂ systems for the microwave assisted oxidation of a lignin model phenolic monomer. *Maderas. Ciencia y Tecnología* 12(3): 181-188.

Herrmann, A.; Stockli, M. 1982. Rapid control of vanilla-containing products using high-performance liquid chromatography. *Journal of Chromatography* 246: 313-316.

James, H.C.; Vitaly, B.; Fabien, E.I.D.; Jeffrey, J.E.H.; Fran, M.K.; Andrew, J.H.; Rafael, L.; Duncan, J.M.; Krzysztosf, M.; Aitana, R.; Owain, S.; Stewart, J.T.; Robin, J.W.; Ashley, J.W. 2006. Green chemistry and the biorefinery: a partnership for a sustainable future. *Green chemistry* 10(8): 853-860.

José, D.P.A.; Carlos, A.G.; Alírio, E.R. 2010. Vanillin production from lignin oxidation in a batch reactor. *Chemical Engineering Research and Design* 88(8): 1024-1032.

Kappe, C.O. 2008. Microwave Dielectric Heating in Synthetic Organic Chemistry. *Chemical Society Reviews* 37(6): 1127-1139.

Kempf, W. 1975. *Chemistry of Delignification with Oxygen, Ozone, and Peroxides*. North Carolina State University School of Forest Resources, UNI Publishers, Tokyo, Japan. pp.207-216.

Kirk, T.K.; Higuchi, T.; Chang, H.M. 1980. *Lignin structure and morphological distribution in plant cell wall*, in *Lignin Biodegradation: Microbiology, Chemistry, and Potential Applications*, CRC Press, Boca Raton, Florida, USA. pp. 1-20.

Kresge, C.T.; Leonowicz, M.E.; Roth, W.J.; Vartuli, J.C.; Beck, J.S. 1992. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature* 359(6397): 710-712.

Lange, W.; Schweers, W. 1980. The carboxymethylation of organosolv and kraft lignins. *Wood Science and Technology* 14(1): 1-7.

Li, J.; Li, B.; Zhang, X.C. 2002. Comparative studies of thermal degradation between larch lignin and manchurian ash lignin. *Polymer Degradation and Stability* 78(2): 279-285.

Lora, J.H.; Glasser, W.G. 2002. Recent Industrial Applications of Lignin: A Sustainable Alternative to Nonrenewable Materials. *Journal of Polymers and the Environment* 10(1): 39-48.

Mathias, A.L.; Rodrigues, A.E. 1995. Production of vanillin by oxidation of pine kraft lignins with oxygen. *Holzforschung* 49(3): 273-278.

Pinto, P.C.; Evtuguin, D.V.; Neto, C.P.; Silvestre, A.J.D. 2002. Behavior of Eucalyptus globulus lignin during kraft pulping I. Analysis by chemical degradation methods. *Journal of Wood Chemistry and Technology* 22(2): 93-108.

Pinto, P.C.; Borges da Silva, E.A.; Rodrigues, A.E. 2010. Comparative study of solid-phase extraction and liquidliquid extraction for the reliable quantification of high value-added compounds from oxidation processes of wood derived lignin. *Industrial & Engineering Chemistry Research* 49(23): 12311-12318.

Pinto, P.C.; Silva E.A.; Rodrigues, A.E. 2011. Insights into oxidative conversion of lignin to high addedvalue phenolic aldehydes. *Industrial & Engineering Chemistry Research* 50(2):741-748.

Reddy, S.S.; Raju, B.D.; Padmasri, A.H.; Prakash, P.K.S.; Rao, K.S.R. 2009. Novel and efficient cobalt encapsulated SBA-15 catalysts for the selective oxidation of cyclohexane. *Catalysis Today* 141(1-2): 61-65.

Sales, F.G.; Maranhão, L.C.A.; Filho, N.M.L.; Abreu, C.A.M. 2006. Kinetic Evaluation and Modeling of Lignin Catalytic Wet Oxidation to Selective Production of Aromatic Aldehydes. *Industrial & Engineering Chemistry Research* 45(20): 6627-6631.

Sales, F.G.; Maranhão, L.C.A.; Filho, N.M.L.; Abreu, C.A.M. 2007. Experimental evaluation and continuous catalytic process for fine aldehyde production from lignin. *Chemical Engineering Science* 62(18): 5386-5391.

Sridhar, P.; Araujo, J.D.; Rodrigues, A.E. 2005. Modeling of vanillin production in a structured bubble column reactor. *Catalysis Today* 105(3): 574-581.

Sultanov, V.S.; Wallis, A.F.A. 1991. Reactivities of Guaiacyl and Syringyl Lignin Model Phenols Towards Oxidation with Oxygen-Alkali. *Journal of Wood Chemistry and Technology* 11(3): 291 -305.

Tarabanko, V.E.; Petrukhov, D. V. 2003. Study of mechanism and improvement of the process of oxidative cleavage of lignins into the aromatic aldehydes. *Chemistry for Sustainable Development* 11: 655-667.

Tarabanko, V.E.; Petukhov, D.V.; Selyutin, G.E. 2004. New Mechanism for the Catalytic Oxidation of Lignin to Vanillin. *Kinetics and Catalysis* 45(4): 569-577.

Tsutsumi, Y.; Kondo, R.; Sakai, K.; Imamura, H. 1995. The difference of reactivity between syringyl lignin and guaiacyl lignin in alkaline systems. *Holzforschung* 49(5): 423-428.

Vázquez, G.; Antorrena, G.; González, J.; Freire, S. 1997. The influencing of pulping conditions on the structure of acetosolv eucalyptus lignins. *Journal of Wood. Chemistry and Technology* 17(1-2):147-162.

Vázquez, G.; Freire, S.; Bona, C.R.; González, J.; Antorrena, G. 1999. Structures and reactivities with formaldehyde, of some acetosolv pine lignins. *Journal of Wood Chemistry and Technology* 19(4): 357-378.

Villar, J.C.; Caperos, A.; García-Ochoa, F. 2001. Oxidation of hardwood kraft-lignin to phenolic derivatives with oxygen as oxidant. *Wood Science and Technology* 35(3): 245-255.

Wool, R.; Sun, X.S. 2005. *Bio-based polymers and composites*. Amsterdam: Elsevier-Academic Press. Burlington, California, USA. pp. 552-557.

Willauer, H.D.; Huddleston, J.G.; Li, M.; Rogers, R.D. 2000. Investigation of aqueous biphasic systems for the separation of lignins from cellulose in the paper pulping process. *Journal of Chromatography B: Biomedical Sciences and Applications* 743(1): 127-135.

Wu, G.; Heitz, M.; Chornet, E. 1994. Improved Alkaline Oxidation Process for the Production of Aldehydes (Vanillin and Syringaldehyde) from Steam-Explosion Hardwood Lignin. *Industrial & Engineering Chemistry Research* 33(3): 718-723.

Xiang, Q.; Lee, Y.Y. 2000. Oxidative Cracking of Precipitated Hardwood Lignin by Hydrogen Peroxide. *Applied Biochemistry and Biotechnology* 84(1):153-162.

Zakzeski, J.; Bruijninx, P.C.A.; Jongerius, A.L.; Weckhuysen, B.M. 2010. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. *Chemical Review* 110(6): 3552-3599.

Zhang, L.X.; Hua, Z.L.; Dong, X.P.; Li, L.; Chen, H.R.; Shi, J.L. 2007. Preparation of highly ordered SBA-15 by physical-vapor-infiltration and their application to liquid phase selective oxidation of styrene. *Journal of Molecular Catalysis A: Chemical* 268(1-2): 155-162.