Comparative Study on the Pyrolysis Behaviors of Pine Cone and Pretreated Pine Cone by Using TGA–FTIR and Pyrolysis-GC/MS

Yu Chen,† Liangcai Wang,† Manqi Zhao, Huanhuan Ma, Dengyu Chen, Yimeng Zhang, and Jianbin Zhou*

ABSTRACT: Pine cone (PC) is a potential biomass energy source and is rich in nonstructural substances (NSS). To understand the impact of these NSS on the pyrolysis behavior and its products, in this study, phenol alcohol extraction was used for the separation of NSS from PC (the PC after separation of NSS was labeled as A-PC), and then thermogravimetric analysis–Fourier transform infrared and PY-gas chromatography/MS detection techniques were used to conduct a systematic comparison of the thermal degradation behaviors and kinetics parameters of PC and A-PC. Results showed that the N content of PC was higher than that of other biomass, and the activation energies of PC and A-PC generally decreased at first and then increased as the conversion rate increased. Furthermore, the activation energy of PC decreased with conversion rates in the range of 0.25–0.30, while A-PC lagged significantly behind PC.

1. INTRODUCTION

With the decline in the number of fossil fuels and an increase in environmental pollution, biomass energy has been receiving considerable interest from relevant researchers because of its advantages of abundance, wide distribution, and CO2 neutrality, as well as low emissions of nitrogen and sulfur compounds.1−5 However, the energy density of biomass is low, leading to some problems such as low combustion efficiency and difficult transportation. Consequently, it needs to be converted into solids, gases, and liquids by thermochemistry or biotechnology, among which, pyrolysis is a promising thermochemical process for the utilization of biomass.6

Numerous studies have reported biomass pyrolysis using thermogravimetric analysis (TGA), differential scanning calorimetry, and Fourier transform infrared (FTIR) combined with the modeless function integration method.7−9 Zhang et al. found that overlapping and continuous chemical reactions occurred during the pyrolysis of grape stems by TGA–FTIR and pyrolysis-gas chromatography (GC)/mass spectrometry (MS).5 Chen et al. employed TGA–FTIR and pyrolysis-GC/MS to analyze the pyrolysis behavior of rice straw after torrefaction. It was presented that torrefaction pretreatment can significantly promote the pyrolysis process.10 Wu et al. investigated the pyrolysis characteristics of cellulose model compounds by TGA–FTIR and pyrolysis-GC/MS and proposed a possible two-step chemical reaction pathway.11

These previous studies achieved remarkable advances in understanding the pyrolysis behavior and its mechanism. However, its investigation object is usually concentrated on biomass whose chemical composition is not particularly complicated.

Interestingly, pine cone (PC) as an agricultural and forest waste is rich in nonstructural substances (NSS), such as wax, fat, resin, tannin, sugars, pigments, and the separation of NSS does not destroy cellulose, hemicellulose, and lignin, which is unmatched by any other biomass. However, the current study of PC mainly focuses on the development and research of natural medicinal extracts, and its pyrolysis behavior has not yet been reported.12 Moreover, pretreatment is a promising method for product upgrading and understanding of its pyrolysis behavior, such as torrefaction, water washing, dilute acid solution washing, and aqueous phase oil washing. However, the separation method is used to pretreat the NSS in the biomass, and a comparative study of the pyrolysis behaviors of the biomass before and after separation has not
yet been reported, as well as the effect of NSS on pyrolysis has not been investigated.

Moreover, nonmechanical function model methods have two categories: differential and integral. Because of employing the instantaneous rate value, the differential isoconversional method is sensitive to experimental noise, leading to the unstable numerical value. However, this phenomenon can be effectively avoided when using the integration methods, especially in the TGA. The Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose are commonly used methods. However, compared with other thermal analysis methods, the FWO integration method can avoid the errors that may be caused by the different assumptions of the reaction mechanism function.

Herein, phenol alcohol extraction was used for the separation of NSS from PC. Subsequently, TGA–FTIR and pyrolysis-GC/MS detection techniques were used to investigate the pyrolysis behavior of PC and A-PC (PC after separation of NSS is labeled as A-PC) at different heating rates (10, 20, 30, and 40 °C/min) and the content of rapid pyrolysis products of PC and A-PC, respectively. Meanwhile, the activation energies of PC and A-PC during pyrolysis were calculated in combination with the FWO integral method.

2. MATERIALS AND METHODS

2.1. Materials. PC was obtained from the Kuandian, Liaoning Province of China. Before the experiment, 100 g of the raw material was taken from which impurities such as pine nuts and sand were removed, and then it was washed with deionized water. Subsequently, it was dried in an oven at 105 °C for 24 h to remove moisture (the sample has almost no change in quality after 22 and 24 h of drying). They were then ground into a powder, and the particle size was 0.130–0.180 mm.

2.2. Separation of NSS and PC. The separation of NSS and PC was performed according to the Chinese National Standards GB/T26777.6-1994 “fibrous raw material-determination of solvent extractives,” and the PC after separation of NSS was named as A-PC.

2.3. Basic Physical and Chemical Properties of PC and A-PC. For PC and A-PC, the proximate analysis and ultimate analysis were performed according to the Chinese National Standards GB/T28731-2012 “proximate analysis of solid biofuels” using an elemental analyzer (Vario macro cube, Elementar, Germany).

2.4. TGA–FTIR Analysis. Weight loss characteristics and identification of volatile components of PC and A-PC were performed with TGA–FTIR (TGA STA8000, PerkinElmer, Waltham, MA, USA coupled with Frontier, PerkinElmer, Waltham, MA, USA). Approximately, 10 mg of the sample was used in each test with heating rates of 10, 20, 30, and 40 °C/min under an atmosphere of high purity nitrogen (carrier gas), and the temperature was set to increase from room temperature to 800 °C, as well as the flow rate was controlled at 50 mL/min. Subsequently, the thermogravimetric curve and the three-dimensional FTIR spectra were recorded.

2.5. Pyrolysis Kinetics Analysis. The reaction of the biomass pyrolysis process could be present as \( A \rightarrow B \rightarrow C \) (gas). The change of conversion rate with reaction time during the reaction is shown as follows

\[
\alpha = \frac{m_0 - m_i}{m_i - m_\infty}
\]

(1)

\[
\frac{d\alpha}{dt} = A \exp\left(\frac{-E}{RT}\right)f(\alpha)
\]

(2)

where \( \alpha, m_0 \) and \( m_i \) are the mass loss number, the initial mass (g), and the mass (g) at a certain time \( \tau \) (s), respectively, and \( m_\infty, A, \) and \( E \) are the final mass (g) (the mass of the sample cannot be finally reacted after completion of the reaction), the frequency factor (S⁻¹), and the activation energy (J/mol), respectively. Finally, \( T, R, \) and \( f(\alpha) \) are the Kelvin temperature, the constant of the molar gas, and the reaction mechanism equation, respectively. The mass loss \( \alpha \) is defined by eq 3.

The heating rate \( \beta \) is defined by \( \beta = dT/dt \), which was obtained by eq 2

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right)f(\alpha)
\]

(3)

After integrating eq 3, we can obtain eq 4

\[
G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = A \int_0^T \exp\left(\frac{-E}{RT}\right)dT = \frac{AE}{\beta R}P(U)
\]

(4)

where \( G(\alpha) \) is an integral form of \( f(\alpha) \), \( P(U) \) is an approximation, \( U \) is defined as \( U = E/R \).

After a series of mathematical simplification and approximation, the FWO model was simplified to eq 5

\[
\log \beta = \log \frac{AE}{RG(\alpha)} - 2.315 - 0.4567 \frac{E}{RT}
\]

(5)

2.6. Pyrolysis-GC/MS Experiments. Approximately, 0.5 mg of PC and A-PC powders were weighed into a quartz tube and were pyrolyzed at 338 and 342 °C, respectively. The heating rate of 20 °C/ms for PC and A-PC, as well as more detailed information regarding the pyrolysis process and instrument can be found in a previously reported study.

3. RESULTS AND DISCUSSION

3.1. Basic Physical and Chemical Properties of PC and A-PC. NSS account for approximately 22.94 ± 0.8% of PC content. Table 1 presents that the ash content of A-PC was higher than that of PC, which resulted from the separation of NSS leading to the relative enrichment of ash content.

Moreover, previous studies reported that the electrochemical performance of carbon-based materials could be further improved by doping with other heteroatoms (N, B, and S). Zhang et al. used petroleum coke as the carbon source, activated with KOH, and then doped with ammonia gas to obtain nitrogen-doped activated carbon with a nitrogen content of 4 wt %, and the specific capacitance was 299 F g⁻¹.
Xiao et al. found that nitrogen-doped porous carbon can be obtained with a specific capacitance of 321.7 F g\(^{-1}\) by carbonizing melamine and citron peel. These previous studies achieved remarkable advances in understanding that doping with N could improve the electrochemical performance. However, with the aid of ammonia as a nitrogen source and protective gas, it is not easy for ammonia molecules to enter the interior of the material, resulting in insufficient doping, and ammonia is expensive, as well as has a risk of operation. Because melamine has an insoluble property in water, it is difficult to evenly distribute in the carbon material, which affects the nitrogen doping effect. The nitrogen content of PC and A-PC was 1.61 and 1.57%, respectively, which was higher than those of other biomass such as grape stem and rice straw. Interestingly, a majority of nitrogen in the PC existed as in situ doped along with PC growing, which was beneficial to nitrogen evenly distributed in PC. Meanwhile, its fixed carbon content was higher than that of palm husk. Moreover, the nitrogen content of activated carbon will enrich during the PC pyrolysis process. Therefore, the preparation of activated carbon for energy-storage materials has the potential to solve the uneven nitrogen doping and improve its electrochemical performance.

### 3.2. Effect of Heating Rate on the Pyrolysis Characteristics of PC and A-PC

The effect of the heating rate on the pyrolysis characteristics of biomass is relatively complicated. Meanwhile, with an increased heating rate, the pyrolysis temperature of biomass decreased, which was in favor of rapid pyrolysis. However, with the further rise of heating rate, the sample particles had a heat transfer time, leading to a temperature difference between the inside and outside of the sample particles. Thus, the degree of biomass pyrolysis depends on the coupling relationship between the two interaction processes.

Figure 1. TG curves of PC (a) and A-PC (c) under different heating rates; DTG curves of PC (b) and A-PC (d) under different heating rates.

#### Table 2. Linear Fitting Equation of the FWO Method for PC and A-PC

| Conversion rates α | PC Conversion Equation | R\(^2\) | A-PC Conversion Equation | R\(^2\) |
|--------------------|------------------------|--------|--------------------------|--------|
| 0.25               | −7730.10x + 15.4177    | 0.96372| −15462.18x + 28.5637     | 0.93417|
| 0.30               | −5031.63x + 10.2372    | 0.91802| −14687.79x + 26.6865     | 0.97621|
| 0.35               | −8236.93x + 15.7617    | 0.98563| −13433.26x + 24.1198     | 0.96761|
| 0.40               | −9746.29x + 18.0526    | 0.92771| −13055.89x + 23.1631     | 0.98927|
| 0.45               | −8815.61x + 16.2214    | 0.95327| −13131.30x + 23.0204     | 0.99979|
| 0.50               | −9770.20x + 17.5318    | 0.93752| −12164.66x + 21.1840     | 0.99767|
| 0.55               | −10172.05x + 17.9433   | 0.96104| −12164.66x + 20.9772     | 0.99767|
| 0.60               | −11148.04x + 19.2003   | 0.99046| −12429.74x + 21.1769     | 0.99691|
| 0.65               | −13711.20x + 22.7857   | 0.97544| −14635.38x + 24.3373     | 0.98618|
| 0.70               | −18734.55x + 29.6801   | 0.96342| −23661.92x + 37.4757     | 0.88958|

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https://dx.doi.org/10.1021/acsomega.0c04456  
ACS Omega 2021, 6, 3490–3498
A-PC move toward the side of high temperature, and the main pyrolysis temperature range also changes. Meanwhile, the thermal hysteresis becomes more notable, and the time for the sample to reach the pyrolysis temperature decreases as the heating rate increases. The maximum rate of weight loss for PC is at 200–500 °C, while for A-PC, it is at 200–400 °C. According to the previous study, the maximum rate of weight loss for grape stalks, palm husks, and rice husks is at about 200–400 °C, which was consistent with that of A-PC.

The DTG curve of PC has two distinct weight loss peaks in the pyrolysis temperature interval of 200–500 °C, which was around 300 and 450 °C, respectively. Among these, the weight loss peak of ~300 °C was caused by the pyrolysis of lignin or hemicellulose, while the weight loss peak of ~450 °C was mainly attributed to the presence of NSS. Moreover, the DTG curve of A-PC has a weight loss peak in the pyrolysis temperature interval of 200–400 °C, which was similar to the DTG curves of pinewood, bamboo, and corn stalk. The yield of the solid product after the pyrolysis of PC was less than that of the solid product after the pyrolysis of A-PC, indicating that the separation of NCC could increase the yield of carbon. Besides, the mass loss rates of PC and A-PC were about 73.98 and 70.04%, respectively, which were consistent with the proximate analysis.

#### 3.3. Pyrolysis Kinetics Analysis of PC and A-PC.

Table 2 lists the fitting results of PC and A-PC at the conversion rate of 0.25–0.7, and the linear fit correlation coefficient ($R^2$) was high, indicating that the fitting results were credible.

Biomass pyrolysis is an overwhelmingly complex process. It involves parallel, competitive, and continuous reactions. Generally, the activation energy of PC and A-PC increased in accordance with increased conversion rates from 0.25 to 0.7, as shown in Figure 2.

![Figure 2. Activation energy change curve of FWO at different conversion rate $\alpha$ of PC and A-PC.](image)

The initial process of PC and A-PC has a relatively low activation energy. With an increase in the temperature, the linear chain of cellulose is broken, and thus the activation energy of PC and A-PC gradually increased. Nevertheless, active cellulose is likely to be generated during the pyrolysis of cellulose in PC, which requires less energy for thermal decomposition because of its lower molecular weight and degree of polymerization. Thus, a declining trend in activation energy was observed when the conversion rate of PC was 0.45. Overall, the activation energy of A-PC was higher than that of PC. It was probably inferred that the presence of NSS significantly improves the reactivity of hemicellulose, cellulose, and lignin, as well as was in favor of the decomposition of structural substances. Therefore, NSS could have potential application value in the field of collaborative biomass reaction. However, the specific mechanism needs further investigation.

Figure 2 presents that the activation energy of PC decreased at first and then increased when $0.25 < \alpha < 0.40$ and reaches the minimum value (91.57 kJ/mol) at $\alpha = 0.3$, which was predictable because when $0.25 < \alpha < 0.30$, there was breaking of hemicellulose branches and the products were volatiles and transition products, and when $0.30 < \alpha < 0.40$, the activation energy gradually increased, and the straight chain weak bonds in the noncrystalline region of hemicellulose and part of cellulose were broken. When $0.40 < \alpha < 0.55$, the activation energy of the PC also decreased at first and then increased. However, compared with $0.25 < \alpha < 0.40$, its activation energy does not change much (160.49–185.18 kJ/mol). According to the pyrolysis temperature region corresponding to $0.40 < \alpha < 0.55$ and compared with A-PC, on increasing the pyrolysis temperature, this region was located between the two weight loss peaks of the PC’s DTG curve. Based on the analysis of the effect of lignin on its DTG curve, it was probably inferred that NSS cooperate with lignin to make the hemicellulose, cellulose, and lignin in PC more cross-linked. Meanwhile, it indicates that not only competitive degradation reactions occur in the cross-linked polymer matrix but also diffusion, which was consistent with the main pyrolysis region of PC wider than that of A-PC. When $0.40 < \alpha < 0.45$, the activation energy of PC decreased and cellulose begins to pyrolyze, and when $0.45 < \alpha < 0.55$, cellulose and lignin cross-decompose. Lignin decomposition requires energy, leading to the increase in the activation energy of PC. When $0.55 < \alpha < 0.70$, there was mainly decomposition of lignin, and because of the three-dimensional network stabilization structure of lignin, its activation energy increased again.

The activation energy of A-PC at $0.25 < \alpha < 0.40$ decreased because of the decomposition of hemicellulose and part of the cellulose noncrystalline region. When $0.45 < \alpha < 0.60$, there was pyrolysis of cellulose, and the activation energy was high resulting from the need for energy to destroy the crystallization of cellulose. However, with a decrease in the degree of polymerization, the activation energy decreased. Moreover, $0.60 < \alpha < 0.70$ was the pyrolysis of lignin, and the reaction mechanism was similar to that of PC. It is not difficult to understand that the activation energies of PC and A-PC were higher than that of xylan (model compound of hemicellulose) (87.65, 69.39 kJ/mol) because PC and A-PC contain hemicellulose, cellulose, and lignin.

#### 3.4. TGA–FTIR Analysis of PC and A-PC Pyrolysis.

At a temperature range of 30–800 °C and a heating rate of 20 °C/min, the three-dimensional infrared spectra of the PC and A-PC pyrolysis processes are shown in Figure 3a,b, respectively. The functional group represented by each characteristic peak can be identified from three-dimensional infrared spectroscopy. Figure 3a presents that the pyrolysis of PC mainly occurs at 200–500 °C, and Figure 3b shows that the pyrolysis of A-PC mainly occurs at 200–400 °C. Meanwhile, compared with the TG (1a,c) and DTG (1b,d) curves at the same temperature region and heating rate, the appearance of infrared absorption peak is consistent with its weight loss time.

The stretching vibration of O–H, C=H, and C=O is observed at 3400–3000 cm$^{-1}$, 2800–2700 cm$^{-1}$, and 2400–2500 cm$^{-1}$, respectively, while the C–O stretching vibration is at 2250–2000 cm$^{-1}$, C=O bending vibration is at 560–500 cm$^{-1}$, and acidic C=O stretching vibration is at 1900–1650 cm$^{-1}$. This peak is caused by the decomposition of structural substances. Therefore,NSS could have potential application value in the field of collaborative biomass reaction. However, the specific mechanism needs further investigation.

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The activation energy of A-PC at $0.25 < \alpha < 0.40$ decreased because of the decomposition of hemicellulose and part of the cellulose noncrystalline region. When $0.45 < \alpha < 0.60$, there was pyrolysis of cellulose, and the activation energy was high resulting from the need for energy to destroy the crystallization of cellulose. However, with a decrease in the degree of polymerization, the activation energy decreased. Moreover, $0.60 < \alpha < 0.70$ was the pyrolysis of lignin, and the reaction mechanism was similar to that of PC. It is not difficult to understand that the activation energies of PC and A-PC were higher than that of xylan (model compound of hemicellulose) (87.65, 69.39 kJ/mol) because PC and A-PC contain hemicellulose, cellulose, and lignin.
Subsequently, the C=O, C−C, and carbon chain stretching vibrations are at 1475−1000 cm−1, the aromatic stretching vibration is at 1900−1650 cm−1, the C−O stretching vibration of the phenolic functional group is at 1300−1200 cm−1, as well as the C−O stretching vibration of the alcohol functional group is at 1200−1100 cm−1. At a heating rate of 20 °C/min for PC and A-PC, the temperatures corresponding to the maximum weight loss peaks of DTG are 338 and 342 °C, respectively. Therefore, this study discusses the volatile products of PC and A-PC at 338 and 342 °C, respectively. The results are presented in Figure 4.

According to the infrared peak range of the above functional groups, the small-molecule gases (H2O, CH4, CO2, and CO) could be identified, among which, CH4 mainly comes from the pyrolysis of methoxy, methyl, and methylene in lignin. Figure 4 shows that the CH4 content of PC was higher than that of A-PC. This result once again indicated that NSS could cooperate with lignin to make the hemicellulose, cellulose, and lignin in PC more cross-linked. Moreover, CO2 was formed via the dehydroxylation reaction and the cleavage of the carbonyl group. The content of CO2 produced by A-PC was higher than that by PC. Studies have reported that the destruction of ether bonds and C=O bonds could form CO. The content of CO produced by A-PC was slightly above that by PC. Besides, organic compounds can be identified by the characteristics of functional groups, and organic compound content of A-PC was higher than that of PC.

3.5. Pyrolysis-GC/MS Analysis of PC and A-PC. At a heating rate of 20 °C/min for PC and A-PC, the temperatures corresponding to the maximum weight loss peaks of DTG are 338 and 342 °C, respectively; that is to say that although 338 °C is near 342 °C, the maximum thermal decomposition rate of PC was at 338 °C. Similarly, the thermal decomposition rate of A-PC was maximized at 342 °C. Thus, PC and A-PC were pyrolyzed at 338 and 342 °C, respectively. However, what difference between PC and A-PC pyrolysis might be caused by 338 and 342 °C will be further verified later in this work.

For pyrolysis-GC/MS results, the chromatographic peak area of a compound is considered linear with its content. Some representative compounds were selected because of their relatively higher peak area %. Table 3 lists the fast pyrolysis products of PC at 338 °C identified by the NIST library; the relative content of individual compound peaks was the percentage of the total compound peak area, and the contents of 39 of the products were above 0.5%. Table 4 lists the fast pyrolysis products of A-PC at 342 °C, and the contents of 24 of the products were above 0.5%.

Table 3 shows that the top five products were isoparvifuran (12.17%), L-(+)-ascorbic acid 2,6-dihexadecanoate (7.73%), N-methyltaurine (6.78%), butanoic acid, 3-hydroxy- (5.41%), and 1,8-naphthalenediol, 2,7-diacetyl-3,6-di (3.67%). The sugar content of the remaining 34 substances was relatively low (0.65%), indicating that the cellulose in PC was rapidly decomposing at 338 °C. Table 4 lists that the top 5 products were hydroxyurea (22.05%), N-methyltaurine (20.41%), N-hexadecanoic acid (11.29%), 2-formylhistamine (9.12%), and (R)-(−)-2-amino-1-propanol (2.84%). Moreover, the observation found that the remaining 19 substances still have lots of acids, which shows that the hemicellulose in A-PC was decomposed at 342 °C, while cellulose and lignin were weakly decomposed. A previous study reported that the decomposition temperature of cellulose is higher than that of hemicellulose. In this study, the fast pyrolysis temperature of PC and A-PC was 338 and 342 °C, respectively. However, even under such pyrolysis conditions, the amount of cellulose decomposed in PC was still higher that of A-PC, again indicating that the presence of NSS could synergistically pyrolyze.
The pyrolysis products are intensely complex and contain an army of compounds. Although it was not possible to identify every product, the pyrolysis products can be divided into several main categories in line with the functional groups detected via pyrolysis-GC/MS: acids, phenols, ketones, esters, N-containing compounds, aldehydes, sugar, and furans. The total content of pyrolysis products, from 70.82% for PC to 83.30% for A-PC, is due to a slice of components that were not calculated.

The main organic products of fast pyrolysis of PC at 338 °C and A-PC at 342 °C are presented in Figure 5a,b, respectively.

As seen in Figure 5a, the relative contents of acids, phenols, ketones, esters, N-containing compounds, aldehydes, sugar, and furans were 17.77, 9.38, 4.71, 11.73, 6.75, 4.36, 0.56, and 15.56%, respectively. However, the relative contents of ketones, aldehydes, and sugar were less than 5%. Compared with the PC pyrolysis products, the A-PC pyrolysis products decreased the relative contents of ester and aldehydes. Meanwhile, the relative contents of phenols, ketones, and furans are not shown in Figure 5b because their relative contents were less than 0.5%. However, the relative contents of acids, N-containing compounds, and sugars increased remarkably.

Because of the presence of NSS in the PC, fast pyrolysis of PC produces more organic species than the fast pyrolysis of A-PC. Meanwhile, the fast pyrolysis of A-PC produces more acids and N-containing compounds than the fast pyrolysis of PC mainly because the acid and nitrogen-containing compounds

| time (min) | relative content (%) | compound name | molecular formula |
|-----------|----------------------|---------------|------------------|
| 23.933    | 7.73                 | L-ascorbic acid 2,6-dihexadecanoate | C_{38}H_{68}O_{8} |
| 1.579     | 6.78                 | N-methyltaurine | C_{3}H_{9}O_{3}NS |
| 26.734    | 6.34                 | isoparvifuran | C_{16}H_{14}O_{3} |
| 25.373    | 5.83                 | isoparvifuran | C_{16}H_{14}O_{3} |
| 2.029     | 5.41                 | butanoic acid, 3-hydroxy- | C_{4}H_{8}O_{3} |
| 26.629    | 3.67                 | 1,8-naphthalenedioli, 2,7-diacytethyl-3,6-di | C_{20}H_{34}O_{2} |
| 25.803    | 3.47                 | 5-(7a-isopropyl)-4,5-dimethyl-octahydro | C_{20}H_{34}O_{2} |
| 1.714     | 2.73                 | hydroyurea | CH_{2}O_{2} |
| 27.534    | 2.61                 | 1-phenanthrene-carboxaldehyde, 1,2,3,4,4a | C_{20}H_{28}O_{2} |
| 1.739     | 2.26                 | hydroyurea | CH_{2}O_{2} |
| 25.133    | 2.21                 | anthracene, 9-butyli,2,3,4-tetrahydro- | C_{14}H_{16}O_{2} |
| 24.718    | 2.18                 | 4b,8-dimethyl-2-isopropylphenanthrene, 4 | C_{14}H_{18}O_{2} |
| 1.534     | 2.10                 | N-methyltaurine | C_{3}H_{9}O_{3}NS |
| 12.418    | 2.06                 | catechol | C_{6}H_{4}O_{3} |
| 24.778    | 1.98                 | 5-inden-1(2H)-one, 3,5,6,7-tetrahydro- | C_{13}H_{18}O_{2} |
| 26.303    | 1.97                 | 1,8-naphthalenedioli, 2,7-diacytethyl-3,6-di | C_{20}H_{34}O_{2} |
| 2.409     | 1.77                 | O-methylisourea | C_{13}H_{20}O_{2} |
| 24.493    | 1.59                 | 2-naphthalenbutanoesnoicic acid, Se-phen | C_{20}H_{34}O_{2} |
| 26.113    | 1.46                 | 1-cyclohexaneone, 2-(1-(2-naphthyl) methyl) | C_{19}H_{29}O_{2} |
| 25.098    | 1.41                 | isoparvifuran | C_{16}H_{14}O_{3} |
| 24.283    | 1.24                 | methyl dehydroabietate | C_{20}H_{34}O_{2} |
| 12.013    | 1.12                 | 2-isopropoxymethyl propionate | C_{14}H_{22}O_{2} |
| 10.457    | 1.11                 | pentanal | C_{6}H_{12}O_{3} |
| 28.214    | 1.10                 | methyl dehydroabietate | C_{20}H_{34}O_{2} |
| 27.364    | 1.03                 | 1-phenanthrene-carboxylic acid, 1,2,3,4,4a | C_{14}H_{20}O_{2} |
| 6.826     | 1.03                 | 1,2-cyclopentanone | C_{11}H_{16}O_{2} |
| 5.330     | 1.01                 | 2-furanmethanol | C_{8}H_{12}O_{2} |
| 9.432     | 0.97                 | 5-hexyl-1,4-dioxepin, 2,3-dihydro-7-methyl- | C_{13}H_{18}O_{2} |
| 26.964    | 0.95                 | retene | C_{13}H_{18}O_{2} |
| 26.414    | 0.95                 | 2H-benz [E]inden-3-ol, 3,3a,4,5-tetrahydro- | C_{14}H_{20}O_{2} |
| 18.500    | 0.90                 | dodecanecarboxylic acid | C_{12}H_{22}O_{2} |
| 22.327    | 0.82                 | phytol, acetate | C_{15}H_{24}O_{2} |
| 28.539    | 0.79                 | 1-phenanthrenemethanol, 1,2,3,4,4a,9,10 | C_{20}H_{34}O_{2} |
| 25.573    | 0.77                 | 4'-((tert-butyl)-2-hydroxystilbene | C_{17}H_{22}O_{2} |
| 14.524    | 0.73                 | 4-hydroxy-3-methylacetoephene | C_{13}H_{18}O_{2} |
| 6.223     | 0.71                 | octadecanoic acid | C_{18}H_{36}O_{2} |
| 17.470    | 0.65                 | β-glucopyranose, 1,6-anhydro- | C_{12}H_{22}O_{2} |
| 26.834    | 0.65                 | N-ethyl-3-methyl-4-N-(2-[1,1,3,3-tetramethyl] | C_{17}H_{34}O_{2}N_{2}Si |
| 23.692    | 0.61                 | 4b,8-dimethyl-2-isopropylphenanthrene, 4 | C_{14}H_{20}O_{2} |
| 10.322    | 0.58                 | phenol, 2-methoxy- | C_{6}H_{12}O_{2} |
| 16.795    | 0.56                 | trans-isoeugenol | C_{14}H_{22}O_{2} |
| 14.114    | 0.55                 | 1,2-benzenediol, 4-methyl- | C_{10}H_{14}O_{2} |
| 5.590     | 0.55                 | 2-propanone, 1-(acetyloxy)- | C_{5}H_{10}O_{2} |
| 22.622    | 0.54                 | 1,2-benzenedicarboxyl acid, bis(2-meth | C_{14}H_{24}O_{4} |
| 24.578    | 0.54                 | 2-naphthalenbutanoselenoic acid, Se-phen | C_{20}H_{34}O_{2}Se |
in A-PC were relatively enriched after the separation of NSS. However, its mechanism needs further investigation. Figure 5a,b shows that the fast pyrolysis products of PC and A-PC contain numerous N-containing compounds, which were 6.75 and 38.84%, respectively. The results correspond to the high nitrogen content in the ultimate analysis results of PC and A-PC. Thus, it was probably inferred that the PC pyrolysis products such as bio-oil, especially the bio-oil derived from A-PC pyrolysis, have promising potential value in the application of liquid compound fertilizers.

### 4. CONCLUSIONS

The nitrogen contents of PC and A-PC were 1.61 and 1.57%, respectively, and their preparation as activated carbon for energy-storage materials has the potential to solve the uneven nitrogen doping. Moreover, NSS could cooperate with lignin to make the hemicellulose, cellulose, and lignin in PC more closely cross-linked. Meanwhile, NSS improve the reactivity of hemicellulose, cellulose, and lignin, as well as reduce their activation energy, which was in favor of the decomposition of structural substances. Therefore, NSS have promising potential application value in the field of cooperative biomass reaction. Finally, the fast pyrolysis products of both PC and A-PC

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**Table 4. Qualitative and Quantitative Analysis of A-PC Fast Pyrolysis Products at 342 °C**

| time (min) | relative content (%) | compound name                              | Molecular Formula |
|-----------|----------------------|--------------------------------------------|-------------------|
| 23.903    | 11.29                | N-hexadecanoic acid                        | C16H32O2          |
| 1.754     | 9.12                 | 2-formylhistamine                          | C6H14O2           |
| 1.674     | 6.99                 | N-methyltaurine                            | C6H14O2NS         |
| 1.564     | 6.98                 | N-methyltaurine                            | C6H14O2NS         |
| 1.534     | 6.44                 | N-methyltaurine                            | C6H14O2NS         |
| 2.029     | 6.26                 | hydroxyurea                                | CH2O2N2           |
| 1.974     | 5.15                 | hydroxyurea                                | CH2O2N2           |
| 2.454     | 3.82                 | hydroxyurea                                | CH2O2N2           |
| 1.724     | 3.50                 | hydroxyurea                                | CH2O2N2           |
| 2.399     | 2.84                 | (R)-(-)-2-amino-1-propanol                 | C3H8O2N2          |
| 17.450    | 2.49                 | β-d-glucopyranose, 1,6-anhydro-            | C6H10O2           |
| 28.209    | 2.43                 | methyl dehydroabietate                     | C21H30O2          |
| 2.209     | 2.21                 | (R)-(-)-2-amino-1-propanol                 | C3H8O2N2          |
| 24.703    | 2.19                 | 4b,8-dimethyl-2-isopropylphenanthrene, 4   | C20H16O2          |
| 18.491    | 2.09                 | dodecanonic acid                           | C12H24O2          |
| 26.949    | 2.06                 | retene                                     | C7H14O2           |
| 2.294     | 2.04                 | hydroxyurea                                | CH2O2N2           |
| 2.613     | 1.58                 | 10,18-bisnorabieta-5,7,9(10),11,13-penta    | C18H22O2          |
| 22.617    | 1.55                 | 1,2-benzenedicarboxylic acid               | C6H12O4           |
| 10.873    | 1.40                 | cyclopentasiloxane, decamethyl-            | C10H20O2Si5       |
| 26.209    | 1.29                 | octodecanonic acid                         | C12H24O2          |
| 2.184     | 1.28                 | hydroxyurea                                | CH2O2N2           |
| 1.394     | 1.02                 | α-alanine                                  | C3H6N              |
| 2.264     | 1.01                 | phenanthenre, 2,3,5-trimethyl-             | C12H10O           |
| 24.273    | 0.82                 | isophthalic acid, di(3-methylphenyl) est    | C8H6O3            |
| 9.172     | 0.64                 | α-limonene                                 | C10H6O2           |
| 24.243    | 0.63                 | 4b,8-dimethyl-2-isopropylphenanthrene, 4   | C18H22O2          |
| 23.808    | 0.59                 | dibutyl phthalate                          | C12H22O4          |
| 32.516    | 0.57                 | tetraccontene                             | C40H82            |
| 30.705    | 0.56                 | hexatriacontane                            | C36H74            |
| 15.965    | 0.50                 | vanillin                                   | C8H8O3            |

**Figure 5.** (a,b) Main organic products of fast pyrolysis of PC at 338 °C and A-PC at 342 °C, respectively.
contain considerable N-containing compounds, especially, the content of nitrogen-containing compounds of A-PC was ~38.84%, which probably infers that its bio-oil has potential value in the application of compound fertilizers.

**AUTHOR INFORMATION**

**Corresponding Author**

Jianbin Zhou — College of Materials Science and Engineering, Nanjing Forestry University, 210037 Nanjing, China; Email: zhoujianbin@njfu.edu.cn

**Authors**

Yu Chen — College of Materials Science and Engineering, Nanjing Forestry University, 210037 Nanjing, China

Liangcai Wang — College of Materials Science and Engineering, Nanjing Forestry University, 210037 Nanjing, China; orcid.org/0000-0002-8906-4638

Manqi Zhao — College of Materials Science and Engineering, Nanjing Forestry University, 210037 Nanjing, China

Huanhuan Ma — College of Materials Science and Engineering, Nanjing Forestry University, 210037 Nanjing, China

Dengyu Chen — College of Materials Science and Engineering, Nanjing Forestry University, 210037 Nanjing, China; orcid.org/0000-0002-5275-3149

Yimeng Zhang — College of Materials Science and Engineering, Nanjing Forestry University, 210037 Nanjing, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c04456

**Author Contributions**

†The authors have contributed equally to this work, and the authors declare no competing financial interest.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Promotion Project of China (no. 20201333136), the National Natural Science Foundation of China (51776100), the Six Talent Peaks Program of Jiangsu Province (XNY-027), and the 333 Project of Jiangsu Province (BRA2019270).

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