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# Char formation during pyrolysis of torrefied cellulose: Role of potassium catalysis and torrefaction pretreatment



Jinzheng Chen, Zhimin Lu<sup>\*</sup>, Zhengyan Bao, Jianfeng Cai, Youxing Wei, Shunchun Yao<sup>\*</sup>

School of Electric Power, South China University of Technology, Guangzhou 510640, China

| ARTICLE INFO   | A B S T R A C T   |
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| Keywords:<br>Cellulose<br>Torrefaction<br>Pyrolysis<br>Char formation<br>Potassium catalysis | Torrefaction is an efficient pretreatment technology for large-scale and high-value utilization of biomass fuel. This study aims to enhance the understanding of the thermochemical conversion of torrefied biomass by delineating the role of potassium and torrefaction on primary/secondary charring reactions during pyrolysis of torrefied cellulose. Celluloses with varying potassium loading levels were torrefied at temperatures ranging from 200 to 320 °C and subsequently pyrolyzed at 1000 °C. Two contrasting pyrolysis conditions, i.e., limiting and enhancing transport resistance, were employed to tune the occurrence of secondary reactions, thereby determining the role of torrefaction and potassium on primary and secondary charring reactions. Potassium content, torrefaction severity, and pyrolysis conditions both profoundly affects char formation during pyrolysis of torrefied cellulose, resulting in a wide range of pyrolysis char yields from 1.95 wt% to 64.35 wt%. The structural changes induced by torrefaction, including the depolymerization of the carbohydrate structure and the formation of crosslinking structures, promote the char formation. Potassium enhances the char formation of torrefied cellulose in two ways: i) by catalyzing the transformation of the carbohydrate structure into the crosslinking structures during pyrolysis. Raman spectral analysis of the char carbon structure indicates that increased potassium loading level and torrefaction severity enlarge the aromatic system of the char. The findings highlight the potential of optimizing biomass pyrolysis through controlled torrefaction and potassium, paving the way for more efficient biofuel production and high-quality biochar applications. |

#### 1. Introduction

The escalating energy demand, rising costs of fossil fuels, and emerging environmental issues have driven efforts toward exploring alternative energy sources [1]. Biomass is an important carbon-containing renewable resource that can be converted into solid, liquid, and gaseous biofuels and chemicals for industries, which can be considered an alternative energy source to fossil fuels. However, utilizing biomass as an energy source comes with its challenges, including its structural diversity, high moisture content, hydrophilicity, low bulk, energy density, and tough fibrous structure [1,2]. Pretreatment or upgrading of biomass helps optimize its utilization in subsequent conversion processes. Torrefaction, a mild pyrolysis, can convert biomass into more coal-like fuel and overcome the shortcomings of raw biomass. Torrefied biomass can be a suitable choice in greening energy production facilities sustainably using residual biomass.

Pyrolysis is an important technology for torrefied biomass

utilization, not only for the production of value-added chemicals, but also as a main sub-process in other thermochemical processes such as gasification or combustion [3]. Char, a key pyrolysis product, holds significant importance as it can either be the desired end product or an undesired byproduct depending on the specific goals of the pyrolysis process [4,5]. Moreover, its conversion is crucial, often serving as the rate-limiting step during the combustion or gasification of solid fuel [6]. Understanding the charring process during pyrolysis is instrumental in enhancing these thermochemical conversion pathways, ultimately leading to improved product selectivity and quality.

Char formation is an intricate process consisting of a complex network of reaction occurring that is highly related to the initial structure of feedstocks, the presence of catalytic agents, and the operating parameters. The torrefaction pretreatment was reported to impact the char formation substantially since it alters the initial structure of feedstocks and hence changes the starting point of the charring process in pyrolysis. Most recent studies reported the influence of temperature,

\* Corresponding authors. *E-mail addresses:* zhmlu@scut.edu.cn (Z. Lu), epscyao@scut.edu.cn (S. Yao).

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Received 13 June 2024; Received in revised form 15 July 2024; Accepted 23 July 2024 Available online 24 July 2024 0165-2370/© 2024 Elsevier B.V. All rights are reserved, including those for text and data mining, AI training, and similar technologies. duration, and carrier gas flow rate and its composition, particle size on the structure of torrefied biomass, which further impacts the subsequent pyrolysis [1]. Experimental studies have highlighted changes in structure resulting from torrefaction, such as decreased crystallinity [7], the depolymerization of biopolymers [7–9], and the formation of crosslinking structure [8,10,11], which play a critical role in affecting char formation. Given that biomass is the multifaceted matrix of cellulose, hemicellulose, lignin, and small extractives [12], differences in the distribution of biomass constitutive polymers and the varying torrefaction reactivity of these polymers lead to the structural diversity of torrefied biomass [8,13]. This variability in the physicochemical structure complicates the understanding of the char formation of torrefied biomass, making the effects of structural transformations after torrefaction on char formation during pyrolysis unclear.

The inherent inorganic metals also influence char formation significantly by serving as catalytic agent in reaction pathways. Their presence affects significantly the chemical composition and the physical properties of the pyrolysis products, sometimes compromising their further utilization or upgrading [14]. Amongst various inherent inorganic metals, potassium emerges as not only the most abundant species [15,16] but also an important catalyst in the chemical reactions of biomass pyrolysis [16,17]. According to the literature, potassium induces different degradation pathways wherein heterocyclic ring opening, cracking reaction, and crosslinking are promoted, favoring the formation of more aromatic structure together with low molecular weight species [16,18,19]. The catalytic influence of potassium has been observed across a wide range of thermal degradation temperatures, from mild pyrolysis (such as torrefaction) [18] to high-temperature pyrolysis [20]. The activity of potassium in catalyzing both torrefaction and pyenriches chemical reaction rolvsis pathways during the torrefaction-pyrolysis process of biomass, bringing complexity into the char formation. Potassium is reported to be a catalyst in the pyrolysis of torrefied biomass, influencing the thermal decomposition pathways and enhancing char yield [20,21]. However, the effects of potassium on the pyrolysis char formation in the context of torrefied biomass, which has undergone structural changes due to torrefaction, are not fully understood.

During pyrolysis, biomass initially degrades to form primary solid and volatile products (so-call primary reactions), and secondary reactions convert primary products into char and gas [17]. When mass transport limitation in the carbonaceous matrix is enhanced, the trapped volatiles react further, promoting secondary reactions and increasing the char yield. The feedstock characteristics and operating conditions, such as particle size [22], pyrolysis pressure[23], and pyrolysis heating rate [24], were found to affect the mass transport limitation and thus determine the occurrence of the secondary reactions. Knowing the primary charring reaction and the subsequent secondary charring reaction induced by operating conditions during the pyrolysis of torrefied biomass is vital for tuning char formation through specific operating conditions. However, existing literature needs more clarity on the effect of torrefaction and potassium on the primary charring reaction and the interplay between torrefaction, potassium, and pyrolysis conditions during the secondary charring reaction.

Given that char is a result of convoluted impacts of the initial structure of the biomass (affected by torrefaction), catalytic effects of potassium, and types of reactions (primary/secondary) prevailing during pyrolysis, understanding of the char formation during pyrolysis of torrefied biomass becomes extremely difficult. A systematic approach to understanding the effects of torrefaction and potassium on the individual components of biomass would provide a foundation for better comprehending the more complex system. This study aims to delineate the role of torrefaction and potassium on the char formation during pyrolysis of torrefied cellulose. The physicochemical structure transformation after torrefaction of cellulose was characterized by scanning electron microscopy (SEM) and <sup>13</sup>C cross-polarization magic angle spinning (CP/MAS) solid nuclear magnetic resonance (NMR). To

delineate the impact of torrefaction and potassium on primary and secondary charring reactions during pyrolysis, we modulated the occurrence of secondary reactions by manipulating transport resistance. Thin-film pyrolysis was conducted under vacuum and high heating rate conditions to limit the secondary reaction, whereas increasing sample dimensions, pyrolysis pressure, and reducing heating rates promoted secondary reactions. SEM and Raman spectra characterized the final char samples.

#### 2. Experiments

#### 2.1. Materials

Microcrystalline cellulose Avicel PH-101 purchased from Sigma Aldrich (USA) was used in this study. Potassium nitrate (KNO<sub>3</sub>) of analytical reagent (AR) grade was obtained from Macklin (China). The preparation of KNO<sub>3</sub>-loaded celluloses involved wet impregnation, resulting in different loading levels (0.002 M, 0.005 M, and 0.015 M). For each impregnation treatment, 200 mL potassium nitrate solution at three concentration levels (0.002 M, 0.005 M, and 0.015 M) was impregnated into 10 g of cellulose. The mixture underwent stirring at room temperature for 12 hours. Subsequently, the potassium-impregnated celluloses were collected by filtration and dried at 70 °C for 12 hours.

In order to clearly reference each impregnation run, we adopted a naming convention based on the potassium nitrate concentration followed by the first three letters of the cellulose name. For instance, 0.002 M-Cel refers to the cellulose impregnated with 0.002 M potassium nitrate. Specifically, 0 M-Cel denotes cellulose without impregnated pretreatment.

#### 2.2. Torrefaction pretreatment

The torrefaction experiment was carried out in a three-stage horizontal tubular oven and the detailed schematic of the tube oven has been described elsewhere [25]. Before heating, N<sub>2</sub> gas with a purity of 99.999 % was purged into the oven under a total gas flow rate of 1 L/min for 20 min to ensure the inert atmosphere before heating. About 1 g of cellulose was put into a porcelain boat, inserted into the center of the temperature-preset oven, and held there for 60 minutes. After torrefaction, the solid residues were cooled down in a cooling zone before exposure to an air-conditioned environment with a constant relative humidity (ca. 50 % RH). The gained torrefied cellulose was ground to less than 50  $\mu$ m and then stored in airtight plastic sample bags for further analysis and testing. In the present study, the torrefaction conditions involved three temperatures, viz-200, 260, and 320 °C.

The mass yield  $(Y_m)$ , as an indicator of how biomass resists thermal degradation [10], is defined as Eq. (1):

$$Y_m(\%) = \frac{M_T}{M_R} \times 100\%$$
 (1)

where  $M_R$  and  $M_T$  are the sample weights before and after torrefaction, respectively.

#### 2.3. Preparation of thin-film and thick-plate sample

A method was developed to create thin-film and thick-layer samples in order to adjust sample thickness, following the protocol of Paulsen et al. [26]. A customized quartz plate measuring 50 mm in diameter and 5 mm in height, with a 45 mm diameter and 4 mm depth groove, was used for preparing samples of varying thicknesses. The thin-film samples were created by suspending cellulose in deionized water with a solid concentration of 10 wt%. These samples were formed by transferring 1 mL of the suspension onto the quartz plate and then allowing the water to evaporate at 60 °C, leaving a micrometer-scale film on the bottom of the groove. On the other hand, thick-layer samples were prepared by depositing 1 g of cellulose directly into the groove of the quartz plate and adding 3 mL of deionized water. These samples were then dried at 60  $^{\circ}$ C to create millimeter-scale plates on the bottom of the groove.

#### 2.4. Pyrolysis reactor description

The pyrolysis experiments were conducted in a hot plate reactor. A schematic representation of the hot plate reactor used is shown in Fig. 1. The body of the reactor is made of stainless steel 304. A thermocouple type B (12 cm long) was installed at the front of the reactor to measure the temperature on the surface of the hot plate platform. A pressure sensor (PG800, Tamagawa) was connected to the reactor for pressure measurement. The reactor was coupled to a vacuum pump to reduce pressure to a vacuum. Two copper electrodes were connected to the tungsten sheet, which were used as terminals to transmit power to the tungsten sheet. The power system and control using the YUDIAN controller have two independent circuits. The first supplies power to the reactor, and the second records data and feeds information to the PID temperature control loop.

#### 2.5. Pyrolysis experimental flow

Each investigation was conducted in triplicate to ensure the reliability and reproducibility of the results. To limit the secondary reaction, the procedure involved loading the thin-film sample onto the heating platform and sealing the reactor chamber. Subsequently, the chamber underwent a 5-minute purge with nitrogen (>99.999 % purity) at a rate of 1 L/min to remove any air within the reactor. The nitrogen was evacuated by the vacuum pump until the absolute pressure reached 0.1 mbar. The reactor was then heated from room temperature to the final pyrolysis temperature (1000 °C) at a heating rate of 200 °C/min, with a holding time of 10 min. In the case of promoting-secondary-reaction condition, N<sub>2</sub> was introduced for 5 minutes at a rate of 1 L/min. Subsequently, a vacuum was reapplied until it reached at least 10 mbar, followed by chamber purging with nitrogen, raising the pressure to approximately 1 bar. The prepared sample was heated to 1000  $^{\circ}$ C at a heating rate of 10  $^{\circ}$ C/min and maintained at this temperature for 10 min for each run of ordinary pressure pyrolysis. Post-experiment, the char yield was obtained from the final weight of the char product. Fig. 2 summarizes the experimental flow diagram for the entire experimental setup.

The yield of pyrolysis char was calculated using the following equation:

$$Y_C(\%) = \frac{M_{char}}{M_{sample}} \times 100\%$$
<sup>(2)</sup>

where  $Y_c$  is the char yield;  $M_{char}$  is the weight of the char, and  $M_{sample}$  is the weight of the pyrolysis sample.

Particularly, accumulated char yield, evaluating char yield in the whole thermal conversion process, was also considered, and calculated using the following equation:

$$Y_{AC}(\%) = Y_c \times Y_m \times 100 \tag{3}$$

Where  $Y_{AC}$  is the accumulated char yield;  $Y_c$  is the pyrolysis char yield;  $Y_m$  is the torrefaction mass yield.

#### 2.6. Characterization of torrefied cellulose by <sup>13</sup>C NMR and SEM-EDX

#### 2.6.1. Solid-state CP/MAS <sup>13</sup>C NMR spectroscopy

Solid-state NMR experiments were performed on a JEOL ECZ-400R/ M1 400 MHz spectrometer with a 3.2 mm HXY MAS probe (JEOL RESONANCE Inc., Japan). The operating 13 C Larmor frequency is



Fig. 1. Schematics of the hot-plate reactor.



Fig. 2. A flowchart of the types of experiments including the impregnation, torrefaction, and the pyrolysis.

100.53 MHz. The magic-angle spinning (MAS) frequency was automatically controlled at 15 kHz for all experiments. The  $^{13}$ C cross polarization (CP) experiments were performed using a contact time of 1.1 ms with a recycle delay of 3 s. A major difficulty in interpreting cellulose NMR spectra arises from signal overlapping. To circumvent this problem, decomposition of the spectra was required. It was performed with DIMFIT software developed by Massiot et al. [27].

Interpretation of the NMR spectra was performed on the basis that each functional group or assignment corresponds to a different chemical shift. Peaks were assigned according to previous studies in the literature [28–30]. Hence, several zones of interest (presented in Table S1) were used to follow the evolution of functional groups in the solid phase during torrefaction. The deconvolutions (displayed in Fig. S1) were processed with Gaussian and Lorentzian lines.

#### 2.6.2. Scanning electron microscopy

Scanning electron microscopy, together with an energy dispersive Xray analyzer (SEM-EDX, Merlin, Zeiss) was used to investigate the surface morphology of torrefied samples. All samples were prepared by coating with 3 nm of platinum to ensure electrical conductivity using a Cressiongton HiRes Sputter Coater. The images were collected under a vacuum with a chamber pressure below 10 mPa. The accelerating voltage was set at 5 kV for all samples. The samples were then analyzed using EDX analysis to analyze for potassium concentration. Because potassium was not evenly distributed in the sample, it can cause problems with inaccurate testing. For accurate semi-quantitative evaluation of potassium content, the EDX analysis was conducted at a low degree of magnification so that more tested samples could be involved in the EDX analysis. The elements C, O, and K were selected to characterize, and the relative weight fraction of K was calculated.

#### 2.7. Characterization of pyrolyzed char by SEM and Raman spectroscopy

Both physical and chemical features of char were investigated. The SEM characterization method is described above. The carbon structure transformation of the char samples was characterized by Raman spectroscopy (LabRAM Aramis) at 532 nm laser excitation. Analytical methods for characterizing chars structure by Raman spectroscopy are typically based on D and G bands. However, more than analysis of the D and G bands is required to capture the full complexity of carbon structure. Deconvolution of spectra from char often utilizes several additional peaks to improve the fit of shoulders not typically represented in spectra from graphitic materials. In this study, the first-order Raman spectra between 800 and 1800 cm<sup>-1</sup> were curve-fitted with 10 Gaussian bands according to the method proposed by Smith et al. [31]. The descriptions of each band are summarized in Table S2 (supplementary material). The Raman spectra obtained were deconvoluted with the software Peakfit 4.0.

#### 3. Result and discussion

#### 3.1. Characterization of torrefied cellulose

#### 3.1.1. Mass yield

Fig. 3 illustrates the mass yields  $(Y_m)$  of torrefied cellulose with different K-loading levels. The  $Y_m$  of cellulose with different K-loading levels decreases with increasing torrefaction temperature, indicating significant mass loss due to thermal degradation at higher temperatures. The presence of potassium exerts varying influences on the thermal degradation of cellulose across different torrefaction temperatures. Under light torrefaction conditions, such as at 200 °C, cellulose exhibits excellent thermal stability, with mass yields stabilizing between 95.23 % and 96.30 % across different K-loading levels, suggesting no significant catalytic effect from potassium. A slight effect of potassium is observed at 260 °C torrefaction, where  $Y_m$  levels off at around 81.29 % before decreasing to 78.42 % for 0.005 M-Cel and then mildly decreases to 77.40 % for cellulose with a higher K-loading level. This indicates a threshold potassium content beyond which catalysis of cellulose decomposition occurs during 260 °C torrefaction. Leng et al. [32] suggested that potassium salts weaken hydrogen bonds and the stability of hydroxyls and glycosidic bonds, accelerating glycosidic bond cleavage when cellulose is pyrolyzed at temperatures close to 260 °C. Potassium's catalytic activity becomes more pronounced at higher torrefaction temperatures. At a torrefaction temperature of 320 °C, the  $Y_m$  exhibits a V-shaped trend with increasing K-loading levels: the  $Y_m$  first falls to the bottom of 22.51 % for 0.002 M-Cel from 28.22 % for 0 M-Cel, then increases to 26.10 % at higher K-loading levels. This trend is similar to that observed by Safar et al. [15] in their torrefaction experiments with nature biomass containing varying K content, suggesting that the V-shaped



Fig. 3. Mass yields of the cellulose with different K-loading concentrations torrefied at different temperatures.

variation in mass yield with increasing K-loading levels in natural biomass is partially attributable to cellulose. The lower mass yield in K-impregnated samples for cellulose compared to unimpregnated ones can be attributed to the enhanced decomposition induced by potassium [18]. Additionally, the increase in mass yield for higher K-loading level cellulose results from the crosslinking promoted by potassium [16]. This indicates that two main competitive pathways, i.e., decomposition and crosslinking, existed in 320 °C torrefaction of cellulose, both of which can be catalyzed by potassium. Potassium mainly accelerates cellulose degradation at low loading levels, leading to lower mass yields. With increasing K-loading content, the pathway to form carbonaceous matrix is promoted.

#### 3.1.2. Morphology transformation after torrefaction

SEM analysis was employed to investigate the morphology of 0 M-Cel, 0.002 M-Cel, 0.005 M-Cel, and 0.015 M-Cel torrefied at different temperatures, as depicted in Fig. S2 of the Supplementary Material. At the same torrefaction temperature, no significant differences were observed in cellulose structures with different K-loading levels. For celluloses torrefied below 320 °C, their structures remained relatively unchanged compared to raw cellulose, as evidenced by SEM images at 200 °C and 260 °C, suggesting maintained rigidity of internal fibrils during low-temperature torrefaction. However, at 320 °C, cellulose with varying K-loading levels underwent significant morphological transformations during torrefaction, becoming more porous due to volatile release. Fig. 4 presents the semi-quantitative analysis of the weight fraction of potassium on the sample surfaces. Raw cellulose with varying K-loading levels follows an expected ratio of 1:2:6, corresponding to the impregnated KNO<sub>3</sub> concentrations. As torrefaction severity increases, the K fraction also increases continuously. This is due to the devolatilization during torrefaction and the subsequent relative potassium enrichment in the remaining solid matrix.

#### 3.1.3. Chemical structure transformation after torrefaction

 $^{13}$ C NMR was employed to track the transformation of C functional groups in cellulose with varying K-doping levels after torrefaction. Fig. 5 presents the evolution of different C functional groups as a function of torrefaction severity. Below 320 °C torrefaction, the chemical structure of torrefied cellulose is dominated by carbohydrate structures, even in samples with added potassium. The introduction of potassium catalyzes the transformation of carbohydrate structures, starting at 260 °C torrefaction. Aliphatic, carbonyl and aromatic structures begin to appear successively in 260 °C torrefaction of 0.002 M-Cel, 0.005 M-Cel, and



0.015 M-Cel compared to the total carbohydrate structure of 0 M-Cel. These structures are significant reaction factors interconnected by ring opening and dehydration processes [30]. Regarding 0.015 M-Cel, the decrease in aliphatic and carbonyl groups alongside the formation of aromatic groups indicates that higher potassium content catalyzes both the decomposition and polycondensation, leading to the formation of aromatic structure by consuming aliphatic and carbonyl structures [28].

Intensive structural rearrangement reactions occur at higher torrefaction temperature (320 °C), transforming carbohydrate structures into other C functional groups. Aromatic structures dominate the chemical structure of cellulose torrefied at 320 °C, along with aliphatic, furanyl, carbonyl, and alkyl-O groups, indicating severe decomposition, dehydration, and crosslinking reactions during torrefaction [30]. Adding potassium alters the chemical structure to a degree, primarily increasing the relative content of aromatic groups while decreasing aliphatic, furanyl, and carbonyl groups compared to 0 M-Cel. This observation may explain the lower mass yield of the K-loading cellulose presented in Fig. 3, as the presence of potassium promotes the decomposition of non-aromatic functional groups, generating more volatile products. Notably, the content of the alkyl-O group as a function of K-loading level exhibits a similar trend to the mass yield presented in Fig. 3, with values showing a noticeable rebound after an initial drop at 0.002 M-Cel. This highlights an important influence of the K-loading level on the catalytic effect. The low K-loading level, corresponding to 0.002 M-Cel, has a strong tendency to catalyze decomposition, as evidenced by the lowest mass yield and the reduction of alkyl-O content. Increasing content enhances the catalytic activity of potassium, thereby enabling more reaction pathways, such as forming a carbonaceous matrix, to be catalyzed by potassium [15].

To distinguish further differences in the carbohydrate structure, Fig. 5 simultaneously provides an additional interpretation of carbohydrate structures of cellulose torrefied at different temperatures, with signals assigned to C-1, C-4, C-2,3,5, and C-6. The evolution of the proportion of C-1 and C-4 shows a similar trend among cellulose with different K-doping levels, which remain stable when torrefaction temperature increases to 200 °C and slightly decreases with increasing torrefaction temperature to 260 °C. Conversely, the peak assigned to C-2,3,5 shows a gradual increase with torrefaction temperature progression, possibly associated with inter-chain cleavage within cellulose leading to depolymerization and formation of anhydrosugars with varying degrees of polymerization [13,23,29]. C-6 seems to be almost stable during 200 °C and 260 °C torrefaction without adding potassium. The presence of potassium catalyzes C-6 cleavage, with the catalytic effect intensifying with increasing potassium content.

#### 3.2. Characterization of pyrolyzed char

#### 3.2.1. Pyrolysis char yield

Fig. 6 illustrates the pyrolysis char yields  $(Y_C)$  in relation to progressive torrefaction temperatures and K-loading level. Notably, Fig. 6a presents the Y<sub>C</sub> obtained under a secondary reaction-constraining condition, while Fig. 6b depicts the Y<sub>C</sub> under a secondary reactionenhancing condition. In Fig. 6a, the  $Y_C$  of raw cellulose with varying K-loading levels follows an expected order, increasing with potassium content: 0.015 M-Cel (10.80 %) > 0.005 M-Cel (7.84 %) > 0.002 M-Cel (7.01 %) > 0 M-Cel (1.95 %). This finding is consistent with previous studies on cellulose char formation [32,33], indicating potassium's catalytic effect on char formation. Under secondary reaction-limited conditions, potassium catalyzes primary reactions, accelerating the char formation path. The impact of torrefaction at 200 °C appears negligible on subsequent torrefied cellulose pyrolysis char formation, with similar char yields and order compared to raw celluloses. Based on the characterization in Section 3.1, the physicochemical structure of cellulose with different K-loading levels remains almost intact until 260 °C

At 260 °C torrefaction, the char yield maintains the same order,



Fig. 5. Functional groups transformation for cellulose with different torrefaction severity: (a) 0 M-Cel; (b) 0.002 M-Cel; (c) 0.005 M-Cel; (d) 0.015 M-Cel.



Fig. 6. Pyrolysis char yield of cellulose with different K-loading concentration torrefied at different temperatures: (a) pyrolysis under condition of limiting secondary reactions; (b) pyrolysis under condition of promoting secondary reactions.

indicating the catalytic effect of potassium on the char formation during pyrolysis. Potassium is highly active in the primary charring reaction of both raw, 200°C-torrefied, and 260 °C-torrefied cellulose. Since the main structure of these samples is carbohydrate-based, it is inferred that potassium significantly promotes the transformation of carbohydrate structure into highly condensed aromatic structure, leading to an increase in char yield. Furthermore, the  $Y_C$  from celluloses torrefied at 260 °C is higher than that at 200 °C. This indicated that the change in chemical structure during the 260 °C torrefaction alter the reaction pathway and promote the char formation. In the absence of potassium, 0 M-Cel only undergoes depolymerization during the 260 °C torrefaction, preserving its carbohydrate structure (as illustrated in Fig. 5a). It is speculated that the depolymerization of the carbohydrate structure during torrefaction favors the char formation in the subsequent pyrolvsis. Additionally, the presence of potassium disrupts the carbohydrate structure, resulting in the formation of carbonyl and aromatic structures (as shown in Fig. 5c&d). This promotes cross-polymerization and char formation [34].

Rising torrefaction temperature to 320 °C drastically increases pyrolysis char yield to over 50 %, as celluloses transform completely from carbohydrate to crosslinking structure composed of aromatic, aliphatic, and furanyl. This crosslinking structure performs well with thermal stability during pyrolysis and tends to form char [8,35]. The lowest pyrolysis char yield of 54.49 % is observed in 0 M-Cel, with added potassium lifting char yield, albeit with fluctuations with increasing K-loading level. This suggests that potassium also can catalyze the char formation of the crosslinking structure, increasing pyrolysis char yield. Additionally, the comparable pyrolysis char yield of the K-loading celluloses indicates that the differences in chemical structure caused by K-loading level have a subtle influence on the char formation.

Fig. 6b illustrates the pyrolysis char yields of thick-plate cellulose samples in relation to progressive torrefaction temperatures and Kloading level. Under the condition of enhancing secondary reaction, the pyrolysis char yield as a function of torrefaction temperature and K- loading level shows the same trend as that collected under the condition of limiting secondary reaction. The difference between these two pyrolysis conditions can be observed in higher pyrolysis char yield gained under the condition of enhancing secondary reaction. Strengthening diffusion resistance promotes heterogeneous reactions between carbonaceous matrix and volatiles, generating more char [36]. This indicates that increased potassium loading levels, increased torrefaction severity, and enhanced secondary reactions all lead to increased char yield.

#### 3.2.2. Char morphology

SEM images were captured for all char samples to compare char morphology after pyrolysis, as depicted in Figs. S3–6 of the Supplementary Material. It can be observed that the raw and 200°C torrefied 0 M-Cel form strings of char. This observation is consistent with the SEM results of cellulose char presented by Montoya et al. [37], who indicated that this is evidence of a liquid intermediate in which crosslinking reactions compete with depolymerization while the liquid intermediate boils. The addition of potassium and the pretreatment with torrefaction shift the interwoven constructure toward char lump, indicating that crosslinking becomes the predominant reaction within liquid intermediate and finally solidifies to form lump char. The fibrous structure remained unchanged despite variations in K-loading level, torrefaction severity, and pyrolysis conditions. However, there were observations of smoothed individual fibers and the initiation of agglomeration. This phenomenon can be attributed to external surface melting while the crystalline structure of internal fibrils maintains rigidity during pyrolysis, leading to crosslinking and polycondensation that form a stable structure before a true melt phase develops in the fiber core[38].

#### 3.2.3. Char carbon structure

Raman spectroscopy was employed to clarify the carbon structure of char samples, utilizing the 10-band deconvolution method developed by Smith et al. [31]. An example of the deconvolution of Raman spectroscopy is presented in Fig. S7 (supplementary material). D band and Ds band are concerned to track the evolution of aromatic cluster size, which the D band assigns to larger aromatic ring systems and the Ds band stands for smaller aromatic ring systems [31,38]. The D band region (including S, D<sub>S</sub>, D, and A<sub>1</sub> bands) and G band region (including A<sub>2</sub>, G<sub>L</sub>, and G<sub>G</sub>) are concerned to track the evolution of crystalline or graphite-like carbon structures[39–41]. For clarity, the D and G bands regions are denoted as D\* and G\*, respectively. The area ratios of  $I_D/I_{Ds}$  for the relative amount of small and large aromatic rings and  $I_{D^*}/I_{G^*}$  for the graphite-like carbon structures are calculated to investigate the evolution of carbon microstructures, shown in Fig. 7.

As can be seen from Fig. 7, the  $I_{D^*}/I_{G^*}$  of char samples fluctuates within a narrow range from 1.17 to 1.60, with an average of 1.35 and 1.44 for the char derived from two contrasting pyrolysis conditions respectively. This indicates that variations in K-loading level, sample dimension, torrefaction severity, and pyrolysis condition (including heating rate and pressure) have an insignificant impact on the graphite-



Fig. 7. Carbon structure parameters of char samples from Raman analysis: (a) char derived from thin film; (b) char derived from thick plate.

like carbon structure. High pyrolysis temperature may be causative of the narrow range of  $I_{D^*}/I_{G^*}$  of the char samples, for which the char produced from high-temperature pyrolysis is highly aromatic [40], rendering I<sub>D\*</sub>/I<sub>G\*</sub> unable to reflect differences in carbon structure due to the mentioned factors. Conversely, the value of the I<sub>D</sub>/I<sub>Ds</sub> values span a broader range, from a minimum of 1.20 to a maximum of 3.53. When the torrefaction temperature is below 320 °C, the I<sub>D</sub>/I<sub>Ds</sub> consistently increase with the K-loading level, indicating that potassium enhances aromatic nuclei polycondensation and promotes aromatic cluster growth [15,42]. At 320  $^\circ\text{C}$  torrefaction, the  $I_D/I_{Ds}$  first fall to the bottom for 0.002 M-Cel from the peak for 0 M-Cel, then increasing gradually with a progressively higher K-loading level. The reduction in  $I_D/I_{Ds}$  in K-loading celluloses may be due to the catalytic role of potassium in crosslinking reactions, which promotes the exposure of small aromatic regions, either isolated or weakly supported benzene rings. Furthermore, increasing the K-loading level accelerates further reactions of the crosslinking structure, leading to condensation and the formation of larger aromatic clusters.

#### 3.2.4. Further discussion on char formation during pyrolysis

Char formation during the pyrolysis of lignocellulosic biomass is significantly influenced by torrefaction pretreatment and potassium catalysis. The impact of torrefaction on char formation during pyrolysis stems from its alteration of the chemical structure of cellulose, which changes the starting point of the charring process. For cellulose without impregnation (0 M-Cel), the chemical structure exhibits varying degrees of transformation when torrefied at different temperatures: the original carbohydrate structure is maintained at 200 °C, depolymerized at 260 °C, and completely transformed into a crosslinking structure at 320 °C. The preservation of the original carbohydrate structure in the 200 °Ctorrefied cellulose leads to pyrolysis behavior similar to that of raw cellulose, resulting in comparable char yield and quality under similar pyrolysis conditions. The depolymerization of the carbohydrate structure after torrefaction at 260 °C reduces the chain length of the carbohydrate structure and results in a higher pyrolysis char yield under limiting secondary reaction conditions. This suggests that reducing the chain length of the carbohydrate structure favors char formation during primary reactions. Recent studies by Mettler et al. [43] and Patwardhan et al. [44] found that cellulose produces much less char than glucose and cellodextrins, indicating that short-chain carbohydrates generate higher char yields. Mettler et al. [43] linked the higher char yield of short-chain carbohydrates to the higher yield of HMF, which has been shown to repolymerize in the intermediate liquid phase to form char precursor. This can also explain the higher pyrolysis char yield under conditions promoting secondary reactions, where the low transport rate enhances the secondary reaction of HMF within the intermediate liquid phase, producing more char [23]. For torrefied cellulose produced at 320 °C, the carbohydrate structure completely transforms into a crosslinking structure along with the release of volatiles. The crosslinking structure is crucial for char production due to its thermal stability and reactive crosslinking sites [35]. Notably, the comparable pyrolysis char yield is observed between conditions limiting and promoting secondary reactions. Generally, lower pyrolysis char yield under conditions limiting secondary reactions is attributed to decreased transport limitation of condensable volatiles, which, through increased heating rate and reduced pressure and sample dimension, enhance the mass transfer of these compounds and limit secondary charring reactions. The comparable pyrolysis char yield between these conditions suggests that non-condensable gases may be the main volatile products rather than condensable compounds.

Potassium also profoundly affects char formation during pyrolysis. In the context of torrefied cellulose pyrolysis, potassium can influence char formation in two ways: i) by catalyzing the pyrolysis of torrefied biomass and ii) by altering the structure of torrefied biomass. The catalytic effect of potassium on pyrolysis is evident in the yield and physicochemical structure of the char derived from non-torrefied cellulose.

Potassium inhibits transglycosylation reactions and accelerates ring opening, fragmentation, dehydration, and crosslinking, possibly through complexation with cellulose hydroxyl and ether groups, stabilizing a particular conformation of the glycosidic bond and promoting ring opening and glycosidic linkage cracking [16,45]. These crosslinking and dehydration reactions, promoted by potassium, lead to higher pyrolysis char yield. Cellulose exhibits thermal stability during 200 °C torrefaction, where thermal degradation and potassium's catalytic effect are inactive. Although potassium favors side chain cleavage, the main carbohydrate structure remains intact. The similar carbohydrate structure between 200 °C-torrefied cellulose and non-torrefied cellulose indicates that potassium's promotion of char formation in 200 °C-torrefied cellulose occurs during the pyrolysis stage. The catalytic effect of potassium starts to manifest at a torrefaction temperature of 260 °C, leading to the partial transformation of carbohydrates and the formation of a crosslinking structure, which becomes more pronounced with increasing K-loading levels. Simultaneously, the pyrolysis char yield of 260 °C-torrefied cellulose increases with higher K-loading levels. Given that crosslinking structures have a high tendency to form char [8,38], the increasing pyrolysis char yield of 260 °C-torrefied cellulose can be attributed to both the enhanced effect of potassium on the char formation of carbohydrates and the crosslinking structures within 260 °C-torrefied cellulose. Admittedly, the results presented in this work cannot separate the respective contributions of these two factors to promoting char formation in 260 °C-torrefied cellulose due to their coupling. Potassium also alters the chemical structure of 320 °C-torrefied cellulose, leading to different distributions of C functional groups within crosslinking structures at different K-loading levels. The change in crosslinking structure appears to have a subtle influence on char formation, as indicated by the similar pyrolysis char yield among K-loaded celluloses. While the change in crosslinking structure caused by potassium has a minimal impact on char formation, adding potassium still promotes the char formation of 320 °C-torrefied cellulose during pyrolysis. This suggests that potassium favors the formation of more char from the crosslinking structure.

Generally, char yield results from the combined contributions of primary and secondary reactions [14]. It has been observed that potassium increases the pyrolysis char yield under conditions where secondary reactions are minimized, demonstrating the effectiveness of potassium's catalytic activity on primary charring reactions. A similar result was reported by Marathe et al. [46], who highlighted that potassium-catalyzed reactions are extremely fast (occurring within milliseconds), making the rapid removal of volatiles insufficient to attenuate potassium's catalytic effect efficiently. Given that the pyrolysis char yield under promoting secondary reaction conditions is the sum of the char yields from both primary and secondary reactions, enhancing primary charring reactions also increases the pyrolysis char yield under these conditions. Another possible reason for the increased pyrolysis char yield under promoting secondary reaction conditions is potassium's catalytic activity in secondary charring reactions. Leng et al. [47] reported a mild catalytic effect of potassium in promoting the formation of secondary char from anhydrosugars.

## 3.3. Estimation of char formation during whole torrefaction-pyrolysis process of cellulose

The pyrolysis of torrefied cellulose can be recognized as a two-stages pyrolysis. Evaluating char formation throughout the entire torrefaction-pyrolysis process is important, as it can provide insight into optimizing both torrefaction and pyrolysis procedures. Accumulated char yield  $(Y_{AC})$ , based on the mass of the raw cellulose, is introduced to assess char formation across the entire thermal conversion process of cellulose with varying K-loading levels, as depicted in Fig. 8. Increasing K-loading level, lifting torrefaction temperature, and enhancing transfer limitation both lead to higher  $Y_{AC}$ . The promoted effect of torrefaction and potassium on  $Y_{AC}$  may attribute to enhancement of the dehydration and



Fig. 8. Accumulated char yield of cellulose with different K-loading concentration torrefied at different temperatures: (a) pyrolysis under condition of limiting secondary reactions; (b) pyrolysis under condition of promoting secondary reactions.

crosslinking. The presence of potassium inhibits the transglycosylation reactions that form oligosaccharide and catalyzes the dehydration and crosslinking [14]. The catalytic effect of potassium is active at low-temperature pyrolysis of cellulose [16]. Different from the catalytic effect of potassium, the torrefaction enhances the dehydration and crosslinking by prolonging the low-temperature pyrolysis period of cellulose, in which the dehydration and crosslinking are favor. In the pyrolysis of cellulose, the dehydration and crosslinking occurred in low-temperature pyrolysis stage lead to the formation of the benzene rings, which can further grow to form char [23,48]. Surprisingly, the result presented in Fig. 8 gives an upper limit of  $Y_{AC}$ , which is about 16 %. The increase in K-loading level and transport resistance can not further lift the accumulated char yield.

Accumulated char yield, reflecting the char formation during whole thermal conversion, was correlated to the char carbon structure parameter ( $I_D/I_{Ds}$ ), characterized by Raman spectra. It can be observed in Fig. 9 that the band area ratio increases with the increasing accumulated char yield. A well linear relationship is built between accumulated char yield and  $I_D/I_{Ds}$ , with a coefficient parameter ( $R^2$ ) of 0.95. This suggests that the char formation is promoted through enlarging the aromatic system.

Since cellulose is the most abundant component within biomass,



Fig. 9. Raman band area ratio  $I_D/I_{Ds}$  as a function of accumulated char yield based on the char data in this study. Linear fitting line based on char data in this study is shown in red and 95 % confidence bands are presented as shadow in the same color. Char data from previous study [8] is shown in hollow circle (pyrolysis temperature: 1028 °C, heating rate: 65 °C /s, pressure: ~1 bar).

tuning the char formation of torrefied cellulose plays a crucial role in tuning the char formation of torrefied biomass. From the perspective of producing liquid products [1,2], limiting the torrefaction temperature below 320 °C is essential, as substantial volatile loss occurs when the temperature reaches 320 °C. When the torrefaction temperature is kept below 320 °C, reducing potassium content can efficiently decrease the accumulated char yield. Since potassium, as an inherent metal, cannot be removed entirely by demineralization and still has a significant catalytic role even at low content, introducing an inhibitor may be a potential method to attenuate potassium's catalytic effect. Some inorganic species, such as Ca(OH)<sub>2</sub>, have been found to react with inherent inorganic elements in biomass, altering their properties and rendering them inactive<sup>[49]</sup>. Mishra et al. <sup>[50]</sup> reported the inhibitory effect of CaO on char yield. From the perspective of valorizing char potential for diverse applications [51-54], increasing the char yield is important for the large-scale utilization of biochar. When the torrefaction temperature is below 320 °C, increasing potassium content and transport resistance can efficiently increase the accumulated char yield. However, at a torrefaction temperature of 320 °C, it does not seem that the accumulated char yield can be further improved by increasing potassium loading levels and transport resistance. Adding other metals may be a potential method to increase accumulated char yield further. Babu et al. [55] reported that biomass ash can create a synergistic environment for pyrolytic products by acting as a catalyst. Considering that potassium catalysis is more active in primary charring reactions, adding catalysts (such as magnesium [56]) to promote secondary charring reactions can further improve accumulated char yield.

#### 4. Conclusion

Based on the present work, some important conclusions can be drawn:

- (1) The initial structure of cellulose is altered by torrefaction, evidenced by the depolymerization of carbohydrate structure at 260 °C and the transformation of carbohydrate structure along with the formation of crosslinking structure at 320 °C. Potassium enhances the change in initial structure of cellulose during torrefaction by accelerating various reaction pathways. K-loading level impacts catalytic activity of potassium in various reaction pathways during severe torrefaction (320 °C), leading to a U-shaped variation in mass yield with increasing K-loading levels.
- (2) The effect of torrefaction and potassium was found to be active in primary charring reactions during pyrolysis, significantly promoting char formation. This is due to the promoted effect of potassium on the char formation of carbohydrate structure and the high tendency of crosslinking structure to form char.

Additionally, the increase in K-loading level and torrefaction severity and enhancement of secondary reaction have a combined promoted influence on char formation and lead to higher pyrolysis char yield.

- (3) Regarding the whole torrefaction-pyrolysis process, K content dominates the char formation of cellulose when the torrefaction temperature is below 320 °C. Torrefaction severity becomes predominant in char formation in the case of 320 °C torrefaction, for the structural transformation caused by torrefaction is more significant in the promotion of char formation than K content.
- (4) Raman spectral parameter ( $I_D/I_{Ds}$ ), reflecting the ratio of the amounts of small and large aromatic ring systems, can describe the change in the carbon structure of pyrolyzed char, and the result indicates that the enhancement in K-loading level and torrefaction severity enlarges aromatic system of char. A linear correlation was built between  $I_D/I_{Ds}$  and the accumulated char yield, with the determination coefficient  $R^2$  of 0.95.
- (5) Future research could investigate the catalytic role of biomass ash on char formation during the pyrolysis of torrefied biomass/ constitutive polymers. Examining the interactions between different inorganic elements in the thermochemical conversion process can provide insights that more closely resemble the conditions of real biomass.

#### CRediT authorship contribution statement

Zhengyan Bao: Writing – review & editing. Jianfeng Cai: Writing – review & editing. Youxing Wei: Writing – review & editing. Shunchun Yao: Resources, Project administration, Funding acquisition. Jinzheng Chen: Writing – original draft, Methodology, Investigation, Data curation. Zhimin Lu: Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

#### **Declaration of Competing Interest**

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Zhimin Lu reports financial support was provided by National Natural Science Foundation of China. Zhimin Lu reports financial support was provided by Ministry of Education of the People's Republic of China. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

#### Data availability

Data will be made available on request.

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#### Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jaap.2024.106644.

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