FAST PYROLYSIS OF ENZYMATIC/MILD ACIDOLYSIS LIGNIN FROM MOSO BAMBOO

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The characteristics of enzymatic/mild acidolysis lignin (EMAL) isolated from moso bamboo were investigated using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). Pyrolysis temperature as a factor on products was studied, and the pyrolysis mechanism was inferred with respect to the dominating products. Research results showed that pyrolysis products derived from EMAL pyrolysis were mainly heterocyclic (2,3-dihydrobenzofuran), phenols, esters, and a minor amount of acetic acid. Pyrolysis temperature had a distinct impact on yields of pyrolysis products. As pyrolysis temperature increased, the yield of 2,3-dihydrobenzofuran rapidly decreased; however, yields of phenols increased smoothly. It can be obtained that, at the low temperatures (250-400^{o}C), pyrolysis products were mainly 2,3-dihydrobenzofuran, and the highest yield was 66.26% at 320^{o}C; at the high temperatures (400-800^{o}C), pyrolysis products were mainly phenols, and yields hit their highest level of 56.43% at 600 ^{o}C. A minor amount of acetic acid only emerged at 800°C. Knowledge of pyrolysis products releasing from EMAL and the pyrolysis mechanism could be basic and essential to the understanding of thermochemical conversion of EMAL to chemicals or high-grade energy.

Keywords: Lignin; Pyrolysis; Thermochemical; Moso bamboo; Py-GC/MS; Mechanism

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INTRODUCTION

As a renewable energy source with enormous reserves worldwide, biomass has been investigated for the thermochemical conversion into new energy. The technique of thermochemical conversion covers gasification, liquefaction, and pyrolysis. The pyrolysis of biomass, as a means of producing liquid fuels and even high-value chemicals, has been the subject of intensive research (Manuel et al. 2008; Liu and Shen 2009). In recent years, fast pyrolysis for liquid fuel production has been widely investigated (Bridgwater and Meier 1999). With pyrolysis, the light decomposed fragments are converted to oily compounds through homogeneous reactions in the gas phase (Demirbas 1998, 2000). The components of biomass depolymerize and disintegrate by thermochemical methods that result in the formation of various products, including a solid residue of charcoal.

Lignin with a high molecular weight polymer has a three-dimensional polymer mainly consisting of phenylpropane units (Lu and Ralph 1999), which is the second largest component in biomass. According to the number of methoxyl groups, the phenylpropane monomers can be classified into three basic units, i.e. syringyl (S-), guaiacyl (G-), p-hydroxyphenyl (p-H-) types, which vary in relative abundance in the polymer, depending on plant species.

In order to thoroughly investigate the properties of lignin, it is necessary to isolate it from biomass. In this work, an enzymatic/mild acidolysis method for lignin preparation proposed by Wu and Argyropoulos was applied to isolate lignin from non-wood fiber to obtain enzymatic/mild acidolysis lignin (EMAL) (Wu and Argyropoulos 2003; Wang and Wu 2006). Lignins can be pyrolyzed reproducibly to produce a mixture of relatively simple phenols resulting from cleavage of ether and certain C-C linkages. Most of these phenols retain their substitution patterns from lignin polymer that can be easily identified the components from p-H-, G-, and S-type lignin moieties. Harris and Hartley (1980) detected in both legumes and grasses a substantial fraction of ferulic acid and p-coumaric acid, and Sarkanen and Ludwig (1971) found that grass lignins differ from wood lignins; grasses contain higher amounts of p-H units resulting from inclusion of p-coumaryl alcohol along with coniferyl and sinapyl alcohols in the monomer pool for free radical-induced polymerization. On pyrolysis of grasses, Faix et al. (1991) examined bamboo pyrolysis coupled to gas chromatography/mass spectrometry. Hartley and Haverkamp (1984) correlated phenolic acids in grasses with total ion pyrolysis-MS, and the abundance of phenols production from beech MWL (milled wood lignin) was expounded by Genuit and Boon (1987) with pyrolysis-gas chromatography-photoionization mass spectrometry. Py-GC/MS analysis gives detailed structural information (Kuroda et al. 1984; Bottcher et al. 1997; Hartley et al. 1984). Lignin is degraded into low molecular weight compounds by pyrolysis or other thermochemical techniques to get detailed information about lignin structure. During thermal degradation, the cleavage and substitution of alkyl groups, ether links, β-O-4 bonds and enough C-C linkages in lignins generate phenols products derived from three basic lignins (p-H-, G-, S-), and the whole side-chains of aromatic subunits lignin are dissociated through bond breaking of α-β and β-γ bonds and dehydrogenation. This paper will present detailed information on the thermochemical characteristics of lignin using Py-GC/MS, and it will help to advance the development on thermochemical conversion and thermal degradation mechanisms of lignin under varied temperature conditions.

EXPERIMENTAL

Materials

Bamboo

Moso bamboo (*Phyllostachys pubescens* Mazel) came from Hunan Province (P.R. China). Removing the leaves, Moso bamboo was ground and then extracted for 48hs with acetone solvent, and milled in a porcelain ball jar for 240hs at a rotational speed of 36rpm. The obtained powder was used to isolate lignin from moso bamboo by the enzymatic/mild acidolysis method (Wang and Wu 2006; Lou and Wu 2008) to obtain EMAL.

Cellulase enzymatic hydrolysis

Milled moso bamboo (10g drybasis) was subjected to enzyme treatment using industrial cellulase with an activity of about 8000 carboxyl methyl cellulose (CMCase) units/mL. The enzymatic hydrolysis was carried out at an enzyme volume concentration of 10% under the acetate buffer solution (pH 4.5) and 40^{o}C conditions in a shaker bed for 48hr with a rotational speed of 240rpm. After the enzymatic hydrolysis, the resulting impure enzymatic hydrolysis lignin, which still contained some carbohydrates in LCC forms, was collected as an acidic insoluble residual by centrifugation and washed twice with acidic deionized water (pH 2.0), then was freeze-dried.

Mild acidolysis

Impure enzymatic hydrolysis lignin (5g drybasis) obtained from the enzymatic treatment was suspended in l00mL acidic dioxane/water (85:15 v/v; 0.05M) and was refluxed at 87^{o}C under nitrogen for 2hr. The resulting mixture solution was filtered, and lignin solution was collected. The solid residue was washed with fresh dioxane/water (85:15 v/v) and fresh dioxane in sequence, until the filtrate was clear. The total filtrated solutions were neutralized with sodium bicarbonate under magnetic stirring for 3h. The neutralized solution was then rotary evaporated at 30^{o}C to be thickened until a syrup-like thickened solution formed. This thickened solution was carefully dropped into a large quantity of acidified deionized water (pH 2.0), and the precipitated lignin was isolated by the centrifugation, washed, and freeze-dried. The obtained lignin was finally washed with HPLC grade hexane and dried in a vacuum oven at room temperature.

Physicochemical properties

Particle sizes of EMAL at 5μm on average were determined by ZEN3600 nano-particle size analyzer. The analysis of the as-received EMAL showed that carbon, hydrogen, nitrogen, and sulfur contents were 58.74wt.%, 5.72wt.%, 2.58wt.%, and 0.06wt.%, respectively, and ash content was 2.80wt.% (on drybasis). The value of C/H mass ratio in EMAL was 10.27/1. Biomass can be transformed into chemicals and fuels by fast pyrolysis, and energy content in biomass is an important factor on behalf of heat productivity. Heat productivity depends on the composition and elements' types and the proportions (especially the carbon content) of the ingredients contained in the biomass. In general, if the carbon content is higher, then the heat productivity will be greater.

Methods

Fast pyrolysis of EMAL was used by Py-GC/MS with carrier gas N_2. Pyrolysis of EMAL samples was carried out in a Chemical Data System (CDS5150, USA) analytical pyrolyzer, consisting of an inductively heated coil to heat the samples at a heating rate of 10°C/ms from room temperature to different terminal temperatures of 250, 320, 400, 600, and 800°C, respectively. The gas chromatograph (QP2010, Japan) with split ratio of 70/1 and linear velocity for 40.0cm/s was used to separate the compounds from EMAL pyrolysis. The temperatures of injector and detector were set at 250°C. The temperature programs started from 50°C to 280°C at 10°C/min, the retention time was kept at 10min, and the interface temperature was set at 250°C. The semipolar column (DB1701, 30m x 0.25mm, film thickness 0.25µm), evidencing an Electron impact mass spectrum, was obtained with a QP2010 Plus at EI ionization energy of 70eV and event time retained for 0.5s. Data processing was performed with a Perkin Elmer NIST spec version 05.

The detected ion peaks were analyzed and compared one by one with the database, and the peak similarity ≤90 point was selected to integrate on the area of peaks. After undergoing normalization, the obtained area fractions act as the yield of pyrolysis products.

RESULTS AND DISCUSSION

Pyrolysis Products Analysis

Depending on the operating conditions, pyrolysis processes can be divided into three subclasses: conventional pyrolysis, fast pyrolysis, and flash pyrolysis. Yields of pyrolysis products depend mainly on the feedstock and the operating temperature. Fast pyrolysis temperature of EMAL was set at 250, 320, 400, 600, and 800°C, and the obtained pyrolysis products were detected to get detailed chemical compounds with GC/MS. Total ion chromatograms of EMAL are shown in Fig. 1, and products analysis of moso bamboo EMAL at each pyrolysis temperature is presented in Table 1.

Figure 1 shows that there was an obviously big signal peak appearing at a retention time of 12.979 min at each pyrolysis temperature, and the peaks increased in number with the increase of temperature. When the temperatures increased to 600°C, phenols appeared, which can be listed corresponding to retention time as the follows: phenol: 8.682 min; p-cresol: 10.578 min; guaiacol: 10.668 min; 2,4-xylenol: 11.875 min; p-ethylphenol: 12.175 min; p-methylguaiacol: 12.562 min; acetic acid (1.971 min) began to emerge from EMAL pyrolysis at 800°C. The compound 2,3-dihydrobenzofuran was generated at retention time 12.979 min. After 12.979 min, the following pyrolysate peaks correspond to: 2-allylphenol: 14.065 min; 4-vinylguaiacol: 14.373 min; syringol: 14.773 min; vanillin: 15.334 min; *E*-isoeugenol: 16.242 min; 3,5-dimethoxyacetophenone: 17.576 min; 4-methoxyeugenol: 19.169 min; syringaldehyde: 18.528 min; acetosyringone: 19.400 min; m-phthalic acid: 21.299 min; syringylacraldehyde: 21.901 min; p-p'-isopropylidenebis-phenol: 23.760min; dotriacontane: 27.010-28.415 min. From the above, the numbers of products increased with increasing pyrolysis temperature, and lower molecular weight of product had a preferential emergence during pyrolysis.

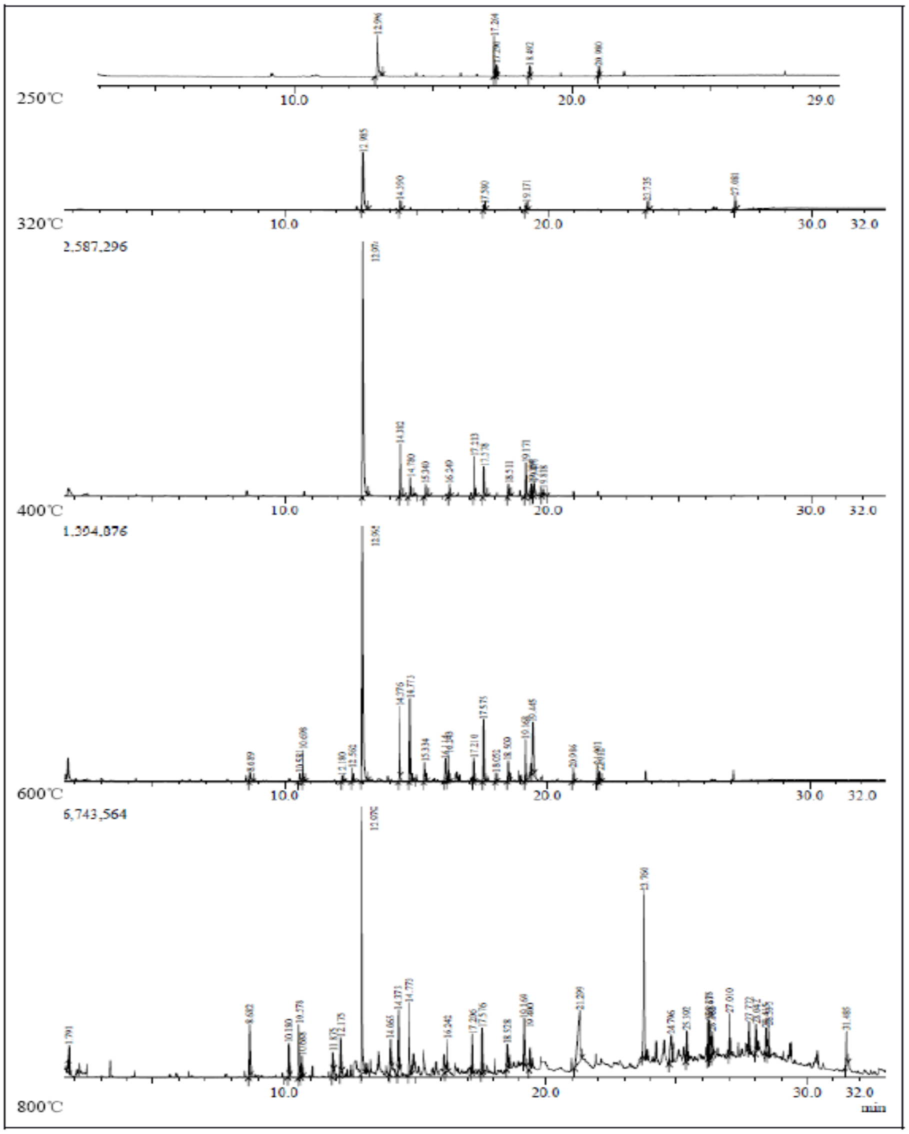

Fig. 1. Total ion chromatograms of EMAL with Py-GC/MS

Yields of Pyrolysis Products

All of products from EMAL pyrolysis can be summarize with heterocycle (2,3-dihydrobenzofuran), phenols, and esters. The yields of products are presented in Fig. 2.

Pyrolysis temperature had a distinct impact on yields of pyrolysis products, as shown in Fig. 2. As pyrolysis temperature increased from 250 to 800^{o}C, the yield of 2,3-dihydrobenzofuran decreased rapidly, and the extrema occurred at 320^{o}C, but the yield of phenols increased smoothly and came to the maximum of 56.43% at 600°C. The esters production was the highest at 320°C. In the low-temperature range (250-400°C), pyrolysis products were mainly 2,3-dihydrobenzofuran, and the highest yield reached 66.26% at 320°C, so the low temperature was favorable for the generation of heterocycle and ester compounds. In the high-temperature range (400-800°C), pyrolysis products were mostly phenols, and their yield hit the highest point of 56.43% at 600°C.

Table 1. Product Analysis of Moso Bamboo EMAL vs. Pyrolysis Temperature

Re.Time[a] /min	Compound	SI	Formular	MW	Area%				
					250°C	320°C	400°C	600°C	800°C
1.971	Acetic acid	96	$C_2H_4O_2$	60	-[b]	-	-	-	0.97
8.682	Phenol	98	C_6H_6O	94	-	-	-	1.61	2.99
10.180	o-Cresol	97	C_7H_8O	108	-	-	-	-	1.68
10.578	p-Cresol	98	C_7H_8O	108	-	-	-	1.01	3.58
10.688	Guaiacol	97	$C_7H_8O_2$	124	-	-	-	3.78	1.08
11.875	2,4-xylenol	97	$C_8H_{10}O$	122	-	-	-	-	0.88
12.175	p-Ethylphenol	98	$C_8H_{10}O$	122	-	-	-	0.74	1.59
12.562	p-Methylguaiacol	93	$C_8H_{10}O_2$	138	-	-	-	1.45	1.72
12.979	2,3-Dihydrobenzofuran	91	C_8H_8O	120	55.66	66.26	56.62	36.05	19.15
14.065	2-Allylphenol	90	$C_9H_{10}O$	134	-	-	-	-	1.84
14.373	Ethenylguaiacol	91	$C_9H_{10}O_2$	150	-	8.18	9.22	7.23	3.16
14.773	Syringol	92	$C_8H_{10}O_3$	154	-	-	3.57	9.69	4.53
15.334	Vanillin	94	$C_8H_8O_3$	152	-	-	2.76	2.64	2.51
16.114	Methylsyringol	90	$C_9H_{12}O_3$	168	-	-	-	2.98	3.01
16.242	E-isoeugenol	93	$C_{10}H_{12}O_2$	164	-	-	1.99	2.66	2.00
17.206	2,6-Di-tert-butyl-p-cresol	96	$C_{15}H_{24}O$	220	24.98	6.91	5.89	2.10	1.67
17.290	3,7-Dimethylnonane	92	$C_{15}H_{24}O$	156	12.80	-	-	-	-
17.576	3,5-dimethoxyphenyl-Ethanone	90	$C_{11}H_{24}$	180	-	4.09	5.10	6.63	2.20
18.528	Syringaldehyde	94	$C_9H_{10}O_4$	182	-	-	2.36	2.42	1.45
19.169	Methoxyeugenol	90	$C_{11}H_{14}O_3$	194	-	4.65	5.67	5.06	2.39
19.400	Acetosyringone	91	$C_{10}H_{12}O_4$	196	-	-	-	-	1.23
19.445	Coniferylalcohol	90	$C_{10}H_{12}O_3$	180	-	-	5.34	9.49	-
21.299	m-Phthalic acid	90	$C_8H_6O_4$	166	-	-	-	-	9.69
21.901	Sinapylaldehyde	91	$C_{11}H_{12}O_4$	208	-	-	1.50	1.96	2.01
23.760	p-p'-Isopropylidenebisphenol	94	$C_{15}H_{16}O_2$	228	-	-	5.72	4.46	15.89
24.796	Allylphthalate	90	$C_{14}H_{14}O_4$	246	6.55	10.01	0.97	1.37	2.69
25.392	Tetracosane	94	$C_{24}H_{50}$	338	-	-	-	-	1.47
26.218	Dotriacontane	95	$C_{32}H_{66}$	450	-	-	-	-	2.18
26.267	2-Phenylbutyrophenone	90	$C_{16}H_{16}O$	224	-	-	-	-	2.61
26.362	Dipropylene giycol dibenzote	90	$C_{20}H_{22}O_5$	342	-	-	-	-	1.63
27.010	Dotriacontane	95	$C_{32}H_{66}$	450	-	-	-	-	2.09
27.772	Dotriacontane	95	$C_{32}H_{66}$	450	-	-	-	-	1.30
28.415	Dotriacontane	95	$C_{32}H_{66}$	450	-	-	-	-	1.50

Note: a—Retention time, b—not existing

Also the related study of Tan (2009) elaborated that the yields of phenols from pyrolysis of bagasse alkali lignin and acidolysis lignin were maximized at 600°C. When the pyrolysis temperature exceeded 400°C, the EMAL began to decompose quickly, and the obtained products consisted of mostly phenolic aromatic compounds.

The amount of 2,3-dihydrobenzofuran in pyrolysis products from EMAL occupied a larger proportion, noting that grass lignin is partially p-coumaroylated, and grass lignins also contain p-coumaric acid that is connected to lignin residues by ester linkages. 2,3-dihydrobenzofuran as a natural organic compound from lignin pyrolysis contains many active ingredients in medicinal plants that can be widely applied in making coumarone-indene resin and also used in the pharmaceutical industry for drugs (Amiodarone) as pharmaceutical intermediates.

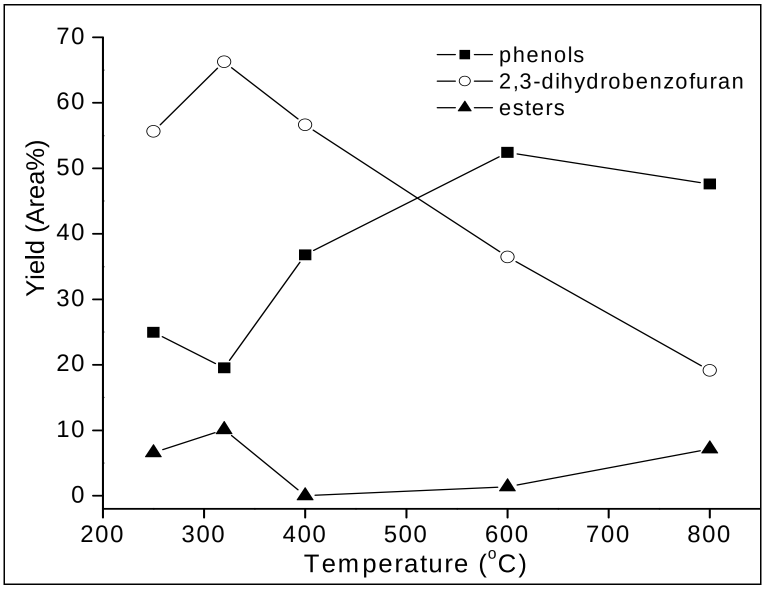

Fig. 2. Yields of pyrolysis products at the varied temperatures

G-, S- and p-H-type phenols in products

Temperature was an important factor affecting the distribution of pyrolysis products. The yields of phenols increased gradually from 24.98% to 62.15% with an increase of pyrolysis temperature, but the highest rate of phenols formation occurred at 600°C. The identified phenols were classified into guaiacols (G-type), syringols (S-type), and cresols (p-H-type) (see Fig. 3.), and the yields of p-H-, G-, and S-type of phenols varied with pyrolysis temperature, as presented in Fig. 4.

Figure 4 reveals that pyrolysis temperature had a distinct impact on G-, S-, and p-H-type phenols from EMAL pyrolysis. According to our laboratory test results, moso bamboo EMAL contained more p-H- and syringyl-lignin units and fewer guaiacyl- lignin units. A study suggested that the G-lignin model compounds are the first to experience bond cleavage during pyrolysis, affecting the C-O bond of methoxyl linked to aromatic ring (Liu 2009). When EMAL was pyrolyzed, the methoxyl was the first to crack and break, hence the G-type phenol was absent in the temperature range 250-400^{o}C. In the low-temperature region (>400°C), the phenol products were mostly p-H-type phenols that had the minimal value at 400°C nearby. G-type phenols were most prominent in the range 400-600^{o}C due to the structure of G-type, which was prone to undergo condensation and coupling reactions. Grass lignins differed from wood lignins, containing higher proportions of p-H-type lignins resulting from p-coumaryl alcohol along with coniferyl and sinapyl alcohols in the monomer pool for free-radical-induced polymerization. With increasing temperature, p-H-type lignins began disaggregating, leading to a decrease of p-H-type phenols. In the high-temperature region (600-800°C), the yield of p-H-type phenols increased because both G- and S-type compounds underwent degradation reactions. Methoxyl had reacted with active hydrogen having weak bond energy, leading to radical-induced reaction to form p-H-type phenols; thus, both yield curves of G- and S-type phenols reached their extrema at 600°C.

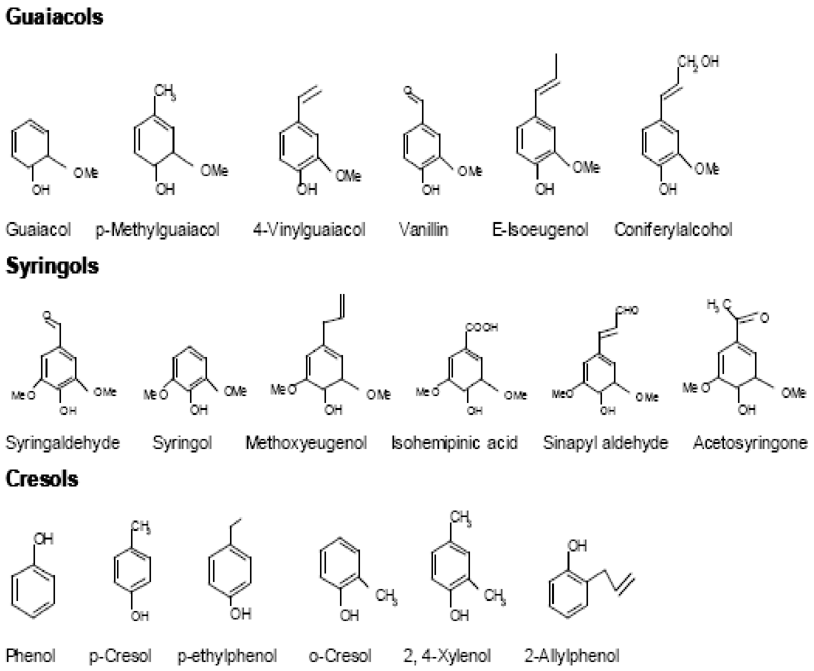

Fig. 3. Chemical structures of phenols derived from EMAL pyrolysis

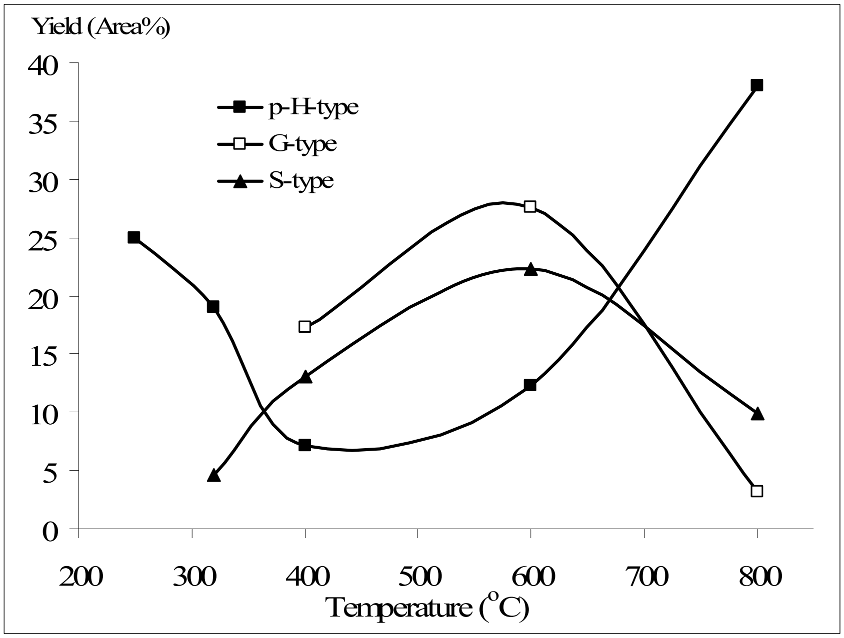

Fig. 4. Yields of p-H-, G- and S-type of phenols varied with pyrolysis temperature

To probe into the dependence of phenols production on pyrolysis temperature, some phenols, i.e. syringol, syringaldehyde, acetosyringone, vanillin, etc., having high frequency appearances in products, were analyzed (see Fig. 5). At 600°C, the yields of

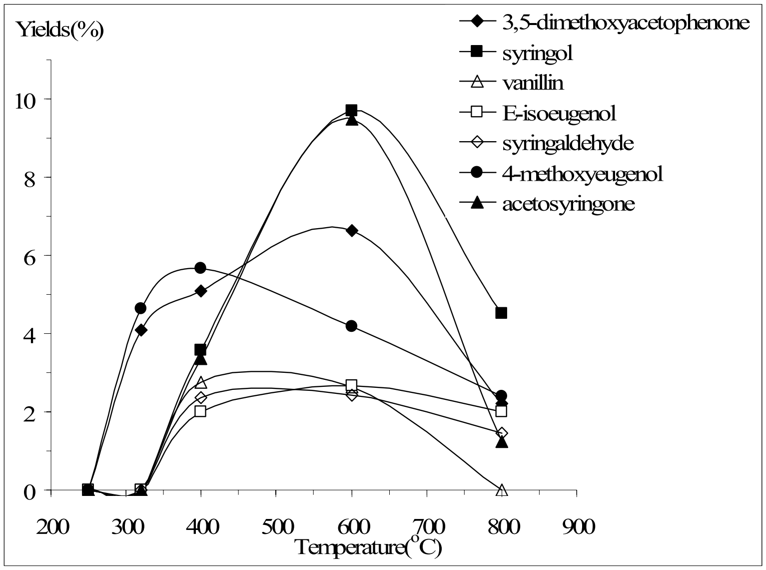

Fig. 5. Yield curves of phenols complying with pyrolysis temperatures

3,5-dimethoxyacetophenone, acetosyringone, and syringol were maximized; however, the yields of vanillin, 4-methoxyeugenol, and syringaldehyde were maximized at ca. 400°C. The yield was related to structure stability of a compound. The stabilities of both ketones and phenols were superior to that of aldehydes; thus, acetosyringone, syringol, and 3,5-dimethoxyacetophenone definitely can exist at 600°C; however, as the temperature increased up to 800°C, the phenols would begin to break and decompose slowly.

Pyrolysis Mechanism of EMAL

With respect to the dominating products of EMAL pyrolysis, the formation mechanism will be partly discussed. Figure 6 shows a proposed formation mechanism of pyrolysis products. In softwood, the guaiacyl units of lignin easily undergo condensation and coupling reactions, which are liable to involve thermal degradation of EMAL at the higher temperatures. The generation of acetic acid is attributable to β-O-4 and C_{α}-C_{β} cleavages of lignin side-chains (1), and the guaiacol, p-ethylphenol, and methylguaiacol are obtained from the cracked lignin via the α-aryl or β-aryl ethers and A_{γ}-C_{α} cleaved during pyrolyzing. Vanillin comes from the degradation of ferulic acid (2). At the higher temperature, the rupture of aromatic rings results in straight-chain alkanes. The pyrolysis products are generated through radical-induced reactions (3) and homolysis reactions (4). o-Quinone methide is an important intermediate, which has an allyl-methyl group with comparatively weak C-H bonds. In the pyrolysis process, the weak C-H bond dissociates through H-abstraction by other radical species to form the ally radical intermediate, and the following cyclization gives 2,3-bezofuran, which goes through the H-reduction reaction to produce 2,3-dihydrobezofuran. The aromatics and phenols and their alkyl substituted fractions are formed by recombination and cyclization reactions.

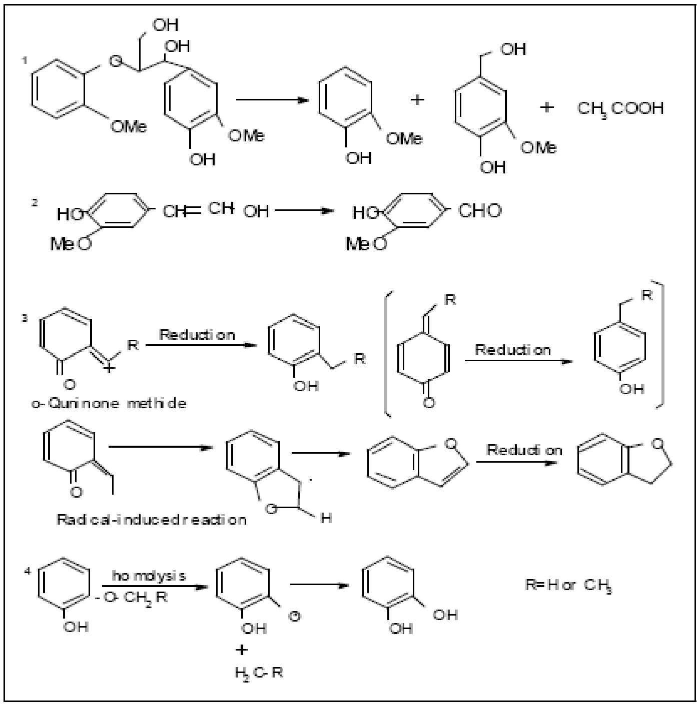

Fig. 6. Proposed formation mechanism of pyrolysis products

CONCLUSIONS

Fast pyrolysis of enzymatic/mild acidolysis lignin (EMAL) isolated from moso bamboo was studied by Py-GC/MS. The obtained pyrolysis products were composed of heterocycles, phenols, esters, and a small amount of acetic acid. Pyrolysis temperature had an obvious impact on the distribution of pyrolysis products from EMAL. At relatively low temperatures (250-400°C), pyrolysis products were mainly 2,3-dihydrobenzofuran, and the highest yield was 66.26% at 320°C; at high temperatures (400-800°C), pyrolysis products were mostly phenols, and their yields reached a maximum of 56.43% at 600°C, while the acetic acid only evolved at 800°C. The pyrolysis products were generated through radical-induced reactions and homolysis reactions. As the pyrolysis temperature increased, besides the species of pyrolysis products increasing, the yields of phenols increased, and the yield of 2,3-hydrobenzofuran decreased. In phenol products, the amount of G- and S-type phenols were maximized at 600°C and the minimization of p-H-type occurred at 400°C.

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