Mechanism study of degradative solvent extraction of biomass

Xianqing Zhu a, Yi Xue a, Xian Li a,⇑, Zong Zhang a, Wei Sun a, Ryuichi Ashida b, Kouichi Miura c, Hong Yao a,⇑

a State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China
b Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan
c Institute of Advanced Energy, Kyoto University, Kyoto 615-8510, Japan

HIGHLIGHTS
• The residence time greatly affected the products yield distributions.
• The residence time exhibited considerable effects on the characteristics of the products.
• Prolonging the residence time can enhance the conversion from Deposit to Soluble.
• The reaction process can be divided into two stages.
• A conversion pathway of the degradative solvent extraction of biomass was proposed.

ABSTRACT
We have recently proposed a novel and effective degradative solvent extraction method to upgrade and convert various types of biomass feedstocks into high-grade carbonaceous materials under rather mild conditions. The feasibility of this method has been preliminarily proven in our previous work. However, the conversion mechanism of this process remains unknown. Hence, in this study the conversion process of the degradative solvent extraction of biomass was investigated in detail. A typical biomass (fir sawdust) was treated in 1-methylnaphthalene at 350°C with the residence time from 0 to 90 min. Three solid products, which were the fraction soluble in the solvent at room temperature (termed Soluble), the fraction soluble in the solvent at treatment temperature but insoluble at room temperature (Deposit) and the unextractable fraction (Residue), were obtained. The products were then characterized by various analysis methods in detail. The oxygen, carbon and minerals in the raw biomass were mainly recovered as CO2/H2O, Deposit/Soluble, and Residue, respectively. With the residence time increasing from 0 to 45 min, the soluble yields increased obviously but the deposit yields decreased significantly. The yield variations of the Solubles and Deposits obtained at residence time longer than 45 min were not significant. The chemical structure and properties of Solubles were independent of the residence time, while those of Deposits varied obviously with residence time. According to the results, the conversion process of the degradative solvent extraction of biomass was proposed. The process can be divided into two stages. The first stage took place at heating up stage from 250 to 350°C and the beginning of the isothermal stage at 350°C. In this stage, the thermal extraction, deoxygenation and aromatization reactions of the raw biomass occurred significantly. The main product was Deposit. The oxygen was removed...
1. Introduction

The rapid depletion and excessive use of fossil fuels (coal, petroleum and natural gas) have brought in serious problems such as the energy crisis and environmental pollution (acid rain, greenhouse gases and particulate matter emissions). Intensive researches have been conducted to seek new and renewable energy resources as substitutes for fossil fuels. Biomass is one of the cheapest and most available renewable energy resources, which accounts for 14–15% of the world's total primary energy consumption [1]. Concerning its zero net emissions of carbon dioxide, renewable characteristic, low sulfur content, and low nitrogen content [2,3], biomass shows great potential in substituting fossil fuels. However, some inherent characteristics of biomass such as high moisture content, high oxygen content, and low bulk density, lead to its low calorific value, hydrophilic nature, high tendency of spontaneous combustion, inconvenience for transportation and storage, and create great challenges for the direct application by the conventional processing technologies (e.g. pyrolysis, gasification, and combustion). Hence, it is essential to dewater and deoxygenate biomass feedstocks prior to introducing them into conventional conversion processes. This is so-called biomass upgrading.

Two primary thermal treatment technologies (torrefaction and hydrothermal upgrading) have been employed to upgrade and convert lignocellulosic biomass into densified biochar or carbon material [4,5]. Torrefaction is the pyrolysis of biomass feedstocks between 200 and 300 °C under an inert atmosphere [6–9]. Hydrothermal upgrading is to treat the biomass feedstocks in a hot (180–300 °C) and pressurized water to produce biochar [5,10–12]. Generally, the properties of the biochar derived from torrefaction are greatly dependent on biomass feedstocks used. The carbon contents of the biochar are generally lower than 60%, and the oxygen contents are still as considerably high as 25–40% [13]. Besides, the ash contents of the biochars from torrefaction are higher than their raw biomasses, which can cause serious problems during further utilization. The hydrothermal upgrading of biomass is to produce biochar which generally has the carbon content ranging from 60% to 75% [4,12]. But it is generally carried out under subcritical or supercritical conditions with the pressure higher than 15 MPa. The severe conditions required for hydrothermal upgrading cause its poor practical applicability.

To overcome the disadvantages in the conventional technologies for biomass upgrading, the authors have recently proposed a novel method to dewater, deoxygenate and separate a wide variety of low grade carbonaceous resources, such as biomass wastes and low rank coals, into several fractions by degradative solvent extraction [14–17]. This method treats the carbonaceous resources in a non-polar solvent below 350 °C under an inert atmosphere by a specially designed batch autoclave. Three solid fractions are obtained, which are the fraction soluble in the solvent at room temperature (termed as Soluble), the fraction soluble in the solvent at treatment temperature but insoluble at room temperature (Deposit) and unextractable fraction (Residue). It was very interesting to find that the physico-chemical properties, chemical composition and structure of Solubles and Deposits prepared from various types of biomass feedstocks were extremely similar to each other, respectively. The carbon contents and oxygen contents of Solubles and Deposits reached as high as 84.9% and as low as 7.3% respectively, significantly different from those of their raw material and similar to those of bituminous coal. It was also found that the low-temperature reactivity of Deposits and Solubles were significantly lower than those of their raw materials [18], demonstrating that the spontaneous combustion tendency of biomass or low rank coal is effectively suppressed by this method. Additionally, the utilization of the Solubles and Deposits obtained from biomass for liquid fuel production and carbon material preparation have been proved preliminarily in our previous work [19,20].

Much works have been performed in our previous study related to the degradative solvent extraction and the utilization of the products. However, the reaction process of this method has not been investigated in detail. In-depth understanding of this process would be rather beneficial for optimizing the treatment conditions and the development of this method. It is well known that the decomposition reactions during the biomass pyrolysis are complex, because the three major components of biomass (cellulose, hemicellulose and lignin) have different thermal decomposition characteristics [21]. Furthermore, the mechanisms of hydrothermal or solvothermal treatments of biomass are not clear. Thus, in this work a typical woody biomass was treated by the degradative solvent extraction at 350 °C. The yields, chemical composition and structure, physico-chemical characteristics of the products obtained at different residence time were investigated and compared in detail. The reaction mechanism of this process was then discussed.

2. Experimental

2.1. Samples and solvents employed

A fir sawdust (abbreviated as SD, from Hunan province, China) was employed as raw biomass material in this work. The proximate analysis and elemental compositions of SD is given in Table 1. A non-polar solvent, 1-methylnaphthalene (1-MN), was chosen as the solvent for the extraction.

2.2. Degradative solvent extraction procedure

It was found in our previous work that 350 °C was the proper temperature for the degradative solvent extraction of biomass [14,16]. So the degradative solvent extraction of SD was conducted at 350 °C in a specifically designed batch autoclave in this study. Fig. 1 shows the schematic diagram of the batch autoclave. The autoclave was equipped with a stainless filter device at the lower end and a valve which connected the autoclave reactor and the reservoir. The detailed procedure of the extraction experiments has been described in our previous papers [16,17]. Around 20 g raw SD (air-dry basis) and 300 mL of 1-MN were placed into the autoclave. After purging the autoclave sufficiently with N2, the autoclave was sealed with 0.2 MPa of N2 and then heated up to 350 °C at an average heating rate of 5 K/min. The residence time at 350 °C were 0, 15, 30, 45, 60, and 90 min. The extracts along with the solvent were transferred to the reservoir through opening the valve immediately after the desired residence time. Therefore,
the in-situ separation of the extracts from the unextractable fraction (Residue) was realized. The autoclave and reservoir were instantly cooled down to room temperature by an electric fan and circulating cooling water, respectively. The fraction precipitated as a solid at room temperature was referred as Deposit and recovered by filtration. The fraction still dissolved in the solvent, was referred as Soluble and recovered as a solid through evaporating the filtrate at around 120°C to remove the solvent by vacuum rotary evaporator. The pressure in the vacuum rotary evaporator was less than 6 × 10⁻² Pa. Then Soluble, Deposit and Residue were further dried under vacuum at 150°C for more than 5 h to remove the residual 1-MN. The produced water and small amounts of hydrocarbons removed together with the solvent were referred as Liquid. The gaseous products (Gas) were collected in a gas bag and quantitatively analyzed by a gas chromatograph. The yields of soluble, deposit and residue were determined through measuring their weights. The yields of Liquid were determined by difference. Each extraction experiment was conducted at least three times, and the experimental errors of the product yields were within 5%.

2.3. Product analyses

The solid products and raw biomass were characterized by various analyses. The elemental composition was determined by an elemental analyzer (Vario, CHN EL-2). The thermal decomposition analysis and proximate analysis of solid products were carried out using a thermogravimetric (TG) analyzer (NETZSCH, STA 449 F3) where 10 mg samples were heated up to 900°C at a heating rate of 10 K/min in a flow of purified nitrogen (100 mL/min). The chemical structure of solid products was analyzed through a Fourier Transform Infrared (FTIR) spectrometer (Bruker, VERTEX-70) and a ¹³C-nuclear magnetic resonance (NMR) spectrometer (Bruker, AVANCE III 600). The FTIR spectra data ranging from 4000 to 600 cm⁻¹ were collected at 4 cm⁻¹ resolution using a mixture of sample and KBr in a sample/KBr ratio (w/w) of 1:100. The ¹³C cross-polarization magic spinning (CP/MAS) solid-sate NMR spectra were recorded using an NMR spectrometer at a resonance frequency of 150.9 MHz, with a spinning rate of 14 kHz, a contact time of 3 ms, and a recycle delay time of 5 s. The chemical shift of ¹³C was externally referenced to tetramethylsilane.

3. Results and discussion

3.1. Yield distributions of products

The product yield distributions of degradative solvent extraction of SD at different residence time (0–90 min) are given in Fig. 2. The Residue was already as low as 3.51% at the residence time of 0 min. It was found that the reactions started from the temperature of 250°C in our previous work[14,16]. It can be seen that the residence time exhibited a great effect on the yield distributions of products. For instance, the yields of Solubles increased obviously from 25.62% at 0 min to 40.91% at 45 min and then almost kept unchanged from 45 min to 90 min. Meanwhile, the proportion of Deposit decreased significantly from 40.91% at 0 min to 24.15% at 45 min and then kept almost constant. The yield of Residue increased from 3.51% at 0 min to 4.35% at 30 min and then gradually decreased to 3.01% at 90 min. The gaseous products (Gas) were collected in a gas bag and quantitatively analyzed by a gas chromatograph. The yields of soluble, deposit and residue were determined through measuring their weights. The yields of Liquid were determined by difference. Each extraction experiment was conducted at least three times, and the experimental errors of the product yields were within 5%.

<table>
<thead>
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<th>RT (min)</th>
<th>Sample</th>
<th>Ultimate analysis (wt%, daf)</th>
<th>Proximate analysis (wt%, db)</th>
<th>HHV(daf) MJ/kg</th>
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<td></td>
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</table>

a Residence time. 

b By difference.
yields of Deposits decreased significantly from 28.71% at 0 min to 12.73% at 45 min and then decreased slowly from 12.73% at 45 min to 8.76% at 90 min. The yields of Residues only slightly increased from 3.51% to 5.24% in the residence time of 0–90 min, which might be caused by the slight polymerization reactions. In the meantime, the yields of Gas and Liquid tended to stay stable throughout the whole residence time. Besides, the CO₂ contents in gaseous products were as high as around 79.8%. The total yields of Soluble and Deposit at all residence time were rather similar to each other, although the Soluble and the Deposit yields changed significantly with residence time. The enhancement in yields of Solubles was attributed to the reduction of Deposits yields, because the yield variations of other products were slight or negligible, as discussed above. The Soluble was comprised of smaller molecular weight compounds than those of Deposit as found in our previous study [16]. So it implies that the Deposit decomposed to generate Soluble with prolonging the residence time. In addition, the nearly similar total yields of Solubles and Deposits at different residence time suggests that the short residence time is sufficient to obtain the extracts. However, it is necessary to investigate and compare the properties of Solubles and Deposits obtained at different residence time.

3.2. Ultimate and proximate analyses

The ultimate and proximate analyses of SD and the three solid products are shown in Table 1. The characterization only focuses on the Solubles and Deposits hereafter in this work, because of the low yields of the Residues. It can be observed that the carbon contents of all Solubles and Deposits were obviously higher than those of their raw material. On the contrary, the oxygen contents of the Solubles and Deposits were obviously lower than those of their raw material. This clearly indicates the raw biomass was indeed deoxygenated and upgraded by the degradative solvent extraction. The carbon contents of the Deposits increased from 71.53% to 77.44% and the oxygen contents decreased from 22.51% to 16.88% with the residence time increasing from 0 min to 90 min. It was also the case for Solubles. This suggests that extending residence time can enhance the deoxygenation of the solid products. The elemental compositions of the Liquid were also calculated by element balance. The results show that the H/O mole ratios of the Liquid were rather close to 2:1, and the carbon contents of the Liquid were less than 20%, indicating that the Liquid was mainly comprised of H₂O. The higher heating values (HHVs) of SD and solid products were calculated by Dulong equation [22]. The HHVs of both Solubles and Deposits were much higher than that of raw SD. The HHVs of the Soluble increased slightly with residence time from 15 to 90 min. In the meantime, the HHVs of the Deposits also increased slightly from 28.25 MJ/kg at 0 min to 30.56 MJ/kg at 90 min. The volatile matter contents of Solubles increased slightly with the residence time from 0 min to 45 min, and then kept constant from 45 min to 90 min. The relatively lower volatile matter content of the Soluble obtained at 15 min should be attributed to the experimental error. While the volatile matter contents of Deposits decreased with residence time.
In addition, the Solubles and Deposits were almost free from moisture and ash. Because most of the moisture was removed as liquid phase, and the ash was concentrated in Residue during the extraction.

It is well-known that the degree of carbonization can be visually described in the Van Krevelen diagram \[23–25\], as shown in Fig. 3. Compared to the raw SD, all Solubles and Deposits had significantly lower O/C atomic ratios. The O/C and H/C atomic ratios of Solubles respectively ranged from 0.12–0.17 and 0.90–1.02. The O/C and H/C atomic ratios of Deposits respectively ranged from 0.80–0.95 and 0.16–0.24. From the viewpoint of elemental composition, the Solubles and Deposits are coal-like products. Deposits contained relatively higher O/C and lower H/C atomic ratios than Solubles at the same residence time. Comparing the elemental compositions of the Solubles and Deposits at different residence time in detail, the O/C and H/C atomic ratios decreased clearly with residence time almost linearly. Furthermore, the interesting phenomenon was that the decrease tendencies of the O/C and H/C atomic ratios were extremely consistent with the dehydration process which was shown by the dotted line for C\(_{123}\)A\(_{130}\)H\(_{2}\)O in Fig. 3, especially for the Deposit. This implies that the product formed from the oxygen removal with the residence time increasing was mainly H\(_2\)O. The evolution of elemental composition from raw SD to Soluble and Deposit generally corresponded to the dehydration and decarboxylation process. This indicates that prolonging the residence time is necessary for the biomass upgrading by the degradative solvent extraction. Similar results were also observed for the hydrothermal carbonization of biomass \[23,26\].

The primary objective of biomass upgrading is to improve its carbon content and lower its oxygen content. Therefore, it is very important and informative to investigate the transformation of carbon and oxygen during the extraction. Fig. 4 shows the carbon and oxygen distributions in products obtained at different residence time. It can be seen that as high as 71.76–81.01% of the carbon in raw SD was transferred into the Soluble and Deposit. The carbon distributions in the Solubles increased from 38.24% at 0 min to 63.00% at 45 min, and then kept almost constant from 45 min to 90 min, similar to the yield variation tendency as shown in Fig. 2. While the carbon distributions in the Deposits decreased significantly from 40.55% to 13.40%. The main transformation of carbon during the extraction was from Deposit to Soluble. The carbon distributions in Liquids obtained from 45 min to 90 min were less than those from 0 min to 30 min. This may be caused by the condensation reactions of the small organic molecules in Liquid. But overall, the condensation reactions were slight. Around 8.80% of carbon was transferred into Gas and formed CO\(_2\) mainly, independent of the residence time. As for the oxygen distribution, more than 73.10% of the oxygen in raw SD was removed as water in the Liquid or CO\(_2\) in Gas. Moreover, prolonging the residence time enhanced the oxygen removal and transformation from raw SD to Liquid. The oxygen removal enhancement should be mainly attributed to the deoxygenation of the Deposit, because both oxygen contents and oxygen distributions in the Deposits decreased with residence time increasing as shown in Fig. 4 and in Table 1. The oxygen distributions in the Residues were rather small and almost constant. The oxygen distributions in Gas were almost
constant from 0 min to 90 min, and were mainly CO₂ as discussed above. On the contrary, the oxygen distributions in Liquid increased with residence time, and were mainly H₂O as discussed above. This implies the product generated from the oxygen removal during the extraction from 0 to 90 min was mainly H₂O, and the oxygen removal as CO₂ mainly occurred at the heating-up stage, consistent with the results of H/C vs O/C diagram as discussed above. Thus, the degradative solvent extraction method can effectively recover the carbon into Soluble and Deposit and remove the oxygen as H₂O or CO₂. Furthermore, prolonging the residence time can enhance the carbon transformation from Deposit to Soluble and oxygen removal from Deposit as H₂O.

3.3. Decomposition behavior of Solubles and Deposits

The thermal decomposition behaviors of Solubles and Deposits, as shown in Fig. 5, were obtained using a thermogravimetric analyzer. The TG curves of the Solubles were similar to each other. A slight difference appeared for the Soluble obtained at 90 min. Another difference for the Soluble obtained at 15 min might be attributed to the experimental error, which was not used for the mechanism investigation. The weight decrease of all Solubles mainly took place at the temperature range of 200–450 °C. Since the Soluble was obtained by the extraction at 350 °C, it was judged that the weight loss of the Solubles at the temperature lower than 350 °C was caused by the devolatilization of the Solubles. However, obvious difference was observed among the decomposition behaviors of the Deposits obtained at different residence time. The TG profiles of the Deposits shifted to higher temperature zone with the residence time increasing. To further elucidate the difference, the differential thermogravimetric (DTG) curves of the Deposits and Solubles were also displayed in Fig. 5. The major weight loss of Deposits happened at the temperature range from 200 to 600 °C, where several overlapped weight loss peaks were observed for all Deposits. Overall speaking, the weight loss rate of Deposits decreased gradually with residence time increasing from 0 to 90 min. The temperature corresponding to the maximum weight loss rate of Deposits shifted to higher temperature region, indicating that the thermal stability of Deposit increased with residence time increasing. A sharp and distinct peak at 200–350 °C attenuated for Deposit at the residence time from 0 to 30 min and almost disappeared at 45 and 60 min. The Deposit yields decreased significantly with the residence time increasing from 0 to 45 min and then decreased slowly from 45 to 90 min, as discussed above. Therefore, it can be judged that the yield reduction of the Deposit was mainly attributed to the volatile matters released at 200–350 °C. These volatile matters in the Deposit were converted to Soluble during the extraction. This is a further evidence for the transformation from Deposit to Soluble during the degradative solvent extraction, especially at the initial stage with the residence time less than 45 min.

3.4. FTIR analysis

FTIR analysis was performed to investigate the variation of chemical structure of Solubles and Deposits with residence time, as shown in Fig. 6. The spectrum of raw SD mainly consisted of OH stretching vibration (3100–3600 cm⁻¹), aliphatic C–Hn stretching vibration (2850–2970 cm⁻¹) and C–O stretching vibration (~1030 cm⁻¹), which were the typical structure of biomass [5]. Compared with raw SD, obvious differences were found for both spectra of the Solubles and Deposits. The wide band centered at 3406 cm⁻¹ (attributed to C–OH group) apparently weakened in the spectra of all Solubles and Deposits in comparison to that of SD, suggesting the removal of hydroxyls or carboxyls due to the dehydratation and decarboxylation reactions. It can also be observed that the aromatic groups prevailed in the spectra of Solubles and Deposits: aromatic out-of-plane C–H bending at 750–875 cm⁻¹, aromatic C=C stretching vibration at 1460–1600 cm⁻¹ and aromatic C–H stretching vibration at 3050 cm⁻¹. This clearly reveals that the aromatization reactions significantly took place during the extraction of biomass. Moreover, the spectra of Solubles obtained at different residence time seemingly resembled each other, except the slight enhancement of the peaks attributed to the aromatic compounds (750–875 cm⁻¹, 3050 cm⁻¹). It suggests the chemical structure of the soluble was almost constant and independent of the varying residence time. So the Soluble should be a stable and final product of the degradative solvent extraction of the biomass. On the contrary, the spectra of Deposits varied obviously with the residence time. The intensity of the OH absorption peak in the spectra of Deposit firstly increased from 0 min to 30 min and then decreased gradually after 30 min. This may be because that a part of the Deposit, which contains less C–OH groups, was largely converted into Soluble from 0 to 30 min as discussed above, resulting in the C–OH groups concentrated in the Deposit. Further increasing the residence time after 30 min, the conversion from the Deposit to Soluble reduced, as shown in Fig. 2. So the removal of C–OH groups dominated, leading to the reduction of C–OH group content in Deposit. On the other hand, the region between 1600 cm⁻¹ and 1460 cm⁻¹ assigned to aromatic structure also increased with the residence time increasing from 0 to 90 min for the Deposit. Therefore, the Deposit underwent further complex reaction process with the residence time increasing, such as decomposition, aromatization, and dehydration.
3.5. Solid-state CP/MAS $^{13}$C NMR characterization

To further estimate the chemical structures of the raw SD, Solubles, and Deposits, the high-resolution $^{13}$C CP/MAS NMR analysis was performed as shown in Fig. 7 to complement the FTIR analysis. The assignment of each carbon type was determined according to several previous publications [27–29]. The spectra of raw SD exhibited sharp and typical peaks ascribed to the carbons in cellulose, hemicellulose, and lignin. There were no obvious peak ascribed to C=O, and only relatively weak peaks attributed to ArC–C, ArC–O, C–CH$_2$, and C–CH$_3$ were observed. Unlike raw SD, the Solubles and Deposits had completely different structures. Most of the standard signals from 60 to 110 ppm attributed to the main components of the raw SD almost disappeared. These signals were mainly assigned to the oxygenated alkyl carbons (O-alkyl), suggesting that the severe scission of C–O bonds occurred during the degradative solvent extraction of SD. Both Solubles and Deposits had rather strong peaks attributed to carbon in alkyl groups (0–50 ppm), such as C–CH$_2$ and C–CH$_3$, methoxy groups (55 ppm) and aromatic groups (110–165 ppm). The chemical structures of the Solubles and Deposits were rather similar to sub-bituminous coal or lignite [27,30].

The $^{13}$C NMR spectra were also curve-fitted [31,32] to obtain the relative percentage of each type of carbon quantitatively. The results are shown in Table 2. Around 7.5–9.9% of carbonyl carbon was detected in Solubles and Deposits. This should be caused by the removal of C–OH from carboxyl groups which were much fewer in Solubles and Deposits compared with those in the raw SD. The aromaticity of raw SD was only 20.3% as shown in Table 2. So the aromatic carbon in raw SD, calculated by the aromaticity × yield (100%), was 20.3%. Fig. 4 shows that the carbon distributions of carbon in Souble and Deposit obtained at 0 min were 38.2% and 40.6%, respectively. The aromaticity of Soluble and Deposit obtained at 0 min was 53.5% and 53.8% respectively, as shown in Table 2. So the aromatic carbon in solid products at 0 min (mainly Soluble and Deposit), calculated by carbon distribution in Soluble × aromaticity of Soluble + carbon distribution in Deposit × aromaticity of Deposit, was 42.3%. Similarly, the aromatic carbon in solid products at 60 min was 46.1%. It is obvious that the amount of aromatic carbon increased dramatically during degradative solvent extraction. These results clearly clarify that significant aromatization reactions occurred during degradative solvent extraction of biomass, which is well consistent with the FTIR analysis as displayed in Fig. 6. Similar proving method was reported in the published paper [33]. The O-alkyl contents (such as CO–CH and CO–CH$_2$) and oxygenated aromatic carbon (ArC–O) in Solubles and Deposits were much less than those in raw SD. Furthermore, the O-alkyl content in Deposits decreased with the residence time increasing. It indicates the cleavage of oxygen containing cross-links, which may result in the conversion of from Deposit to Soluble. Thus, it clearly shows that the C–OH, ArC–O, O-alkyl groups in raw SD were significantly removed during the degradative solvent extraction. These were the main deoxygenation reactions occurred during the extraction. The aromaticity of the Deposit increased from 53.8% at the residence time of 0 min to 58.7% at the residence time of 60 min, implying that the Deposit experienced further aromatization reaction with prolonging residence time.

According to the results obtained in this work and in our previous papers [14,16], the conversion process of the degradative

![Fig. 7. Cp/Mas $^{13}$C NMR spectra of raw SD, Solubles and Deposits prepared at 0, 30, 60 min.](image)

<table>
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<th>Samples</th>
<th>Carbonyl</th>
<th>Carboxyl</th>
<th>ArC–O</th>
<th>ArC–C</th>
<th>ArC–H</th>
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<td>8.3</td>
<td>3.9</td>
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<tr>
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<td>12.3</td>
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A degradative solvent extraction method of biomass was proposed. The whole process can be divided into two stages. The first stage took place at heating up stage from 250 to 350 °C and the beginning of the isothermal stage at 350 °C. At first stage, the thermal extraction, deoxygenation and aromatization reactions of the raw biomass occurred significantly. The main product was Deposit. At the second stage, the Deposit was further deoxygenated and converted into Soluble. In this stage, the Deposit underwent complex reactions, such as the cleavages of oxygen containing cross-links and aromatization reactions. The oxygen was mainly removed as H₂O at the second stage. During the whole extraction process, the extracts (Soluble and Deposit) were well dispersed in the solvent. So the intermolecular reactions, such as polymerization reactions, were inhibited. The reactions in this process were mainly intramolecular. This is the main difference between degradative solvent extraction and torrefaction of the biomass. The oxygen, carbon and minerals in the raw biomass were mainly recovered as CO₂/H₂O, Deposit/Soluble, and Residue by the degradative solvent extraction, respectively. The proposed conversion pathway was shown in Fig. 8.

4. Conclusion

A degradative solvent extraction method of biomass was proposed in our previous work. To elucidate the conversion mechanism of this process, a typical woody biomass was treated in 1-MN at 350 °C with the residence time ranging from 0 to 90 min. The oxygen, carbon and minerals in the raw biomass were mainly recovered as CO₂/H₂O, Deposit/Soluble, and Residue by the degradative solvent extraction, respectively. The residence time exhibited considerable effects on the yield distributions and characteristics of the products. The Soluble yields increased obviously from 0 min to 45 min and then almost kept unchanged from 45 min to 90 min. Meanwhile, the Deposit yields decreased significantly with the residence time from 0 min to 45 min and then decreased slowly from 45 min to 90 min. Prolonging the residence time can enhance the transformation from Deposit to Soluble and oxygen removal of the products. The chemical structure and properties of Solubles were independent of the residence time, while those of Deposits varied obviously with residence time. Significant aromatization reactions occurred during solvent extraction. The reaction process of the degradative solvent extraction of biomass can be divided into two stages. The first stage took place at heating up stage from 250 to 350 °C and the beginning of the isothermal stage at 350 °C. At first stage, the thermal extraction, deoxygenation and aromatization reactions of the raw biomass occurred significantly. The main product was Deposit. The oxygen was removed as CO₂ and H₂O. At the second stage, the Deposit was further deoxygenated and converted into Soluble. In this stage, the Deposit underwent complex reactions, such as the cleavages of oxygen containing cross-links and aromatization reactions. The oxygen was mainly removed as H₂O at the second stage.

Acknowledgments

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