Effect of torrefaction temperature on Reverse Chemical Looping Pyrolysis Characteristics of Pine Wood Biomass

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Abstract. Torrefaction treatments play a crucial role in upgrading the quality of pyrolysis bio-oils. In this study, the impact of torrefaction temperature (200, 230, 260, and 290°C) on the reverse chemical looping pyrolysis characteristics of pine wood biomass was investigated at 550°C. The findings revealed that torrefaction processes markedly decreased both water and oxygen levels in the biomass, ultimately improving the yield characteristics of the pyrolyzed materials. Specifically, when the torrefaction temperature reached 230°C, the phenol content in the pyrolysis liquid peaked at 73.4%, while the proportion of oxygen-containing compounds was minimized to 16.7%. With increasing torrefaction temperature, the content of hydroxyphenyl type (H) phenols increased, whereas the contents of guaiacyl type (G) and syringyl type (S) phenols gradually decreased.

Keywords: torrefaction temperature; pine wood biomass; reverse chemical looping pyrolysis; bio-oils.

1. Introduction

Biomass resources are vast in quantity, yet the excessive moisture in raw biomass can disrupt the pyrolysis process and compromise the stability of pyrolysis products. Although biomass is a plentiful resource, it frequently presents several disadvantages, such as excessive oxygen content, reduced calorific value, and logistical issues related to storage and transport[1]. To address these issues, pretreatment methods including drying, crushing, torrefaction, and acid treatment play a crucial role. By modifying the complex physical and chemical properties of biomass, these methods substantially improve the output quality of pyrolyzed bio-based products. Currently, bio-oil produced via biomass conversion technologies confronts major challenges, namely high acidity and elevated oxygen content, which pose significant hurdles to its long - term storage. This study introduces an innovative approach termed reverse chemical looping pyrolysis (RCLP), wherein a pre-reduced oxygen carrier is employed to facilitate oxygen-lean pyrolysis of biomass. Upon oxygen abstraction from the biomass, the regenerated oxygen carrier subsequently serves as an oxygen donor for the subsequent gasification stage, thereby establishing a closed-loop oxygen cycling mechanism. To address excessive oxygen content in bio-oil, torrefaction pretreatment has emerged as an efficient deoxygenation technique[2]. During this treatment, biomass is heated between 200 and 300°C under inert or oxygen-limited atmosphere[3, 4]. Beyond optimizing feedstock properties, torrefaction generates premium-grade solid fuels with enhanced suitability for thermochemical conversion processes. Previous research has provided valuable insights into torrefaction. Matali et al.[5] investigated oil palm fronds and Leucaena leucocephala at varying torrefaction temperatures and discovered that as the temperature increased, the pyrolysis reaction became more intense, leading to a notable decrease in the oxygen - carbon ratio (O/C) and hydrogen - carbon ratio (H/C) of solid products. Zhao et al.[6] explored the hydrophobicity of torrefied rice husks and found that higher torrefaction temperatures and oxygen concentrations facilitated the removal of hydrophilic groups. Additionally, Chen et al.[7] analyzed the pyrolysis of cotton stalks and demonstrated elevating torrefaction temperatures between 220-280°C resulted in increased production of bio-oils Compared with directly pyrolyzed biomass, the torrefied samples produced more biochar, and the resulting pyrolysis gas and bio-oil exhibited improved quality and higher calorific values.

This study focuses on pine wood, conducting pyrolysis experiments in a fixed bed reactor to systematically investigate how torrefaction temperature influences the composition of gas, oil, and carbon deposition in pyrolysis products. The findings aim to offer theoretical support for the advancement of torrefaction technology and the efficient conversion of biomass resources.

2. Materials and Methods

2.1 Material Preparation and Characterization

At the outset of the experiment, a calcium–iron composite oxygen carrier was synthesized via the sol–gel technique.1:1 molar mixture of ferric nitrate and calcium nitrate was dissolved in DI water. Citric acid served as the chelating agent. The solution was heated at 80°C in an oil bath with constant agitation until gel formation. The resulting gel was oven-dried at 80°C, then calcined in two stages: 300°C (1 h) followed by 900°C (5 h). The cooled product (labeled OX-OC) was ground and reduced under CH4 at 850°C for 45 min. After argon-cooling, the final material was designated Re-OC.

2.2 Experimental Apparatus and Procedure

In this study, a fixed-bed reactor was employed. Prior to the pyrolysis experiment, pine wood was heated in an argon (Ar) atmosphere at a flow rate of 150 ml/min to the designated temperatures (200, 230, 260, 290°C) with a heating rate of 10°C/min. After a torrefaction duration of 30 minutes, the temperature was reduced to ambient. Subsequently, a reverse chemical looping pyrolysis experiment was conducted at 550°C. During the pyrolysis process, 5 g of pine wood biomass and an equivalent mass of the Re-OC oxygen carrier were used. The pine wood and Re-OC oxygen carrier were thoroughly mixed and placed on a sieve plate within the reactor. The reactor system underwent thorough inert gas purging using high-grade argon (30 min flow) to eliminate reactive gases. Following the thermal process, gradual cooling to ambient temperature was maintained under continuous argon flow. The bio-oil components resulting from pyrolysis were condensed and collected in a gas-washing bottle containing isopropanol.

2.3 Product Analysis Method

Compositional analysis of the liquid pyrolysis products was performed using an Agilent Technologies GC-MS system (Model 7890A-5975C). For structural characterization of the oxygen carriers, powder X-ray diffraction measurements were conducted on a Rigaku D-MAX 2500/PC instrument equipped with a Cu-Kα radiation source, scanning across 10-80° 2θ angles. The acquired diffraction patterns were processed and interpreted using Jade 7.5 analytical software.

3. Results and Discussion

3.1 XRD of the Oxygen Carrier

Fig. 1 illustrates the X-ray diffraction (XRD) patterns of both the freshly prepared oxygen carriers and those subjected to reduction. XRD analysis indicates that the fresh oxygen carriers exhibit a crystalline structure characteristic of Ca2Fe2O5. After being reduced with CH_4 for 45 minutes in an Ar atmosphere, the oxygen carriers primarily contain metallic Fe and CaO phases, demonstrating a substantial change in structure.

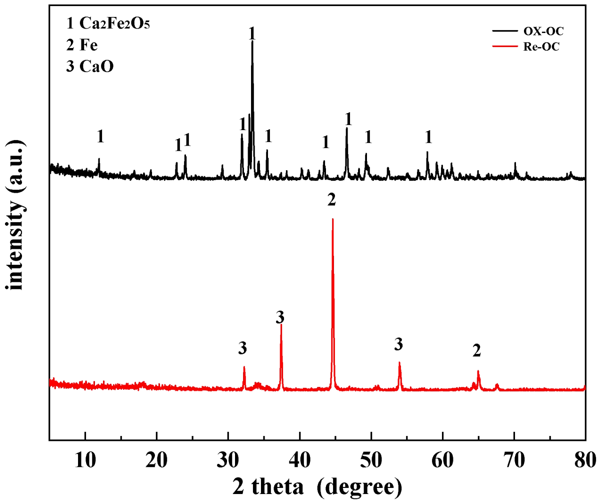

Fig. 1 XRD patterns of oxygen carriers

3.2 Influence of torrefaction on the Surface Morphology and Structure of Pine Wood

Fig. 2 shows the apparent morphologies of the raw pine wood biomass and the samples pretreated at different roasting temperatures. It can be observed that the color of the pine wood changes after the roasting treatment. As the roasting temperature increases, components such as hemicellulose and lignin in the wood undergo pyrolysis, and the color of the pine wood gradually changes from yellow to brown and eventually to black. Torrefaction, to a certain extent, alters the microscopic structure of the pine wood itself. Generally, roasting at around 250°C can yield solid products with a relatively small average pore size and the largest specific surface area, as well as a better pore structure. Such solid products are conducive to heat and mass transfer during the thermochemical conversion process, thereby promoting the rapid progress of the gas-solid reaction.

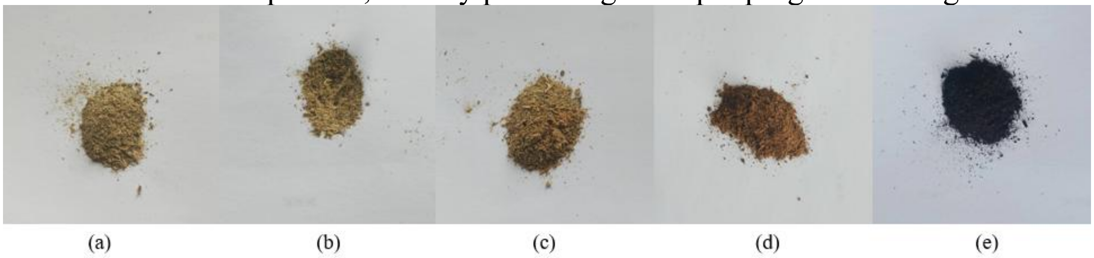

Fig. 2 Surface morphology of pine wood after torrefaction pretreatment
(a)untreated, (b)after torrefaction at 200°C, (c)after torrefaction at 230°C,
(d)after torrefaction at 260°C, (e)after torrefaction at 290°C

3.3 Influence of torrefaction on the Pyrolysis Characteristics of Pine Wood

Table 1 presents the elemental analysis outcomes for pine biomass following torrefaction across various temperatures. As torrefaction temperature ascended, the carbon (C) concentration within the biomass progressively augmented, whereas the oxygen (O) concentration diminished. This shift precipitated a decline in both the O/C and H/C ratios, signaling that dehydration and carbonization processes transpired within hemicellulose and lignin, thereby augmenting aromaticity. This trend is likely due to decarboxylation and carbonylation during torrefaction, which expedited oxygen removal. Post-torrefaction, the biomass's energy density markedly enhanced, and its combustion characteristics were refined.

Table 1 Elemental analysis of pine wood before and after torrefaction

temperature	C	H	N	O	O/C	H/C
untreated	44.78	4.2	3.45	47.57	1.06	0.09
200	52.8	5.6	6.61	34.99	0.66	0.66
230	52.99	5.59	6.71	34.71	0.66	0.11
260	56.15	5.41	6.19	32.25	0.57	0.1
290	66.23	4.5	5.52	23.75	0.36	0.07

Fig. 3 shows the influence of the presence or absence of an oxygen carrier on the yields of the three phases of pyrolysis of pine wood under torrefaction treatment at different temperatures. "Raw" represents the pine wood that has not been torrefaction treated, and "T200" represents the sample that has been torrefaction treated at 200°C. According to the results, the torrefaction temperature has a significant impact on the production amount of pyrolysis products. Specifically, the torrefaction temperature is positively correlated with the production amount of pyrolytic char, while it shows a negative correlation with the production amount of liquid products. In contrast, the influence of the torrefaction temperature on gas products is relatively weak. The reason for this analysis is as follows: During the pyrolysis process, the main sources of char, pyrolysis oil, and pyrolysis gas are lignin, cellulose, and hemicellulose in the biomass. Due to its unstable structure and poor thermal stability, hemicellulose decomposes first during torrefaction treatment, and its content will decrease sharply as the temperature rises; the structure of cellulose is relatively more stable, and it will decompose to a certain extent under high-temperature torrefaction, resulting in a gradual decrease in its content; lignin has a relatively wide decomposition temperature range and a low degree of decomposition, so it will be relatively enriched during the torrefaction process, which will promote an increase in the yield of solid-phase products. As the torrefaction temperature rises, the production amount of liquid-phase products decreases significantly. This is mainly because the hemicellulose that forms pyrolysis oil decomposes during the torrefaction process, and the intensification of the carbonization degree of the sample is also one of the reasons for the decrease in the yield of liquid products. The yield of gas products is jointly affected by the content of volatile matter and the degree of chemical bond cleavage, and the change in yield is relatively small. After adding the calcium-iron oxygen carrier, the solid-phase yield increases and the liquid-phase yield decreases because part of the oxygen-containing volatile matter is converted into carbon deposition. Compared with the reverse chemical looping pyrolysis process of biomass alone, the solid-phase yield obtained after torrefaction treatment increases, the gas yield decreases, and the liquid phase decreases. As the torrefaction temperature rises, the amount of carbon deposition generally shows an increasing trend.

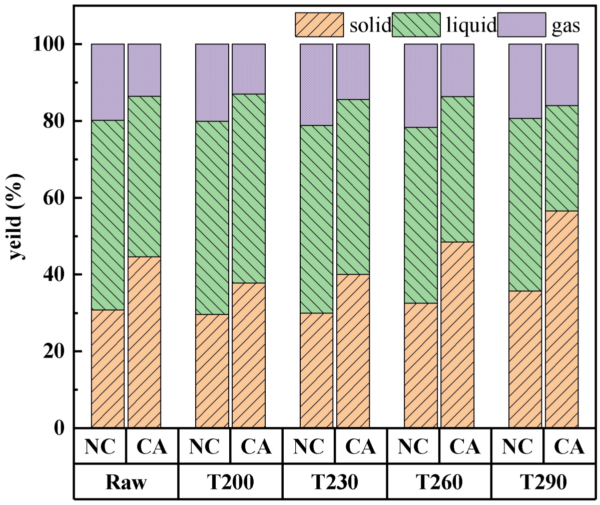

Fig. 3 Three-phase yields of pyrolysis of pine wood treated at different roasting temperatures with or without oxygenated carriers

Fig. 4 shows the distribution of liquid-phase products from the pyrolysis of pine wood at different torrefaction temperatures. Fig. 4(a) presents the distribution of pyrolysis liquid-phase products. It can be observed that the content of phenols reaches its maximum value of 73.4% at a torrefaction temperature of 230°C. At this temperature, the proportion of oxygen-containing compounds is the lowest, at 16.7%. This is mainly because phenols are derived from the pyrolysis of lignin. After torrefaction treatment, partial depolymerization of lignin occurs, leading to an increase in phenols. As the temperature rises, phenols further undergo condensation reactions to produce oxygen-containing compounds. This is manifested by an increasing trend in the content of oxygen-containing compounds during high-temperature torrefaction (>230°C). Meanwhile, cellulose and hemicellulose undergo pyrolysis and rearrangement reactions at high temperatures, which also promotes the formation of some complex oxygen-containing compounds. As the torrefaction temperature increases, the content of hemicellulose decreases, resulting in a decreasing trend in the content of aromatics in the pyrolysis liquid phase. Fig. 4(b) shows the change in the content of phenols in the liquid-phase products. It can be seen that during low-temperature torrefaction (<230°C), weak bonds such as β-O-4 bonds in lignin break, the contents of guaiacyl type (G) and syringyl type (S) phenols increase, the demethoxylation reaction is weak, and less hydroxyphenyl type (H) phenols are generated. As the torrefaction temperature rises, it promotes the condensation of lignin free radicals. The G- and S-type monomeric phenols undergo secondary cracking, and their contents decrease. The methoxy groups are removed to generate H-type phenols. Moreover, the originally stable H-type structures in lignin, such as p -coumaric acid esters, will further decompose at high temperatures, releasing free H-type phenols.

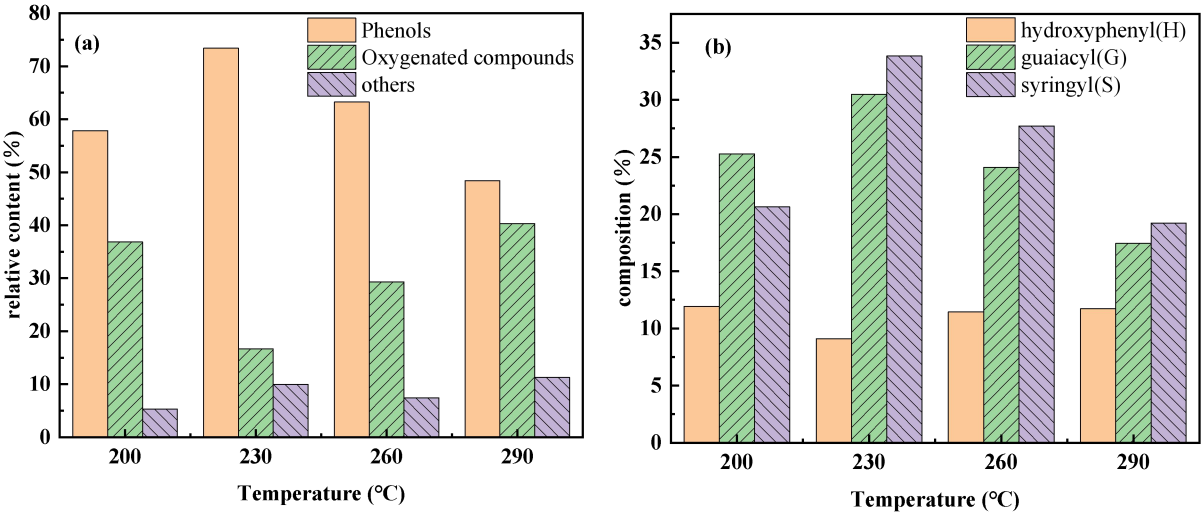

Fig. 4 Effect of torrefaction temperature on pyrolysis products of pine wood
(a) liquid phase product distribution, (b) distribution of phenolic compounds

4. Summary

Torrefaction pretreatment can effectively reduce the oxygen-to-carbon ratio of biomass, thereby improving the energy density and combustion performance of biomass. As the torrefaction temperature increases, the amount of carbon deposition increases. Low-temperature torrefaction can promote an increase of phenols (G- and S-type phenols) in the pyrolysis oil, while decreasing oxygen-containing compounds, which indicating that low-temperature torrefaction can effectively enhance the stability of bio-oil. The content of phenols in the bio-oil obtained from the reverse chemical looping pyrolysis of pine wood at a torrefaction temperature of 230°C reaches 73.4%, indicating that low-temperature torrefaction is beneficial for producing phenol-rich bio-oils.

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