



The Effect of ^{60}Co γ -Irradiation on the Structure and Thermostability of Alkaline Lignin and Its Irradiation Derived Degradation Products

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Abstract

To elucidate the degradation mechanism of lignin treated by irradiation, alkaline lignin was used as the material treating with different dosage (0, 100, 200, 400, 600, 800, 1000, 1200 kGy). The morphology, molecular weight, structure, thermostability and degradation products of alkaline lignin irradiated by gamma ray were investigated by a set of experiments. The results observed in scanning electron microscopy showed that there were more cracks and small protuberances on the morphological surface of irradiated-lignin in comparison with untreated lignin. The gel permeation chromatography results showed that weight-average molecular weight and number-average molecular weight of lignin decreased from 17829 and 590 Da to 13526 and 444 Da, respectively, when irradiation dose increased from 0 to 1200 kGy. The absorption bands of hydroxyl group at 3237 cm^{-1} detected by Fourier transform infrared (FT-IR) analysis decreased with irradiation dose increased from 0 to 1200 kGy. FT-IR and solid state ^{13}C nuclear magnetic resonance (^{13}C CP/MAS NMR) confirmed that benzene ring skeleton structure of lignin disrupted when the absorbed dose was > 800 kGy. Thermogravimetry/differential thermogravimetry curves revealed thermostability and activated energy (E_a) of lignin were slightly decreased after irradiated. The irradiation derived degradation products of lignin were analyzed by gas chromatography and mass spectrometry, indicated presence of 22 aromatic compounds and 18 aliphatic acids. Moreover, the relative peak area of aromatic compounds and aliphatic acids in un-irradiated lignin (0 kGy) were 4.48 ± 0.42 and $23.81 \pm 1.85\%$, respectively, and these two types of degradation products reached a maximum of 23.81 and 6.10% at 800 and 1200 kGy, respectively. In summary, the findings in this work provide a basic scientific support on the mechanism of irradiation and full utilization of lignin.

Keywords Lignin · γ -Irradiation · Structure · Thermostability · Degradation products

Introduction

Lignocellulose, the largest abundant renewable resources on earth, is a promising alternative source for producing bio-energy and bio-chemicals. It consists of three major components: cellulose, hemicellulose and lignin. Holocellulose is

considerably converted to bio-based liquid fuel by saccharification and fermentation [1, 2]. Lignin, a non-carbohydrate tri-dimensional heteropolymer consists of three different monomeric units: *p*-hydroxyphenyl (H), syringyl (S) and guaiacyl (G). It accounts for 15–30% by weight of plants [3]. When lignocellulose is used to produce bio-fuels, the

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cellulose in the natural lignocellulosic material is encapsulated by highly polymerized lignin, which hinders the contact of the cellulose with the hydrolysis catalyst and seriously reduces the reaction efficiency. Thus, prior to the hydrolysis reaction, the pretreatment is a necessary step for effectively destroying the lignocellulosic structure and expose the cellulose component [4].

In recent years, a large number of basic and applied researches have focused on high-energy radiation pretreatment. It is an effective means for lignocellulose desorption, and gradually formed a new research field, widely used in the efficient degradation of lignocellulose conversion such as pulp, cotton fiber, linen, all kinds of wood, wheat straw, rice straw, corn stalk, reed, bagasse and other lignocellulosic materials [5–7]. Irradiation can decrease cellulose crystallinity, the degree of disruption of cellulose increased with the increase of irradiation dose. So, the irradiation enhances the enzymatic hydrolysis rate of cellulose, which is faster than single acid hydrolysis [8]. Wang et al. used rice straw and reed as the materials, and they found the cellulose structure was destroyed, and water-soluble reducing sugars and total sugars of straw fiber were significantly increased after irradiation, which reached to 214.4 and 758.5 mg g⁻¹, respectively, after irradiation coupled with enzyme treatment [9, 10]. Liu et al. compared the effect of different pretreatment on lignocellulose fermentation on ethanol productivity. It was found that the ethanol production effect of lignocellulose fermentation after irradiation was equivalent to that of ionic liquid pretreatment, which was significantly higher than that of 1% diluted hydrochloric acid, 1% diluted sulfuric acid and acidified ionic liquid pretreatment [11].

However, irradiation depolymerization of lignocellulosic macromolecule is a random reaction. It can not only be cleavage of glycosidic bond of cellulose and hemicellulose to produce glucose and xylose, but also may generate a certain amount of organic acids, aldehydes, ketones and other products [12, 13]. Meanwhile, lignin also undergoes a certain degree of degradation, and produces some degradation products such as aromatic acids and aromatic aldehydes after irradiation. Many of these by-products are secondary reactants in the irradiation process, which will directly affect the subsequent bioconversion efficiency of biomass [14]. Therefore, it is important to investigate the changes in the physicochemical properties of lignin and the regularity of degradation products after irradiation treatment. It will provide a theoretical basis for further use of lignin from irradiated lignocellulose materials, and play an important role on whether it is necessary to carry out detoxification in the process of production of bio-based liquid fuel by bioconversion of cellulose.

Alkaline lignin (solid state) was degraded by ⁶⁰Co γ -irradiation with different dosage from 0 to 1200 kGy in this work. The physico-chemical properties, such as

morphology, molecular weight and molecular weight distribution, structure, thermostability, and irradiation derived degradation products, were systematically characterized by scanning electron microscopy (SEM), gel permeation chromatography (GPC), Fourier transform infrared (FT-IR), Solid state cross-polarization/magic angle spinning Solid state ¹³C nuclear magnetic resonance (¹³C CP/MAS NMR), thermogravimetry/differential thermogravimetry (TG/DTG) and gas chromatography and mass spectrometry (GC-MS). The results of this research will provide powerful information supporting on irradiation degradation mechanism and full use of lignin.

Materials and Methods

Materials

Alkali lignin (CAS: 8068-05-1) was bought from Sigma-Aldrich Co. (Shanghai, China). *N,O*-bis (trimethylsilyl) trifluoroacetamide (BSFTA) and pyridine of chromatographically grade were purchased from Sigma-Aldrich Co. (Shanghai, China). The chromatographically grade ethyl acetate was purchased from Shanghai Wokai Biotechnology Co., Ltd (Shanghai, China). Other reagents used in this work were analytical grade and bought from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Deionized water was used in this study.

Irradiation Pretreatment of Lignin

The processing method of lignin irradiation pretreatment was modified according to the method reported by Liu et al. [11]. In brief, all irradiation treatment experiments were performed using a ⁶⁰Co gamma ray irradiation facility in the Hunan Institute of Nuclear Agricultural Science and Space Breeding (Changsha, China), irradiation source strength was 9.99×10^{15} Bq, the average dose rate was 2.0 kGy h⁻¹. The specific irradiation dose of lignin was 0 (blank control), 100, 200, 400, 600, 800, 1000, 1200 kGy, respectively.

Scanning Electron Microscopy (SEM)

First, the lignin was dried at 60 °C for 24 h. Then, the samples were attached to a cylindrical microscope stub using a conductive adhesive, and coated with gold using a EMS 150 T sputter (Quorum Technologies Inc., England). The surface morphology of lignin was analyzed by a JSM-6380LV SEM (Japan Electron Optics Laboratory Co., Ltd, Japan) at an accelerating voltage of 10 kV.

Gel Permeation Chromatography (GPC)

The specific procedure of GPC was referred to the method by Luo et al. [15]. Agilent 1260 Series Gel Permeation Chromatography (Agilent 1260 series, Santa Clara, USA) and Agilent PL aquagel-OH MIXED-H (7.5 mm × 300 mm, 8 μm) gel column (Agilent 1260 series, Santa Clara, USA) were used in this experiment. The sample was dissolved with 0.01 mol L⁻¹ NaCl solution, filtered through a 0.45 μm microporous membrane and tested for injection. The mobile phase was 0.01 mol·L⁻¹ NaCl, flow rate 1.0 mL·min⁻¹, column temperature 30 °C, injecting volume 50 μL. Calibration was carried out on the basis of polyethylene glycol (PEG) and polyoxyethylene (PEO).

Fourier Transforms Infrared (FT-IR) Analysis

The dried lignin powder was mixed with an appropriate amount of KBr, made into a tablet using a HY-12 standard device (Tianjin Tianguang Optical Instrument Co., Ltd., China) under the pressure of 25 MPa. FT-IR spectra of lignin before and after irradiation were carried out with a Nicolet 670 FT-IR spectrometer (Nicolet NicPlan IR microscope, USA), the scanning range was about 4000–400 cm⁻¹, scanning speed 20 kHz, scan 64 times, resolution 2 cm⁻¹. All the original data of FT-IR spectra were baseline correction and normalization.

Solid State ¹³C Nuclear Magnetic Resonance (¹³C NMR)

The cross-polarization/magic angle spinning (CP/MAS) solid state ¹³C NMR spectroscopy was performed at an Avance III 600 NMR spectrometer (Bruker, Switzerland). The experiment conditions of ¹³C NMR were as follows: resonance frequency 150.9 MHz, CP contact time 2 ms, delay time 5 s. The probe size of CP/MAS was 4 mm and the rotation speed of the rotor was 8 kHz.

Thermogravimetry (TG) and Differential Thermogravimetry (DTG) Analysis

The TG and DTG measurements were recorded on TGA Q50 thermogravimetric analyzer (Waters Co., Milford, USA). Approximately 5 mg of lignin for each measurement was sealed into a platinum crucible and heated from 30 to 900 °C at a heating rate of 20 °C·min⁻¹. All measurements were carried out under a nitrogen atmosphere at a gas flow rate of 40 mL·min⁻¹.

Gas Chromatography and Mass Spectrometry (GC–MS) Analysis

The extraction method of irradiation derived degradation fractions was modified according to the method reported by Jiang et al. [16]. To determine the irradiation derived degradation fractions of lignin, about 1.0 g lignin was dissolved in 30 mL deionized water, the solution was acidified with hydrochloric acid at a pH value of 3.0, extracted three times with 30 mL ethyl acetate. The fractions of the ethyl acetate extracted were mixed, concentrated, and redissolved by 2 mL ethyl acetate.

The silyl derivatization of extraction was according to the method reported by Zhu et al. [17]. Derivative products were used for GC–MS analysis (Agilent 7890, USA) with capillary column of DB-5 (30 mm × 0.25 mm, 0.25 μm). The temperature was began at 60 °C for 2 min, increased to 200 °C at a rate of 15 °C·min⁻¹ for 2 min, then increased to 310 °C at a rate of 10 °C·min⁻¹ for 15 min. The injector temperature was 300 °C, and injecting volume was 1 μL. The products were identified by comparison with library spectra supplied by the NIST database.

Results and Discussion

Effects of ⁶⁰Co Gamma-Irradiation on the Structure of Lignin

SEM Analysis

The surface morphology of lignin with different irradiation dose were observed by SEM, the results are shown in Fig. 1. Untreated lignin (0 kGy) was found to have smooth surface with little irregular fragments and crevices. The damaged degree of lignin surface morphology was much greater with the irradiation dose increased. There were a lots of small embossment appeared in the surface of lignin with > 800 kGy, the surface became very rough when the irradiation dose reached 1200 kGy. This result agrees well with that by Rao et al. [18], who observed the morphology structure of lignin was damaged by irradiated processing, the average diameter of lignin particles decreased from 100 to 60 μm when the irradiation dose increased from 0 to 90 kGy. The observation was also demonstrated by our previous work, and it was also found the damaged of lignin apparent structure when irradiation treatment was used to black liquor lignin [19].

GPC Analysis

In order to study the change of molecular weight and molecular weight distribution of lignin after irradiation,

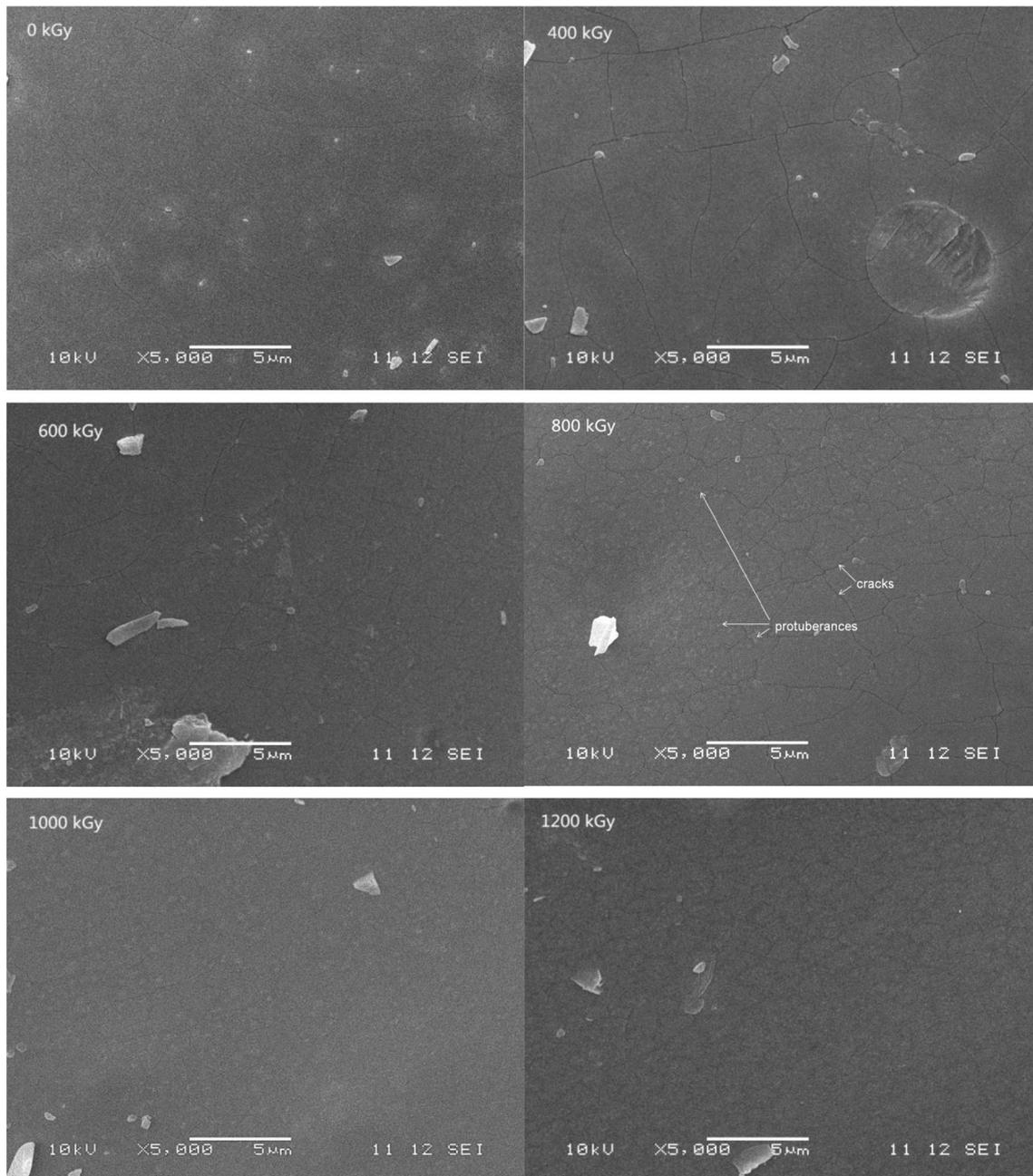


Fig. 1 The SEM diagrams of unirradiated lignin (0 kGy) and irradiated lignin at different irradiation dose (400, 600, 800, 1000, 1200 kGy)

the weight-average molecular weight (M_w), number-average molecular weight (M_n) and polydispersity index (M_w/M_n) of lignin were measured by GPC, and the results are

summarized in Table 1. As it can be seen from the data in the table, the weight-average molecular weight and number-average molecular weight of lignin decreased with the

Table 1 Effect of irradiation on the molecular weight and molecular weight distribution of lignin

Irradiation dose (kGy)	0	400	600	800	1000	1200
Weight-average molecular weight (M_w , Da)	17,829	17,583	17,183	16,737	15,184	13,526
Number-average molecular weight (M_n , Da)	590	579	560	548	496	444
Polydispersity index (M_w/M_n)	30.22	30.36	30.68	30.54	30.61	30.46

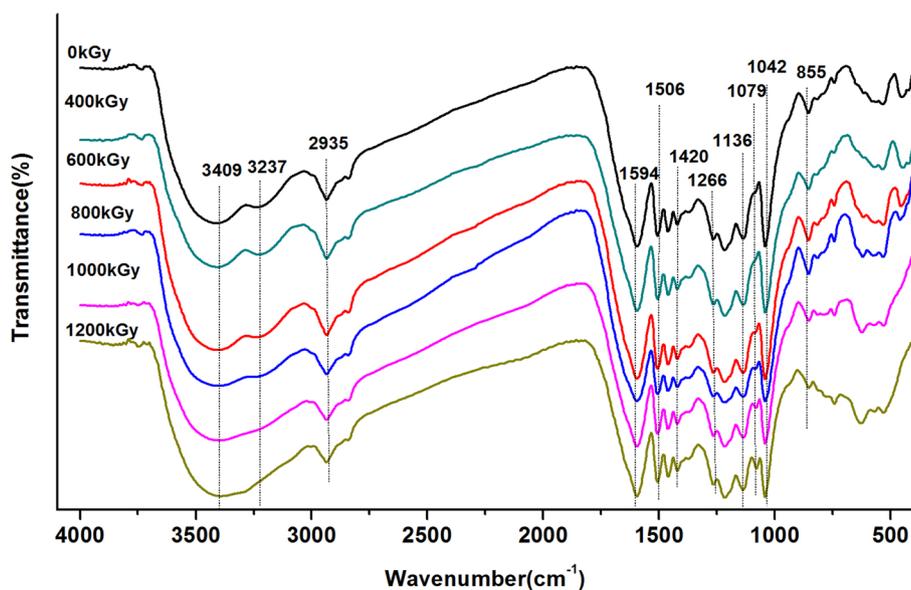
increase of irradiation dose, while there were little changes of the polydispersity index (M_w/M_n). Compared with untreated samples (0 kGy), the weight-average molecular weight and number-average molecular weight of lignin decreased from 17,829 and 590 Da to 13,526 and 444 Da, respectively, after 1200 kGy irradiated. This indicated that the lignin polymer was depolymerized, and resulting in a decrease in molecular weight after the irradiation treatment.

FT-IR Analysis

The chemical structure changes reflected by FT-IR spectra of before (0 kGy) and after irradiated lignin at different dosage from 400 to 1200 kGy are shown in Fig. 2. The absorption bands at 3392–3410 and 3227–3248 cm^{-1} are caused by the stretching vibration of hydroxyl group, the peak at 2935 cm^{-1} is the adsorption peak of C–H stretching vibration of methyl, methylene and mythine, the adsorption peaks at 1594–1595, 1506 and 1420–1421 cm^{-1} are attributed to skeleton vibrations of benzene ring, the absorption peaks at 1266 and 1136 cm^{-1} are carbonyl group stretching vibration of Guaiacyl units and Syringyl units, respectively, the peak at 1079–1084 cm^{-1} is attributed to C–O bending vibration of secondary alcohol and ether, the absorption bands at 1042–1043 and 853–855 cm^{-1} are in-plane and out-of-plane deformation vibration of aromatic ring, respectively [20, 21].

After irradiation, the absorption band of hydroxyl group at 3237 cm^{-1} was decreased with irradiation dose increase from 0 to 1200 kGy, it is probably indicated that the content of hydroxyl group in lignin decreased after irradiated. Meanwhile, the characteristic peak of aromatic ring at 1042 and 855 cm^{-1} decreased when the irradiation dose was > 800 kGy, illustrating the benzene ring skeleton structure of lignin was

Fig. 2 The FT-IR spectra of lignin treated with different irradiation doses at 0, 400, 600, 800, 1000, 1200 kGy



degraded after high dose irradiation. The observation agrees with that by Wang et al. [19]. Furthermore, the intensity of the absorption bands at 1079 cm^{-1} increased gradually with the irradiation dose increased from 400 to 1200 kGy.

^{13}C CP/MS NMR

In order to an further investigation on the effect of irradiation on the chemical linkage bonds cleavage in lignin, solid-state ^{13}C CP/MS NMR spectroscopy was used to evaluate the chemical bonds changes of lignin, and the results are shown in Fig. 3. The chemical shift at 147.0–147.3 ppm is assigned

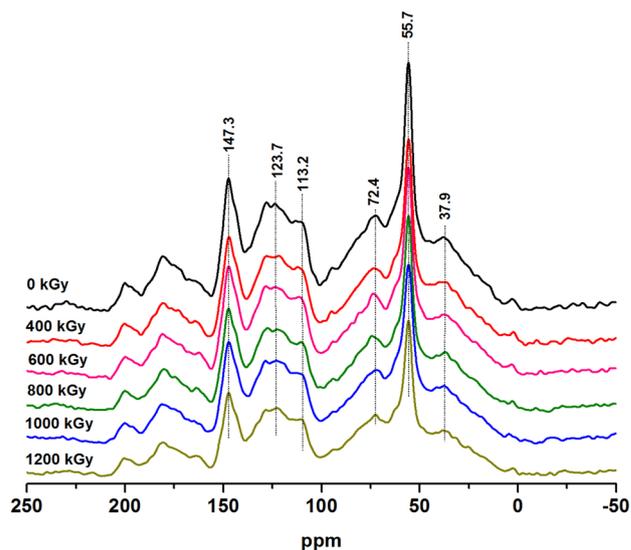


Fig. 3 The ^{13}C CP/MS NMR spectra of lignin treated with different irradiation dose at 0, 400, 600, 800, 1000, 1200 kGy

to C₄ in ether Guaiacyl unit, 121.7–123.7 ppm is ascribed to C₁ and C₆ in Ar–C(=O)C–C, 110.6–113.2 ppm is attributed to C₂ in Guaiacyl units, 72.1–74.3 ppm is ascribed to C_γ of β–β and β–O-4 structure, 55.7 ppm is assigned to C in methoxyl group of Ar–OCH₃, 36.6–38.2 ppm is attributed to C in methyl group of aliphatic [22–24].

As seen in Fig. 3, the signal intensity of chemical shifts at 55.7 and 72.4 ppm were decreased with the irradiation dose increased, it probably due to the cleavage of C–C linkage bonds in lignin after irradiation. In addition, the significantly weakened signal intensity of chemical shifts at 113.2, 123.7 and 147.3 ppm when the irradiation dose was > 800 kGy,

indicating the benzene ring of lignin was damaged after high dose irradiation. This results were consistent with FT-IR.

Effects of ⁶⁰Co Gamma-Irradiation on the Thermostability of Lignin

In order to evaluate the effect of ⁶⁰Co gamma-irradiation on the thermostability of lignin, TG and DTG were used to analysis the thermal properties changes of lignin before and after irradiated. The results are shown in Fig. 4 and Table 2.

As seen in Fig. 4, the TG and DTG curve of lignin pyrolysis process were mainly divided into three stages. At the first

Fig. 4 The change of TG and DTG curves of lignin before and after irradiated at 0, 400, 600, 800, 1000, 1200 kGy

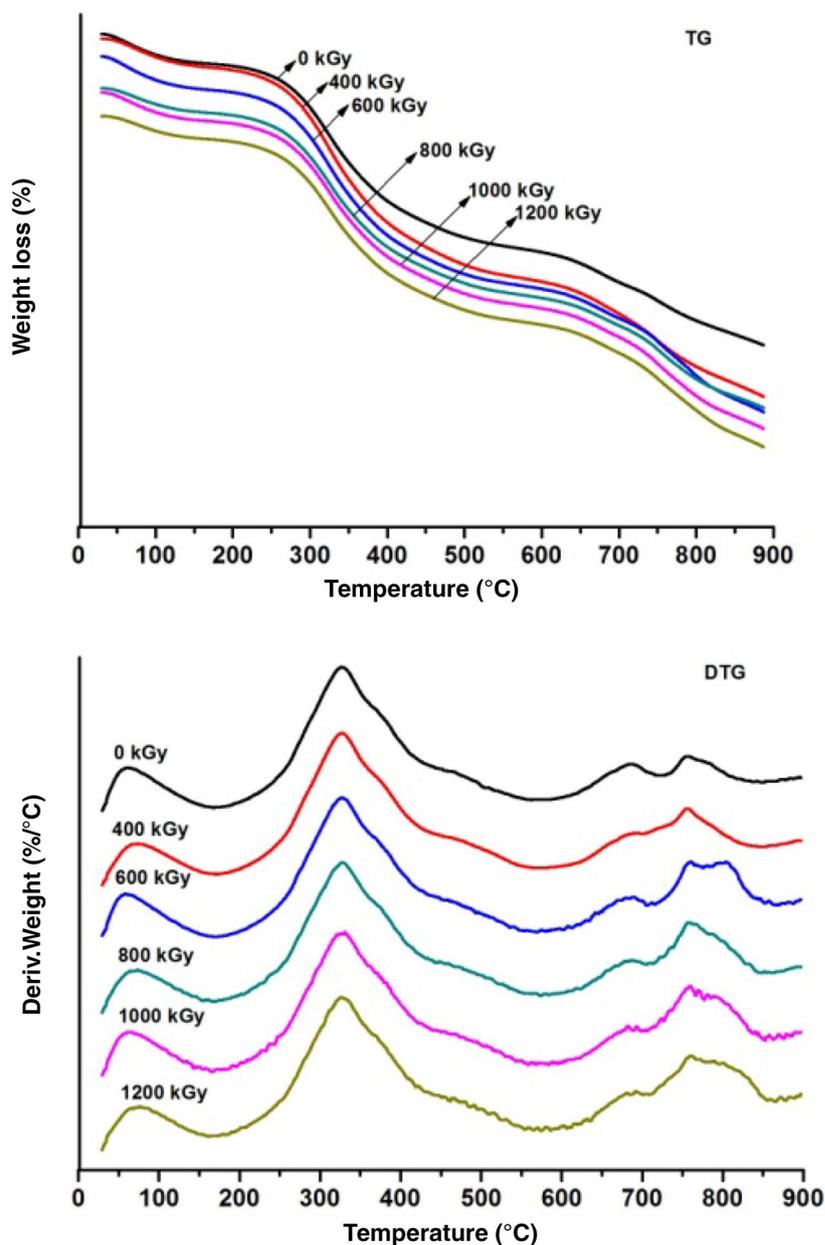


Table 2 The change of thermostability parameter of lignin pyrolysis with different irradiation dose at 0, 400, 600, 800, 1000, 1200 kGy

Irradiation dose (kGy)	Peak temperature (°C)	Maximum rate of weight loss n (%·°C ⁻¹)	Solid residues left (%)
0	331.40	0.2119	43.62
400	327.42	0.2138	42.06
600	326.71	0.2109	39.38
800	327.04	0.2102	39.02
1000	326.29	0.2094	38.04
1200	325.22	0.2098	37.85

stage, the weight loss was range from 4.24 to 7.28%, in the reign between 30 and 170 °C, due to the free water and part of bound water evaporated [25]. The second stage was the major weight loss stage (31.79–42.05%) occurring in a wide temperature range between 170 and 575 °C, in this stage, intra-molecular dehydration of lignin was happened, meanwhile, lignin was pyrolysis into lower molecular weight monomer [26]. The peak temperature (T_p) of maximum weight loss decreased from 331.40 to 325.22 °C with the irradiation dose increased from 0 to 1200 kGy in this step, indicated that the thermostability of lignin was slightly lower after irradiation treatment. At the third phase, the monomer of lignin was cracked between 575 and 900 °C, the solid residue left reduced from 43.62 to 37.85% after irradiation [27].

To further clarify the changes of thermogravimetry of lignin after different irradiation dose pretreatment, the degradation activated energy (E_a) was employed to assessed the thermogravimetry kinetics through Coats–Redfern equation [28, 29], the results are shown in Table 3. In the main pyrolysis stage (300–350 °C) of lignin, the E_a value was decreased from 33.17 to 30.52 kJ·mol⁻¹ with the increasing irradiation dose, it is likely speculated that the structure of lignin was destroyed after irradiation, giving rise to the decrease of thermal stability. This result was consistent with those reported by Rao et al. [18], who found that the Glass transition temperature (T_g) was increased from 130 to 142 °C with the irradiation dose increased, indicating the

inter-molecular interaction of lignin was disassociated after gamma irradiation.

Effects of ⁶⁰Co Gamma-Irradiation on the Irradiation-Derived Products of Lignin with Different Irradiation Dose

During the processing of irradiation, gamma-ray attacked the chemical bonds between monophenolic, side chain and benzene ring skeleton structure of lignin, generating macromolecular radicals, which results in the degradation of lignin to form all sorts of small molecular components [30]. The changes of the comparing peak area % (the area are relative to the total area of all peaks detected, not the relative abundance) of aromatic compounds and aliphatic acids in ethyl acetate extractives of untreated- and irradiated-lignin were listed in Tables 4 and 5, there were 22 kinds of aromatic compounds and 18 kinds of fatty acids were detected.

As the results shown in Table 4, the comparing peak area of aromatic compounds was $4.48 \pm 0.42\%$ in the lignin before irradiated, it was probable caused by lignin degradation occurring in the process of ethyl acetate extract. With the increase of irradiation dose from 0 to 800 kGy, the comparing peak area of aromatic compounds was gradually increased to the maximum value $23.81 \pm 1.85\%$. It was likely damaged the β -O-4-linkage, ether bond and C–C-linkage of lignin at low irradiation dose due to the relative weak bond energy, generating aromatic aldehyde, acid, alcohol, ketone and ester compounds [21, 31]. Jia et al. evaluated the degraded products of lignin by GC–MS during GIF biomimetic bleaching of bamboo pulp, who discovered that syringaldehyde (3,5-dimethoxy-4-hydroxy benzaldehyde) and vanillin (4-hydroxy-3-methoxy benzaldehyde) were the primary degraded components of Syringyl and Guaiacyl, respectively, due to the oxidative cleavage of β -O-4 linkage and C _{α} –C _{β} linkage [32]. It was interesting that 4-hydroxy-3-methoxy benzoic acid, 4-hydroxy-3-methoxy benzenepropanoic acid, 4-hydroxy-3-methoxy benzaldehyde, 3,5-dimethoxy-4-hydroxy benzaldehyde, 4-hydroxy-3-methoxy cinnamaldehyde, 4-hydroxy-3-methoxy acetophenone and 4-hydroxy-3-methoxy phenylpropanol were the main degradation products of lignin treated by gamma irradiation,

Table 3 The change of activated energy of lignin after different dose irradiated

Irradiation dose (kGy)	Temperature range (°C)	Linear fitting equation	R ²	Activated energy (kJ·mol ⁻¹)
0	300–350	$y = -3.9894x - 7.1767$	0.9981	33.17
400	300–350	$y = -3.8476x - 7.3380$	0.9984	31.99
600	300–350	$y = -3.8832x - 7.3918$	0.9982	32.29
800	300–350	$y = -3.8905x - 7.4436$	0.9982	32.35
1000	300–350	$y = -3.6353x - 7.7586$	0.9984	30.23
1200	300–350	$y = -3.6701x - 7.7477$	0.9984	30.52

Table 4 The changes of aromatic compounds in ethyl acetate extractives of untreated- and irradiated-lignin analyzed via GC–MS (area %)

No.	Compounds	0 kGy	100 kGy	200 kGy	400 kGy	600 kGy	800 kGy	1000 kGy	1200 kGy
1	Benzoic acid	0.10±0.07	0.11±0.03	0.28±0.07	0.28±0.03	0.21±0.03	0.26±0.03	0.29±0.03	0.13±0.04
2	Benzoic acid, 4-hydroxy-3-methoxy	0.86±0.34	2.48±0.68	3.47±0.50	4.01±0.78	4.70±0.89	4.83±0.41	3.53±0.70	2.80±0.56
3	Benzoic acid, 2-hydroxy-3-methoxy	–	0.17±0.03	0.40±0.09	0.60±0.16	0.63±0.14	0.45±0.06	0.33±0.04	0.19±0.04
4	Benzeneacetic acid	–	0.02±0.01	0.08±0.01	0.10±0.05	0.08±0.02	0.03±0.02	0.03±0.01	0.03±0.02
5	Benzeneacetic acid, 4-hydroxy-3-methoxy	0.07±0.03	0.09±0.05	0.19±0.05	0.20±0.06	0.27±0.03	0.31±0.05	0.20±0.03	0.06±0.01
6	Benzenepropanoic acid, 4-hydroxy-3-methoxy	0.05±0.03	0.30±0.01	0.77±0.05	0.75±0.16	0.75±0.08	0.79±0.15	0.76±0.23	0.21±0.07
7	Cinnamic acid, 4-hydroxy-3-methoxy	–	0.13±0.04	0.15±0.04	0.15±0.03	0.16±0.03	0.17±0.04	0.14±0.04	0.12±0.04
8	Benzaldehyde, 4-hydroxy	0.15±0.01	0.18±0.05	0.32±0.05	0.32±0.10	0.35±0.07	0.30±0.04	0.29±0.04	0.16±0.03
9	Benzaldehyde, 4-hydroxy-3-methoxy	0.71±0.15	2.20±0.44	4.44±0.77	4.84±0.45	4.95±0.95	5.86±0.55	6.01±0.46	5.13±0.79
10	Benzaldehyde, 3,5-dimethoxy-4-hydroxy	0.19±0.08	0.24±0.08	0.43±0.06	0.46±0.03	0.61±0.15	0.98±0.18	0.65±0.09	0.63±0.15
11	Cinnamaldehyde, 4-hydroxy-3-methoxy	0.27±0.06	0.29±0.06	0.68±0.08	0.69±0.05	0.71±0.26	0.72±0.12	0.73±0.22	0.28±0.05
12	Acetophenone, 4-hydroxy	–	–	0.13±0.05	0.19±0.05	0.16±0.05	0.16±0.05	–	–
13	Acetophenone, 4-hydroxy-3-methoxy	0.47±0.12	1.35±0.49	3.30±0.44	3.16±0.47	3.55±0.58	3.63±0.48	2.37±0.46	1.54±0.29
14	Acetophenone, 4-methoxy-2-hydroxy	0.35±0.04	–	–	–	–	–	–	–
15	Benzoic acid, 3,5-dimethoxy-4-hydroxy, methyl ester	0.11±0.03	0.12±0.03	0.20±0.04	0.19±0.03	0.19±0.02	0.21±0.01	0.21±0.03	0.26±0.03
16	Benzeneacetic acid, 3-methoxy, ethyl ester	–	–	0.43±0.05	0.67±0.19	0.59±0.02	0.61±0.07	0.43±0.08	0.14±0.04
17	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	0.01±0.01	0.10±0.04	0.13±0.04	0.14±0.03	0.13±0.04	0.14±0.05	0.15±0.07	0.08±0.02
18	2-Methoxyphenol	0.08±0.02	0.09±0.03	0.25±0.05	0.25±0.02	0.18±0.04	0.23±0.05	0.25±0.06	0.10±0.03
19	Benzyl alcohol, 4-hydroxy-3-methoxy	–	0.15±0.06	0.16±0.03	0.20±0.03	0.19±0.02	0.20±0.03	0.20±0.03	0.12±0.05
20	Phenyl ethanol, 4-hydroxy-3-methoxy	–	0.33±0.13	0.48±0.07	0.51±0.15	0.50±0.14	0.47±0.05	–	–
21	Phenyl propanol, 4-hydroxy-3-methoxy	1.06±0.27	1.32±0.42	3.38±0.44	3.22±0.34	2.91±0.81	2.93±0.72	3.63±0.37	1.48±0.29

Table 4 (continued)

No.	Compounds	0 kGy	100 kGy	200 kGy	400 kGy	600 kGy	800 kGy	1000 kGy	1200 kGy
22	(4-Hydroxy-3-methoxy phenyl)ethylene glycol	–	–	0.15 ± 0.04	0.39 ± 0.03	0.71 ± 0.24	0.54 ± 0.15	0.27 ± 0.08	–
Total area		4.48 ± 0.42	9.35 ± 0.99	19.82 ± 1.62	21.34 ± 1.11	22.51 ± 2.16	23.81 ± 1.85	20.46 ± 1.69	13.47 ± 0.96

– Not detected

Table 5 The change of aliphatic acids in ethyl acetate extractives of untreated- and irradiated-lignin analyzed via GC–MS (area %)

No.	Compounds	0 kGy	100 kGy	200 kGy	400 kGy	600 kGy	800 kGy	1000 kGy	1200 kGy
1	Propanoic acid, 2-methyl-2-hydroxy	0.05 ± 0.02	0.08 ± 0.03	0.14 ± 0.05	0.14 ± 0.07	0.15 ± 0.04	0.10 ± 0.03	0.12 ± 0.01	0.07 ± 0.01
2	Propanoic acid, 2-hydroxy	0.37 ± 0.03	0.57 ± 0.09	0.74 ± 0.08	1.17 ± 0.33	1.84 ± 0.25	1.79 ± 0.32	1.91 ± 0.45	2.21 ± 0.47
3	Hexanoic acid	–	0.02 ± 0.01	0.02 ± 0.01	0.03 ± 0.01	0.03 ± 0.00	0.05 ± 0.03	0.04 ± 0.02	–
4	Acetic acid, 2-hydroxy	0.07 ± 0.02	0.15 ± 0.02	0.53 ± 0.08	0.61 ± 0.10	0.50 ± 0.05	0.55 ± 0.04	0.95 ± 0.39	1.20 ± 0.30
5	Pentanoic acid, 2-hydroxy	0.03 ± 0.03	0.05 ± 0.02	0.21 ± 0.04	0.20 ± 0.05	0.16 ± 0.05	0.18 ± 0.05	0.20 ± 0.02	0.12 ± 0.03
6	Butanoic acid, 2-methyl-2-hydroxy	–	0.05 ± 0.02	0.07 ± 0.02	0.07 ± 0.03	0.07 ± 0.04	0.06 ± 0.03	0.07 ± 0.01	0.06 ± 0.01
7	2-Propenoic acid	0.08 ± 0.03	–	–	–	–	–	–	–
8	Propanoic acid 3-hydroxy	0.05 ± 0.01	0.07 ± 0.02	0.13 ± 0.04	0.12 ± 0.01	0.10 ± 0.02	0.10 ± 0.02	0.12 ± 0.03	0.23 ± 0.04
9	3-Hydroxybutyric acid	–	–	0.04 ± 0.02	0.03 ± 0.02	0.03 ± 0.01	–	–	–
10	Butanoic acid, 4-hydroxy	0.09 ± 0.04	0.09 ± 0.04	0.23 ± 0.04	0.21 ± 0.08	0.20 ± 0.02	0.25 ± 0.04	0.27 ± 0.08	0.32 ± 0.06
11	Butanedioic acid	0.23 ± 0.03	0.30 ± 0.08	0.87 ± 0.33	0.84 ± 0.28	0.77 ± 0.08	0.85 ± 0.21	0.97 ± 0.26	0.87 ± 0.04
12	Methylbutanedioic acid	0.29 ± 0.08	0.33 ± 0.03	0.65 ± 0.24	0.61 ± 0.22	0.58 ± 0.09	0.56 ± 0.03	0.53 ± 0.05	0.44 ± 0.06
13	2-Butenedioic acid (E)	–	–	0.08 ± 0.02	0.12 ± 0.03	0.10 ± 0.05	0.10 ± 0.03	0.09 ± 0.01	0.11 ± 0.04
14	Butanedioic acid, 2,3-dimethyl	–	–	0.09 ± 0.04	0.12 ± 0.05	0.09 ± 0.06	0.10 ± 0.03	0.09 ± 0.01	0.07 ± 0.03
15	Pentanedioic acid	–	0.05 ± 0.02	0.12 ± 0.03	0.12 ± 0.02	0.12 ± 0.05	0.11 ± 0.03	0.15 ± 0.06	0.13 ± 0.04
16	Pentanedioic acid, 2-hydroxy	–	0.15 ± 0.05	0.28 ± 0.11	0.33 ± 0.11	0.30 ± 0.11	0.29 ± 0.03	0.24 ± 0.01	0.20 ± 0.03
17	Octanedioic acid	0.16 ± 0.04	–	0.06 ± 0.04	0.11 ± 0.03	0.07 ± 0.02	0.04 ± 0.02	0.10 ± 0.03	0.08 ± 0.03
18	Azelaic acid	0.18 ± 0.04	0.19 ± 0.04	0.29 ± 0.07	0.14 ± 0.08	–	–	–	–
Total area		1.61 ± 0.10	2.12 ± 0.23	4.56 ± 0.20	4.99 ± 0.24	5.14 ± 0.02	5.13 ± 0.07	5.85 ± 0.27	6.10 ± 0.02

– Not detected

and its relative peak area reached 75.21–89.00% of the total aromatic degradation products. However, the relative peak area of aromatic compounds was declined with the irradiation dose increased continuously (800–1200 kGy). Especially, the relative peak area of aromatic degradation products significantly dropped to 13.55% at 1200 kGy. This phenomenon was in agreement with the results reported by Jiang et al. [16] where they also found that the aromatic degradation components were reached to the maximum at 800 kGy, however, in analysis of the irradiation-derived degradation products, it is presumably due to the benzene ring cracked into small molecular compounds at high irradiation dose (> 800 kGy). These results were consistent with foregoing studies of FT-IR and ¹³C CP/MS NMR reported in this study.

As seen in Table 5, the variation trend of aliphatic acids was different from aromatic compounds. The comparing peak area of aliphatic acids in untreated-lignin was 1.61%,

which was increased with the increasing irradiation dose, reaching the maximum value (6.10 ± 0.02%) at 1200 kGy. Meanwhile, 2-hydroxy propanoic acid, 2-hydroxy acetic acid, butanedioic acid and methylbutanedioic acid were the main irradiation-derived degradation products of lignin, and its comparing peak area were 2.21, 1.20, 0.87 and 0.44%, respectively, when the irradiation dose was 1200 kGy. The formation of aliphatic acids may due to the cleavage of side chain or benzene ring from lignin [33, 34].

Conclusions

The ⁶⁰Co gamma irradiation pretreatment can disrupt the structure, reduce thermal stability and increase degradation products of lignin. The cracks and small protuberances on

the morphology surface of lignin enhanced, the weight-average molecular weight and number-average molecular weight of lignin decreased, with increasing of irradiation dose. C–C bond were damaged after irradiation pretreatment, benzene ring skeleton structure of lignin degraded when the irradiation dose was greater than 800 kGy. The thermal stability and activated energy (E_a) were reduced after irradiation. GC–MS analysis revealed 22 kinds of aromatic compounds and 18 kinds of aliphatic acids were detected after irradiation pretreatment, the comparing area of these two types of degradation products reached a maximum of 23.81 and 6.10% at 800 and 1200 kGy, respectively. In conclusion, the results in this study provide a basis support on the mechanism of irradiation and full utilization of lignin.

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