Research paper

Characterization of free radicals by electron spin resonance spectroscopy in biochars from pyrolysis at high heating rates and at high temperatures

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ABSTRACT

The concentration and type of free radicals from the decay (termination stage) of pyrolysis at slow and fast heating rates and at high temperatures (above 1000°C) in biomass char have been studied. A room-temperature electron spin resonance spectroscopy study was conducted on original wood, herbaceous biomass, holocelluloses, lignin and their chars, prepared at high temperatures in a wire mesh reactor, an entrained flow reactor, and a tubular reactor. The radical concentrations in the chars from the decay stage range up between $7 \cdot 10^{16}$ and $1.5 \cdot 10^{18}$ spins g^{-1} . The results indicated that the biomass major constituents (cellulose, hemicellulose, lignin) had a minor effect on remaining radical concentrations compared to potassium and silica contents. The higher radical concentrations in the wheat straw chars from the decay stage of pyrolysis in the entrained flow reactor compared to the wood chars were related to the decreased mobility of potassium in the char matrix, leading to the less efficient catalytic effects of potassium on the bond-breaking and radical re-attachments. The high Si levels in the rice husk caused an increase in the char radical concentration compared to the wheat straw because the free radicals were trapped in a char consisting of a molten amorphous silica at heating rates of 10^3 – 10^4 K s^{-1} . The experimental electron spin resonance spectroscopy spectra were analyzed by fitting to simulated data in order to identify radical types, based on g-values and line widths. The results show that at high temperatures, mostly aliphatic radicals ($g = 2.0026$ – 2.0028) and PAH radicals ($g = 2.0027$ – 2.0031) were formed.

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1. Introduction

Understanding pyrolysis of biomass-derived materials is an important step in optimization of biochar production. The application of biomass as a substitute for coal as a reducing agent in metallurgical processes can decrease the direct CO₂ emissions [1]. The present technology allows conversion of biomass to biochar, but due to limited knowledge about biochar properties and high costs, the application of biochars is limited [2]. The yield and properties of the biochar, including size, morphology, composition,

and reactivity depend strongly on the pyrolysis conditions. Knowledge of the char structure at the molecular level including the presence of free radicals and oxygen heteroatoms is essential for the understanding and prediction of biochar valuable properties in metallurgical applications. The highly reactive biochars are required in a blast furnace, whereas in iron sintering processes, the low reactive biochars are desired [3]. High heat treatment temperature and mineral matter produce free radicals [4,5], which are accumulated at the biochar surface and consequently the reactivity of the sample is increased [6,7]. The mechanical strength of biochars affects significantly the application in metallurgical processes [3]. Higher free radical concentrations favor chemical activity and cross-linking reactions, which enhance the physical and mechanical strength of composites [8,9]. Little is known about the influence of feedstock type on the biochar production and pyrolysis by-products.

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Electron spin resonance spectroscopy (ESR) has been used in many investigations since the discovery of free radicals in coal by Uebersfeld et al. [10]. The electron spin resonance spectroscopy has been used to describe the concentration and chemical structure of free radicals in different coals as reported in the previous studies [10–13]. The majority of investigations on free radical reactions of biomass focused on char generated at slow heating conditions ($1\text{--}50\text{ K min}^{-1}$) and long holding times [14–20].

Bourke et al. [7] investigated high temperature pyrolysis ($750\text{--}1000^\circ\text{C}$) under slow heating of corncob and sucrose, and detected the presence of carbon-centered radicals as a narrow electron spin resonance signal. Moreover, they observed a mixture of narrow and broad ESR signals, arising from two different types of radicals which were a disorganized carbon with unpaired electrons (narrow signal) and an organized carbon with a conductive electron (broad signal). Schurr et al. [18] showed that in a pyrolyzed biomass the g-factor of the ESR signals was related to the remaining oxygen in the char, and when the heat treatment temperature increased, the g-factor decreased and approached the free electron g-factor with a value of 2.0023. As the g-factors were close to the g-factor of a free electron, the EPR signal in the char was mainly derived from unpaired electrons associated with aromatic delocalized π system [19]. Similar to coal pyrolysis [12,13,20–23], increasing heat treatment temperature decreased the O/C and H/C ratios in the biomass, leading to a reduction of the oxygen-centered radicals relative to the original biomass ($g = 2.0040\text{--}2.0060$), and formation of the carbon-centered radicals in the char ($g = 2.0025\text{--}2.0040$). Moreover, they observed that more stable carbon-centered radicals than the $\sigma\text{-CH}_2\text{-carbon-centered}$ type were formed. The relevant g-factors for biomass pyrolysis are summarized in Table 1.

The formation of free radicals is initiated by primary pyrolysis reactions, where the organic compounds are cracked to small unstable radical fragments [23]. These radicals react with more stable low-molecular weight PAH such as naphthalene and may grow into larger high-molecular PAHs structures, containing delocalized unpaired carbon-centered π -electrons with an additional presence of aliphatic radicals. Due to the homolytic cleavage of β -aryl-ether bonds of lignin, highly reactive and unstable free radicals are initially obtained that may react through rearrangement, electron abstraction or interactions between radicals, to form stable products as described in the literature [24–26].

During pyrolysis free radicals may detach from the fuel macromolecules, and leave the particle as volatile matter if they have a sufficiently high vapor pressure [27,28]. However, most of them, being reactive, seek stabilization by reacting with reactive species near them [27]. The stabilization of free radicals (cracking,

condensing) results in the formation of char and tar from the larger fragments, manifested by the char fluidity decrease [29]. The char may release more volatile matter during reaction stages where radicals are present in high concentrations [27]. More free radicals were proposed to be present in the char matrix. However, many of the radicals generated during pyrolysis were hypothesized to be ESR silent [30] or to disappear from the char matrix after pyrolysis [31–34]. Kihedu et al. [35] reported that free radicals produced during bond breaking in fuels with a high hydrogen level, may prevent repolymerization/cross-linking reactions by the hydrogen donor-acceptor mechanism and therefore decrease the char yield.

The effect of free radicals from the decay stage of pyrolysis (termination stage) at fast heating conditions and at high temperatures (above 1000°C) on the biomass char yield has not been discussed previously. The objective of the present work was to characterize experimentally the remaining free radicals after pyrolysis. The knowledge about remaining free radicals will help to understand the role of free radicals trapped in the solid matrix on the biomass cross-linking/depolymerization. A primary emphasis of the present study was placed on the influence of heating rate and biomass composition effect on the free radical yield and type in the solid char matrix, generated from wood and herbaceous lignocellulosic materials.

2. Material and methods

2.1. Char preparation

The char samples were obtained in separate pyrolysis experiments performed at a slow heating rate (10 K min^{-1}) in the tubular reactor, and at an intermediate heating rate (1000 K s^{-1}) in the wire mesh reactor and at a fast heating rate ($10^3\text{--}10^4\text{ K s}^{-1}$) in the entrained flow reactor.

Wire-mesh reactor. The wire mesh reactor at TU Munich, previously described by Tremel et al. [36], can be operated up to a temperature of 1400°C , has a maximal heating rate of 3000 K s^{-1} , and a maximal pressure of 50 bar. The investigations on the wire mesh reactor were conducted at 1000, 1250 and 1400°C with a heating rate of 1000 K s^{-1} . The holding time on the mesh was 1 s or 2 s. The schematic top view of the wire mesh reactor is shown in Fig. 1. The temperature distribution on the wire mesh was assumed to be uniform. However, on the mesh side near the electrodes, the temperature was proposed to be lower than in the middle as reported by Hoekstra et al. [37]. In order to ensure high reproducibility of char yield data, the sample was therefore placed centrally. A biomass initial weight of ca. 3 mg was applied for all experiments.

Table 1
g-Factors of radicals found in lignocellulosic materials and their chars.

g-factor	Description	Ref.
Carbon-centered radicals		
2.0025–2.0026	Aliphatic π type radicals located on hydrocarbons	[12]
2.0026–2.0028	Simple 1–5 rings aromatic hydrocarbons	[12]
2.0028	Graphitic carbon, unsubstituted aliphatic radical	[61,62]
2.0029	Complex aromatic hydrocarbons (coronene, benzoperylene)	[12]
2.003–2.004	Carbon-centered with an oxygen atom	[78]
2.0030–2.0035	Azaaromatics	[50]
2.0035–2.0042	Azo compounds	[50]
Oxygen-centered radicals		
2.0038–2.0047	π type radicals (quinones, 1–3 rings)	[12]
2.0035–2.0040	Ethers (mono-, di- and trimethoxybenzenes)	[12]
2.0040–2.0060	Semidione, semiquinone, ketyl anions	[50]
Nitrogen-centered radicals		
2.0031	Nitrogen-containing radicals	[12]
2.0045–2.0055	Nitro compounds	[50]
2.0055–2.0065	Nitroxyls	[50]

Fig. 1. Schematic top view of the wire mesh reactor at TU Munich: 1. Reactor steel casing; 2. Electrodes and holder of the wire mesh with a sample; 3. Thermocouples B-type; 4. Thermocouples S-type; 5. Thermocouples K-type; 6. Wire mesh with a sample; 7. Intensifier; 8. PC with LabVIEW software; 9. Vacuum pump; 10. Gas bottle; 11. Valves [52].

Tubular reactor. A tubular reactor, placed in a furnace (Entech, ETF 3050/15S) was used for the fixed-bed pyrolysis experiments with a heating rate of $<10 \text{ K min}^{-1}$ and at a temperature of 1000°C . The reactor consists of a stainless steel tube with an alumina tube fitted with electrical heating elements and gas supply (Fig. 2). 5 mg of the virgin sample was loaded into the alumina boat placed in the reactor middle. Once the preset temperature was reached, the sample was kept for about 10 min in the reactor to ensure complete conversion.

Entrained-flow reactor (BabiTER). The entrained flow study was carried out with the Baby High Temperature Entrained Flow Reactor (BabiTER) at TU Munich. The layout of the entrained flow reactor is shown in Fig. 3 [38,39]. The mass flow of the pulverized biomass can be varied from 50 g h^{-1} to 1 kg h^{-1} and is controlled by

a software connected to the balances. The pre-heated nitrogen is mixed with the biomass in the entry of the reaction tube. In this work, the experiments were carried out with the entrained flow reactor at temperatures of 1000 , 1250 and 1500°C . The BabiTER system is limited to use particles with a characteristic length $<0.5 \text{ mm}$. A biomass feeding rate of 300 g h^{-1} was selected for the rice husk. At 1000 and 1250°C , the wheat straw and leached wheat straw was fed with 200 g h^{-1} , and at 1500°C with 100 g h^{-1} to ensure continuous biomass feeding. The sampling probe was kept at a constant height, enabling a residence time of about 1 s during all experiments.

Char yield determination in the wire mesh and entrained flow reactors. The average char yield was determined from at least five pyrolysis experiments in the wire mesh reactor for each condition. The char yield (Y_s) in the wire mesh reactor was calculated according to equation (1):

$$Y_s = \frac{m_{\text{mesh+char}} - m_{\text{mesh}}}{(m_{\text{mesh+biomass}} - m_{\text{mesh}}) \cdot (1 - X_{\text{water}})} \cdot 100 \quad (1)$$

where X_{water} is the mass fraction of moisture in the original biomass. The char yield of the Si-rich wheat straw and rice husk in the entrained flow reactor including ash was quantified by using Si as a non-volatile tracer element, as proposed by Damø et al. [40], according to equation (2):

$$Y_s = 100 \cdot \frac{c_{\text{Si,fuel}}}{c_{\text{Si,char}}} \quad (2)$$

$c_{\text{Si,fuel}}$ is Si mass fraction of the dry fuel, $c_{\text{Si,char}}$ is Si mass fraction of the dry char. The method with application of silicon as an ash tracer is based on the assumption that all Si is retained in the char.

2.2. Materials and methods

2.2.1. Biomass composition

Prior to the pyrolysis experiments, pinewood, beechwood, wheat straw and rice husk were comminuted on a hammer mill and sieved to the particle size fractions 0.05 – 0.2 mm for the wire mesh and tubular reactor experiments and to 0.09 – 0.18 mm for the entrained flow reactor study. The raw Scots pinewood (*Pinus sylvestris* L.) originates from Jylland (Denmark), whereas beechwood (*Fagus sylvatica*) was harvested in Hannover (Germany). The raw rice husk (*Oryza sativa* L.) and wheat straw (*Triticum aestivum* L.) originate from North Vietnam (Sapa plantage) and Denmark (Aabenraa plantage). For the individual biomass compounds organosolv lignin (Alcell) from loblolly pinewood (*Pinus taeda*) (BOC Sciences, US) and lignin from wheat straw (BOC Sciences, US), xylan from beechwood (purity 97.3%, Sigma-Aldrich, St. Louis, US) and cellulose (Avicel PH-101, Sigma-Aldrich, US) were used. Xylan from beechwood (*Fagus sylvatica*) originates from North America, and consists of 1,4-linked β -xylopyranosyl units substituted by 4-O-methyl- α -D-glucopyranosyl uronic acid units [41]. The xylosyl-to-uronic acid ratio is 8:1. Organosolv lignin from wheat straw originates from wheat residues in Eastern Oregon (US), whereas organosolv lignin from softwood was harvested in Arkansas (US).

The wheat straw was leached in deionized water (room temperature) by continuous stirring for 12 h, followed by drying at 30°C in an oven desiccator without any ventilation. The mineral content after biomass leaching was determined by ash analysis. Due to the wheat straw leaching, the metal content was reduced to $\approx 60\%$ of the original value and the Cl, S, K, Na and P contents were strongly reduced.

The proximate and ultimate analyses of fuels are shown in Table 2. The compositional analysis of lignocellulosic materials

Fig. 2. Schematic view of the tubular reactor at DTU: 1. Gas bottle (N_2); 2. Valve; 3. Ceramic tube; 4. Horizontal tubular reactor; 5. Quartz boat; 6. Electric heater and temperature controller; 7. Exhaust gas.

Fig. 3. Schematic view of the entrained flow reactor (BabiTER) at TU Munich [38,39]: 1. Feeding gas (N_2); 2. Main gas (N_2); 3. Fuel feeding system; 4. Pre-heater; 5. Tube furnace; 6. Water quench; 7. Collection probe; 8. Solid residue char bin; 9. Metal filter; 10. Impinger bottle; 11. Gas analyzer; 12. Pump (Venturi); 13. Gas analysis/measurement controller; 14. Exhaust gas [84].

(cellulose, hemicellulose, acid-soluble lignin, acid-insoluble lignin, protein and extractives) was conducted according to NREL technical reports [42–44] and Thammasouk et al. [45], and shown in Table 3. The water-ethanol extraction was performed on wheat straw, alfalfa straw and rice husk which contain a high level of hydrophilic and lipophilic extractable compounds [45]. The extraction comprised of a water extraction after which the remaining solid was extracted in 95% ethanol, as described by Thammasouk et al. [45]. In addition, the original sample was also extracted using 95% ethanol. These operations allowed for the determination of the total amount of water-soluble extractives, ethanol-soluble extractives, and water-insoluble but ethanol-soluble extractives, as well as the total extractives removed under a sequential extraction using water and then ethanol.

2.2.2. Methods

Elemental analysis. The elemental analysis was performed in quadruplicates on two instruments of the same model (Eurovector, model EA3000) to determine CHN and oxygen contents of chars

prepared in the tubular, wire mesh, and BabiTER reactors. Acetanilide was used as a reference standard. The ash content of the chars was determined using a muffle oven.

Ash compositional analysis. The ash content of 1 g raw biomass and char samples was determined in triplicates by oxidation at 550°C for 7 h in the muffle oven [46]. The ash compositional analysis was performed by an X-ray fluorescence instrument (Shimadzu, model EDX 800-HS) at TU Munich. The ash (about 200 mg) which was generated at 550°C was initially mixed and then pressed with a special wax (mixture ratio 1:5). The Cl and S content in the ash was analyzed by ion chromatography (IC) at TU Wien. The ash sample was dissolved in ultrapure water at 120°C for 1 h, and then the solution was filtered and analyzed by IC.

^{13}C solid state NMR spectroscopy. Solid-state NMR analysis was carried out on a Bruker Avance 400 NMR spectrometer (9.4 T) operating at Larmor frequencies of 400.13, 100.58 and 79.48 MHz for 1H and ^{13}C respectively. All experiments were conducted using a double resonance probe equipped with 4 mm (o.d.) rotors. Samples were analyzed at room temperature by single-pulse (SP) magic angle spinning (MAS) as well as cross polarization (CP) MAS [47] utilizing high-power 1H two-pulse phase-modulated decoupling (TPPM) [48] during acquisition and employing a spin-rate of 9 kHz. The ^{13}C CP/MAS spectra were recorded using a recycle delay of 8 s, a contact time of 1 m, an acquisition time of 45.9 m and 4096 scans, whereas the ^{13}C SP/MAS spectra were recorded using a recycle delay of 128 s, an acquisition time of 45.9 m and 1080 scans. All ^{13}C NMR spectra were referenced to the carbonyl resonance of an external sample of α -glycine at 176.5 ppm.

Electron spin resonance spectroscopy. Electron spin resonance (ESR) spectra were recorded on a Jeol JES-FR30 ESR spectrometer (JEOL Ltd., Tokyo, Japan). Samples were placed in a closed-bottom quartz capillary tube with a wall thickness of 0.75 mm and an outer diameter of 5 mm. The measurements were carried out at room temperature with a microwave power of 4 mW, and a modulation width of 0.1 mT, sweep width of 50 G, sweep time of 0.5 min, time constant of 0.3 s. The intensity of all signals was recorded relative to the intensity of a Mn (II)-marker (JEOL Ltd., Tokyo, Japan) attached to the cavity of the spectrometer. Since the area under the ESR adsorption curve is directly proportional to the number of paramagnetic centers contributing to the resonance, the spin concentration (spins g^{-1}) of a sample, $N_{s,spin}$, was calculated by comparing the double integrated areas of the sample signals, A_{sample} , and the Mn (II) internal marker signals as shown in equation (3) [49]:

$$N_{s,spin} = \frac{N_{marker} \cdot A_{sample}}{A_{marker}} \quad (3)$$

A solid sample of $CuSO_4 \cdot 5H_2O$ of known weight was used as a standard for calculating the number of spins in the Mn (II)-marker signals as shown in equation (4) [50]:

$$N_{marker} = \frac{n_{CuSO_4 \cdot 5H_2O} \cdot N_A \cdot A_{marker}}{A_{CuSO_4 \cdot 5H_2O}} \quad (4)$$

The calculation of a spin sample concentration ($c_{s,spin}$) is based on the ratio of a number of spins and a sample weight (m_s) using equation (5) [50]:

$$c_{s,spin} = \frac{N_{s,spin}}{m_s} \quad (5)$$

The ESR g -factor is determined in equation (6) [50]:

$$g = \frac{g_1 \cdot H}{H + H_1} \quad (6)$$

Table 2

Proximate and ultimate analysis of fuels and ash analysis.

Fuel	Pinewood	Beechwood	Wheat straw	Leached wheat straw	Rice husk	Lignin wheat straw	Lignin softwood	Xylan from beechwood
Proximate analysis								
Moisture, (% as received)	5.1	4.5	5.5	4.3	4.5	4.4	6.1	3.3
Ash (550°C), (% dry basis)	0.3	1.4	4.1	2	21.7	3.6	1.3	2
Volatiles, (% dry basis)	86.6	79.4	77.5	84.2	64.3	66.3	67.3	81.6
HHV, (MJ kg ⁻¹)	21.6	20.2	18.8	18.7	15.5	26.7	26.4	14
LHV, (MJ kg ⁻¹)	20.2	19	17.5	17.4	14.5	25.5	25.2	14
Ultimate analysis, (% dry basis)								
C	50.5	46.7	42.4	45.7	35.5	61.8	64.6	39.7
H	6.8	6.3	6.3	6.6	5.5	3.8	5.3	6.1
O	42.3	45.3	46.2	45.4	37.2	29.4	28	51.9
N	0.1	0.3	1	0.3	0.1	1.4	0.8	0.3
S	<0.01	0.02	0.1	0.02	0.03	0.8	0.1	0.02
Cl	0.01	0.02	0.1	0.01	0.05	0.03	0.5	0.01
Ash compositional analysis, (mg kg ⁻¹ dry basis)								
Al	10	10	150	100	70	300	100	10
Ca	600	2000	2500	1300	750	200	250	5700
Fe	20	10	200	350	80	1400	600	150
K	200	3600	11000	1300	2500	270	80	180
Mg	100	600	750	350	400	40	<30	80
Na	30	100	150	50	70	6800	4100	19200
P	6	150	550	80	600	30	30	150
Si	50	200	8500	6200	98500	4000	900	3
Ti	2	<8	10	10	5	100	50	100

In equation (6), g_1 -factor of a digital marker (1.981), H_1 and H are positions of the digital marker ($H = 335.7$ mT) and signal center ($H = 337.1$ mT).

Fitting of experimental ESR-spectra to simulated data was done using WinSim software, as described by Duling et al. [51]. The WinSim software is based on the LMB and simplex optimization methods to fit an experimental ESR spectrum to a combination of simulated free radical ESR spectra. Each spectra was assumed to be isotropic, spin = 1/2 without contributions from hyperfine splittings. The simulation of spectra gave the relative amounts of radical derivatives as well as optimized values of line widths and g -factors. Optimizations gave best fits to the experimental ESR spectra with a root mean square (RMS) > 0.85.

The ESR analysis of biomass char was conducted the next day after char generation, and compared with the results seven month later. The radical concentration showed negligible differences (<5%) over a period of seven month, and therefore being independent on the storage time.

3. Results

3.1. Char characterization

3.1.1. Char yield

The char yields generated at 1000°C in the wire mesh reactor and at 1000–1500°C in the entrained flow reactor were determined for all lignocellulosic materials (Fig. 4(a)). The char yields on dry ash

free basis (daf) of rice husk, leached wheat straw and pinewood in the wire mesh reactor were equally similar and low (ca. 4% daf). The alkali lean rice husk, leached wheat straw and pinewood show a significant variation in biomass major compounds. This indicates that any differences in biomass composition (cellulose, hemicellulose and lignin) between straw and wood only result in small char yield differences. The char yields of beechwood (rich in Ca, K) and wheat straw (rich in Ca, K, Si) were 4–10% points higher than char yields from pyrolysis of other lignocellulosic materials which was associated with the catalytic effect of alkali metals that affect polymerization/cross-linking [52].

The char yield from pyrolysis of wheat straw at 1000°C in the entrained flow reactor was 7% lower than the char yield in the wire mesh reactor, due to the differences in heating rate and residence time (Fig. 4(b)). The pyrolysis in the wire mesh reactor was carried out with a lower heating rate (1000 K s⁻¹) than in the entrained flow reactor (10⁴ K s⁻¹). The char yield of wheat straw decreased with increasing temperature, indicating a dependency of the char yield on the heat treatment temperature. An opposite tendency was observed during the rice husk pyrolysis, where the char yield decreased only slightly from 5 to 3.5% by weight in a temperature range of 1000–1500°C. The heat treatment temperatures and silica contents did not seem to affect the char yield of rice husk, based on the small differences in char yields obtained at 1000, 1250 and 1500°C.

The wheat straw and rice husk chars were collected from the fast pyrolysis in the entrained flow reactor, and were analyzed by

Table 3

Biomass feedstock composition, calculated in percentage based on dry weight (% dry basis).

Biomass	Cellulose	Hemi-cellulose	Lignin		Totallignin	Extractives	Protein
			Acid insoluble	Acid soluble			
Pinewood	38.3	17.8	29.6	1.8	31.4	8.8 ^a	0.6
Beechwood	35	19.2	32	1.5	33.5	7.5 ^a	1.9
Wheat straw	35.9	18	19.2	6.5	25.7	10.1 ^b	6.3
Leached wheat straw	32.1	23.5	13.8	2	15.8	13.3 ^b	1.3
Rice husk	36.7	17.7	21.6	1.2	22.8	1 ^b	—

^a Acetone extraction.

^b Ethanol-water extraction at room temperature.

X-ray fluorescence (XRF), Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) and Ion Chromatography (IC). The results of ash compositional analysis of original wheat straw, rice husk and their chars are shown in Fig. 5. The analysis of rice husk chars generated at temperatures of 1000–1500°C indicated high concentrations of silicon oxides along with smaller amounts of potassium, aluminium, iron, sodium and magnesium. The wheat straw char at all applied heat treatment temperatures contained potassium and calcium along with a high concentration of silicon, leading to the formation of silicates [53]. About 70% of potassium has been released during wheat straw pyrolysis in a temperature range of 1000–1500°C, and potassium at 1500°C is bound to silicates (Fig. 5). The ash compositional analysis of wood and herbaceous biomass chars obtained in the wire mesh and tubular reactors was not performed due to the limited amount of the biomass chars.

(a): Char yield and radical concentrations in the WMR

(b): Char yield and radical spin concentration in the EFR

Fig. 4. Char yields (blue-red diamonds) and ESR concentration (spins $\times 10^{16} \text{ g}^{-1}$): 4(a) pinewood, beechwood, rice husk, leached wheat straw and wheat straw chars prepared in the wire mesh reactor (heat treatment temperature: 1000°C, heating rate: 1000 K s⁻¹, holding time: 1 s) and shown as green stars; 4(b) wheat straw and rice husk chars prepared in the entrained flow reactor (heat treatment temperatures: 1000, 1250 and 1500°C) versus potassium content in the original lignocellulosic materials. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.1.2. Elemental analysis

Fig. 6 shows a Van Krevelen plot of original lignocellulosic materials and their chars, generated in the wire mesh, tubular and entrained flow reactors to study the effect of heating rate and heat treatment temperature on the char composition. The results in Fig. 6(a) indicate that the oxygen content in rice husk char is higher than in beechwood and wheat straw chars. Fig. 6(b) shows that temperatures above 1000°C led to an increase in the carbon content of the rice husk and wheat straw chars due to the preferential release of hydrogen, oxygen and nitrogen.

3.1.3. ¹³C solid state NMR spectroscopy

The effect of temperature on the organic matter transformation of char prepared in the wire mesh reactor and tubular reactor, was investigated using ¹³C CP/MAS and ¹³C SP/MAS NMR. The NMR spectra are displayed in Fig. 7 and the associated spectral assignments are shown in Table 4.

The most intense resonance in the ¹³C MAS NMR spectra of chars is a broad resonance centered at 125 ppm indicating the presence of disordered aromatic residues, whereas resonances originating from cellulose (amorphous and crystalline), hemicellulose and lignin were observed in the spectra of the original lignocellulosic materials. It was noted that the CP/MAS and SP/MAS spectra of original lignocellulosic materials were almost identical, whereas differences between these two spectra were observed for the chars. During the char formation charged species are formed and some of these are paramagnetic. As reported previously [54], the presence of paramagnetics will increase relaxation rates and line widths. In close proximity of the paramagnetic sites this may even broaden the resonances beyond the limit of detection. For the wheat straw and rice husk heated at 10 K min⁻¹ no resonances were observed in the CP/MAS spectra. The remains of polysaccharides and lignin were detected in the CP/MAS spectra of beechwood and rice husk samples heated at 1000 K s⁻¹. This indicates the increased aromatization of the lignocellulosic material and formation of more graphene-like structures compared to chars generated in the wire mesh reactor [55]. Since these compounds were not observed in the corresponding SP/MAS spectra, this means that it is only a small fraction of the immobile part of the sample that contained polysaccharides and lignin.

No resonances were observed in the CP/MAS spectra of wheat straw and rice husk chars generated at slow heating rate (10 K min⁻¹) whereas a resonance in the spectrum of beechwood

Fig. 5. Ash compositional analysis of rice husk and wheat straw pyrolyzed in the BabITER reactor at 1000, 1250 and 1500°C. The ash composition of both lignocellulosic materials and their chars is shown in g kg⁻¹ on dry basis [84].

(a): Van Krevelen plot of chars prepared in the wire mesh and tubular reactors

(b): Van Krevelen plot of chars prepared in the entrained flow reactor

Fig. 6. Van Krevelen plot of original biomass and their chars prepared 6(a) in the tubular reactor (heat treatment temperature: 350, 600 and 1000°C; heating rate: 10 K min⁻¹; holding time: 10 min) and in the wire mesh reactor (heat treatment temperature: 600 and 1000°C; heating rate: 10 K s⁻¹ and 1000 K s⁻¹; holding time: 1 s); 6(b) in the entrained flow reactor (heat treatment temperatures: 1000, 1250 and 1500°C).

was present. Comparison with the H/C- and O/C-ratios in Fig. 6 shows that H/C ratios of beechwood are similar to the values for wheat straw, whereas the O/C ratio for slowly heated beechwood is a factor of 8–10 lower than wheat straw and rice husk. The lower oxygen content makes the beechwood less sensitive to effects of charged species such as paramagnetics. According to Fig. 8(a), the number of paramagnetic spins in beechwood is higher than in wheat straw and rice husk. Therefore, it is not the amount of paramagnetics that is the main reason for the lack of CP efficiency for wheat straw and rice husk. It is rather a high oxygen abundance that leads to a higher sensitivity towards paramagnetics in the sample.

3.2. Electron spin resonance spectroscopy

3.2.1. Spin radical concentration

Spin concentrations of free radicals trapped in the chars were measured using electron spin resonance spectroscopy (ESR). The effects of heating rate (10 K min⁻¹ or 1000 K s⁻¹), holding time (1 or

2 s) and biomass origin (wood or herbaceous biomass) on the spin radical concentration at 1000°C were investigated.

Fig. 8(a) shows that the radical concentrations in wood chars were significantly higher than in herbaceous chars at 1000°C. The radical concentration in biomass chars, pyrolyzed in the wire mesh reactor was up to 60% higher than in chars from the tubular reactor. The ESR signal intensities decreased when holding time was increased from 1 to 2 s in the wire mesh reactor (Fig. 8(b)). The ESR signal intensities in chars from beechwood hemicellulose and lignin are compared in Fig. 8(c). The Avicel cellulose char, prepared at 1000°C in the wire mesh reactor, did not show ESR signals of any free radicals (data not shown). Chars produced by pyrolysis of hemicelluloses had lower concentration of radicals than chars from pyrolysis of lignin due to the aromatic structure of lignin. This results suggest a significantly influence of lignin on the radical concentration of chars at the decay stage [8]. Radicals generated from the primary pyrolysis reactions can be trapped in the polyaromatic matrix of lignin [56], and stabilized by the delocalized unpaired electrons [57,58]. The major products from cellulose pyrolysis (levoglucosan and other light oxygenates) do not have unpaired electrons [59], and therefore, the radical concentrations in the char from the decay stage are low. The char prepared from softwood lignin at 1000°C with 1 s holding time showed a higher concentration of radicals than the wheat straw lignin char. However, smaller differences in radical concentrations between leached wheat straw and beechwood chars indicate a minor effect of the lignin composition than the alkali influence on remaining radical concentrations.

In the entrained flow reactor, free radicals were not observed in the wood and leached wheat straw chars at 1000–1500°C. The concentrations of radicals in the wheat straw char changed only slightly with increasing temperature in the entrained flow reactor. In contrast, the concentrations of remaining radicals in the rice husk char increased above 1000°C (Fig. 8(d)).

3.2.2. g-Factors and radical types

The experimental ESR-spectra were analyzed by fitting to simulated spectra in order to identify radical species. A model based on a mixture of two radical types which were assigned to carbon-centered and oxygen-centered polyaromatic radicals was found to adequately fit the experimental ESR spectra. This allowed determination of relative amounts of the radicals and their g-values and line widths. The fitting of simulated ESR-spectra to the experimental spectra of the original beechwood and rice husk chars prepared in the wire mesh reactor are shown in Fig. 9. The ESR signals were symmetric without hyperfine splittings for the original biomass and as well as its chars formed under both slow and fast heating (Fig. 10(a)). The ESR lines were a mixture of Lorentzian and Gaussian fitting, yet with the dominating Lorentzian shape.

The fitted ESR spectra of the original lignocellulosic materials had line widths (LW) in the range 1.7–7.1 G and g-factors in the range 2.0031–2.0052, while the spectra of the chars gave LW = 2.5–7.1 G and g = 2.0026–2.0046 (Tables 5 and 6). Radicals with g-factors outside the range 2.002–2.006 were not observed in the present study. Sulfur radicals were probably not present in the char matrix due to the higher g-values of sulfur-containing radicals (g = 2.0080–2.0081). Nitrogen-containing radicals that have g-values similar to the oxygen-containing radicals (g = 2.0031), but usually have broad line widths (5.7–8.2) G [60], cannot be excluded based on values (Tables 5 and 6). However, the hyperfine coupling to ¹⁴N was not detected. Thus, the presence of nitrogen-containing radicals is less likely.

The original lignocellulosic materials and compounds gave ESR spectra with radicals with higher g-values than their derived chars, indicating higher levels of oxygen-containing radicals (Tables 5 and

Fig. 7. ^{13}C CP/MAS and ^{13}C SP/MAS NMR spectra of the original beechwood, wheat straw, and rice husk and their chars pyrolyzed in the tubular reactor (heat treatment temperature: 1000°C ; heating rate: 10 K min^{-1} ; holding time: 10 min) and chars pyrolyzed in the wire mesh reactor (heat treatment temperature: 1000°C ; heating rate: 1000 K s^{-1} ; holding time: 1 s).

Table 4

Assignment of resonances in the ^{13}C CP/MAS NMR and ^{13}C SP/MAS NMR spectra of the original beechwood, wheat straw and rice husk [79–83].

Chemical shift, ppm	Description
172–174	Carbohydrate; $-\text{COO}-\text{R}$, $\text{CH}_3-\text{COO}-$
153–154	Lignin; S3(e), S5(e)
145–148	Lignin; S3(ne), S5(ne), G1(e), G4(e)
133–138	Lignin; S1(e), S4(e), G1(e)
121–122	Lignin; G6
105–106	Carbohydrates; C1, Lignin; S2, S6
89–92	C4 in cellulose (cr)
84–85	C4 in cellulose (am)
72–75	C2, C3 in carbohydrates; C5 in cellulose
63–65	$\text{CH}_2\text{ OH}$ (C6 in cellulose, C5 in xylan)
56–57	Lignin, OCH_3
30–38	CH_2 in aliphatics
21	Carbohydrates; $\text{CH}_3-\text{COO}-$

Abbreviations: S, syringyl; G, guaiacyl; ne, in non-etherified arylglycerol β -aryl ethers; e, in etherified arylglycerol β -aryl ethers.

6). The chars prepared under slow heating could be fitted by two spectra with g -values (2.0026–2.0046), indicating two radical types which were assigned to oxygen-centered radicals ($g = 2.0038\text{--}2.0047$) [12] and carbon-centered radicals ($g = 2.0025\text{--}2.003$) based on their g -values [12,61,62].

The simulated spectra indicated two slightly different species in the wood and herbaceous chars generated by fast heating with 1 s holding time. These radical were most likely of a polyaromatic origin ($g = 2.0029$) with either 1–5 ring aromatic hydrocarbons ($g = 2.0026\text{--}2.0028$) or carbon-centered radicals with containing oxygen [13]. When the holding time increased from 1 to 2 s, the spectra could be described by only one type of radicals, which was proposed to consist of a complex polyaromatic structure with more than five rings like benzoperylene or coronene ($g = 2.0029$) [13]. Interestingly, only rice husk char, prepared in the wire mesh reactor with 2 s holding time, showed the presence of two types of radicals. The g -factors of hemicellulose and lignin char radicals decreased with oxygen elimination and formation of PAH structures with the stable aromatic radicals ($g = 2.0031$). The remaining radicals in the hemicellulose char are most likely of a similar carbon-centered type with the negligible structural differences ($g = 2.0029\text{--}2.0031$) (Table 6).

The results of the present study indicate that the free radicals in softwood and wheat straw lignin chars form more complex polyaromatic radical structures with an oxygen, corresponding to investigations of Tian et al. [23]. The wheat straw and rice husk chars, generated in the entrained flow reactor, formed aromatic radicals of a similar type as it was observed in the chars, prepared at a lower heating rate in the wire mesh reactor.

Fig. 8. ESR concentration (spins $\times 10^{16} \text{ g}^{-1}$) of original lignocellulosic materials and their chars in: 8(a) Pinewood, beechwood, wheat straw, leached wheat straw, rice husk pyrolyzed in the wire mesh reactor (heat treatment temperature: 1000°C, heating rate: 1000 K s⁻¹, holding time: 1 s) and in the tubular reactor (heat treatment temperature: 1000°C, heating rate: 10 K min⁻¹, holding time: 10 min); 8(b) Beechwood, wheat straw and rice husk pyrolyzed in the wire mesh reactor (heat treatment temperature: 1000°C, heating rate: 1000 K s⁻¹, holding time: 1 s or 2 s); 8(c) Hemicellulose, lignin (wheat straw) and lignin (softwood) pyrolyzed in the wire mesh reactor (heat treatment temperature: 1000°C, heating rate: 1000 K s⁻¹, holding time: 1 s); 8(d) Wheat straw and rice husk pyrolyzed in the entrained flow reactor (heat treatment temperature: 1000, 1250 and 1500°C). No free radicals were detected in the pinewood and leached wheat straw chars from the decay stage of pyrolysis in the entrained flow reactor.

4. Discussion

The ESR analysis was performed on the original wood, herbaceous biomass and plant cell wall compounds and their chars, prepared at different heating rates and at temperatures above 1000°C in the tubular, wire mesh and entrained flow reactors. The free radicals were detected by ESR in the char matrices obtained during the decay stage after pyrolysis was completed. The decay stage of pyrolysis is characterized by the radicals, which are stabilized by entrapment in the solid biomass char matrix at room temperature [23].

The wood, leached wheat straw and rice husk gave a lower char yield and higher free radical concentrations than wheat straw in the wire mesh reactor with a heating rate of 1000 K s⁻¹ and at a temperature of 1000°C. The high levels of carbon-centered radicals, which were detected in the chars from the decay stage, may inhibit repolymerization/cross-linking [24], and decrease the wood char yield. The cross-linking of wheat straw char prepared in the wire mesh reactor was proposed to be additionally affected by the high potassium level, leading to the higher char yield and lower radical concentrations than in wood and leached wheat straw chars. High heating rates cause a strong bond-breaking in lignocellulosic materials before it starts to cross-link and therefore becomes fluid, leading to a significant tar release. The high levels of potassium

cause less severe plasticization by catalyzing the conversion of bridges into char links, and therefore increasing polymerization/cross-linking and reducing char fluidity. The wood and leached wheat straw chars, generated in the entrained flow reactor, had no remaining free radicals, indicating an efficient recombination of radicals. The radical quenching (recombination reaction) of wood and leached wheat straw was mainly affected by the higher heating rate in the entrained flow reactor than at slow and intermediate heating rates in the tubular and wire mesh reactors. The tubular reactor at slow heating rate conditions provides a longer time of radical stabilization, and thus, longer reaction times to form non-radical products in the char matrix.

The high potassium content in the wheat straw affected catalytically the radical concentration in the char matrix. Sancier et al. [63] discussed the mechanism of potassium effect on the radical concentration in catalytic coal gasification. The high potassium levels accelerate the formation of reactive aliphatic radicals ($g = 2.0030$). The formation of potassium-carbon bonds, such as in the potassium rich wheat straw, can weaken carbon-carbon bonds in aromatic rings and thereby facilitate bond breaking at high temperatures. This leads to formation of aliphatic radicals which react further to produce stable polyaromatic compounds through polymerization/cross-linking reactions at an early stage of the pyrolysis [64–67]. At temperatures of 1000–1500°C close to 70%

(a): ESR-spectra of original beechwood

(b): ESR-spectra of rice husk char prepared in the WMR

Fig. 9. Experimental ESR-spectra of 9(a) original beechwood and 9(b) rice husk char (or PAH radical type 3 from Table 5) pyrolyzed in the wire mesh reactor (1000°C , 1000 K s^{-1} , 1 s) and fitted to simulated data with RMS = 0.85 (original beechwood) and RMS = 0.999 (rice husk char). The experimental ESR-spectra are shown (black line), the simulated spectra (red line), fitting peak 1 (red dotted line) and fitting peak 2 (black dashed line). The Mn (II) internal marker signals are marked by stars. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

potassium in the wheat straw has been released (Fig. 5), and the remaining potassium was probably bonded to the wheat straw char in phenolate groups or intercalated in graphene layers [68], reducing the mobility of potassium in the char matrix. The higher radical concentrations in the wheat chars from the decay stage of pyrolysis in the entrained flow reactor compared to the wood chars may be related to the decreased mobility of potassium in the char matrix, leading to the less efficient catalytic effects of potassium on the bond-breaking and radical re-attachments.

The increased radical concentrations in the rice husk chars, generated in the entrained flow reactor, were caused by the formation of carbon-centered radicals. The rice husk sample contains high concentrations of silicon that is present as silicon oxides with small amounts of alkalis and other trace elements. Lanning [69] concluded that silicon occurs in rice husk in a hydrated amorphous form (opal or silica gel), located mainly in the outer epidermis and filling the inner channels in the spiral structure of the epidermal cells. In addition, Liu et al. [70] and Sharma et al. [71] proposed that the silica in the rice husk is combined with

(a): ESR-spectra of rice husk

(b): ESR-spectra of wheat straw

Fig. 10. ESR-spectra of 10(a) rice husk (raw (RMS = 0.86) and their chars prepared in the entrained flow reactor at 1000°C (RMS = 0.94), at 1250°C (RMS = 0.85), at 1500°C (RMS = 0.959), and in the wire mesh reactor at (1000°C , 1000 K s^{-1} , 1 s or 2 s (RMS = 0.999))); 10(b) wheat straw (raw (RMS = 0.85) and their chars prepared in the entrained flow reactor at 1000°C (RMS = 0.85), at 1250°C (RMS = 0.86), at 1500°C (RMS = 0.87), and in the wire mesh reactor (1000°C , 1000 K s^{-1} , 1 s or 2 s (RMS = 0.87)). The Mn (II) internal marker signals are marked by stars.

carbohydrates. In the present study, the ash compositional analysis showed that the elemental silicon content in the rice husk chars generated in the entrained flow reactor remained unchanged (Fig. 5). The radicals formed at rapid heating rates were proposed to be trapped upon fast cooling in a glassy char structure composed of an amorphous silica phase (glass transition temperature $\approx 730^{\circ}\text{C}$) [72]. Trapping of organic radicals in amorphous silicon has been reported by Friebele et al. [73], who detected methyl radicals in a heat-treated synthetic silicon fused in a hydrogen-oxygen flame.

Two types of free radicals were identified by fitting the ESR-spectra to the simulated data. Biomass chars, generated at different operational conditions, showed almost negligible differences in the radical structure. The original lignocellulosic materials contained mostly oxygen-centered radicals, whereas at high temperatures aliphatic carbon-centered radicals ($g = 2.0026\text{--}2.0028$) and PAH radicals ($g = 2.0027\text{--}2.0035$) were formed during pyrolysis in the wire mesh and entrained flow reactors. The decreased experimental sensitivity of ^{13}C CP/MAS and ^{13}C SP/MAS NMR

Table 5

Simulation results of original biomass and chars prepared in the wire mesh and tubular reactors.

Biomass	Reactor/holding time	Heating rate	Area, %	g-factor	Line width (Gauss)
Pinewood	Original biomass	10 K min ⁻¹	72	2.0052	5.9
			28	2.0033	4.3
	Tubular reactor		94.9	2.0028	5.2
			5.2	2.0034	4.1
	Wire mesh reactor, 1 s		54.5	2.0030	4.3
			45.5	2.0029	5.1
Beechwood	Original biomass	1000 K s ⁻¹	5.9	2.0031	2.2
			94.1	2.0048	4.7
	Tubular reactor		17.3	2.0030	5
			82.7	2.0039	4
	Wire mesh reactor, 1 s		21.8	2.0035	2.9
			78.2	2.0028	4.1
Wheat straw	Wire mesh reactor, 2 s	1000 K s ⁻¹	100	2.0031	4.3
			86.5	2.0050	5.1
	Original biomass		13.5	2.0035	3.4
			17.6	2.0033	4
	Tubular reactor		82.4	2.0026	5.6
			100	2.0031	2.5
Leached wheat straw	Wire mesh reactor, 2 s	1000 K s ⁻¹	100	2.0027	2.3
			66	2.0046	5.1
	Original biomass		34	2.0033	3.5
			100	2.0030	4.4
	Tubular reactor		100	2.0029	3.8
			98.4	2.0043	7.1
Rice husk	Original biomass	10 K min ⁻¹	1.6	2.0027	1.7
			27.7	2.0026	2.5
	Tubular reactor		72.3	2.0046	7.1
			100	2.0030	7.5
	Wire mesh reactor, 1 s		100	2.0028	9.8
			Wire mesh reactor, 2 s	1000 K s ⁻¹	100

Table 6Simulation results of biomass compounds and chars generated in the wire mesh reactor (heat treatment temperature: 1000°C; heating rate: 1000 K s⁻¹; holding time: 1 s) and wheat straw and rice husk chars generated in the entrained flow reactor (heat treatment temperatures: 1000, 1250 and 1500°C).

Biomass	Condition	Area, %	g-factor	Line width (Gauss)
<i>Hemicellulose</i>	Original compound	100	2.0047	5.8
	Wire mesh reactor, 1 s, 1000 K s ⁻¹	100	2.0030	5
<i>Lignin (softwood)</i>	Original compound	100	2.0037	5
	Wire mesh reactor, 1 s, 1000 K s ⁻¹	100	2.0029	4.3
<i>Lignin (straw)</i>	Original compound	100	2.0046	4.2
	Wire mesh reactor, 1 s, 1000 K s ⁻¹	26.1	2.0028	3
<i>Wheat straw</i>	Wire mesh reactor, 1 s, 1000 K s ⁻¹	73.9	2.0034	4.3
		86.5	2.0050	5.1
	Original biomass	13.5	2.0035	3.4
		100	2.0028	3.1
		100	2.0030	2.8
		100	2.0029	2.9
<i>Rice husk</i>	Entrained flow reactor, 1500°C	98.4	2.0043	7.1
		1.6	2.0027	1.7
	Original biomass	100	2.0032	15.8
		100	2.0031	10.1
		100	2.0030	7.8
		100		

analysis was caused by the isolated free radicals in the carbonaceous bulk as it was proposed by Bardet et al. [74].

The heating rate and heat treatment temperature affected the dominating ESR signal shape less than the high Si mass fraction in the rice husk that caused an ESR line broadening (≈ 7.1 G) in the pyrolysis. Moreover, the fitting of ESR-spectra to the simulated data showed that the line width of ESR-spectra remained between 4 and 6 G for the wood chars independent on the heating rate and holding time, whereas the herbaceous biomass chars obtained a narrow line width (2.3 and 3.4 G) and broad line width (4 and 7.1 G) which did not change significantly during pyrolysis. Both line types were narrower than the line widths of radicals obtained for carbon black (23–66 G) [75]. The ESR signal of pyrolyzed lignocellulosic materials is often only a broad

featureless singlet without the hyperfine splitting which is caused by the presence of multiple radical species or strong matrix interaction occurred between the products [76]. In addition, the heterogeneity of biomass samples and that the radicals are not exclusively centered on single atoms could lead to broad featureless singlets, as reported by Herring et al. [76]. Investigations of Ross et al. [77] showed that the differences in line widths were caused by the formation of the disorganized carbon with unpaired electrons (narrow signal) and organized carbon with the conductive electrons (broad signal). In the present study, the line broadening of rice husk chars was associated with the radicals of carbon-centered type, encapsulated in the chars due to the amorphous silicon melting at high temperatures.

5. Conclusion

High concentrations of free radicals were detected by ESR in wood and herbaceous chars from the decay stage of pyrolysis at slow and fast heating rates and at temperatures above 1000°C. The free radicals in the lignocellulosic chars from the decay stage of pyrolysis were stable at room temperature and showed similar structural characteristics. The radical concentrations ranged up between $7 \cdot 10^{16}$ and $1.5 \cdot 10^{18}$ spins g^{-1} . The results showed that the radicals in wood and herbaceous biomass chars were mainly aliphatic and PAH radicals, whereas the original lignocellulosic materials contained mainly oxygen-centered radicals. The ESR spectra of radicals showed the narrower line widths of <6 G. The g -factors (2.0026–2.0030) in the chars from the decay stage of pyrolysis were attributed to π -hydrocarbon radicals, embedded in larger polycyclic aromatic hydrocarbon structures of biomass chars.

Similar radical concentrations were detected by ESR in the chars generated in the wire mesh reactor from pinewood, beechwood and leached wheat straw. The original lignocellulosic materials showed differences in the distribution among the three major biomass constituents (cellulose, hemicellulose, lignin), whereas the alkali content was similarly low compared to rice husk and wheat straw. The results indicate that the biomass major constituents had a minor effect on remaining radical concentrations compared to potassium and silica contents.

Potassium was proposed to catalyze the reaction between radicals forming larger and stable structures. The higher radical concentrations in the wheat straw chars from the decay stage of pyrolysis in the entrained flow reactor compared to the wood chars were related to the decreased mobility of potassium in the char matrix, leading to the less efficient catalytic effects of potassium on the bond-breaking and radical re-attachments. The high levels of radicals in the rice husk chars generated in the wire mesh and entrained flow reactors were related to the trapping of free radicals in a molten Si-rich char with increasing temperature, and followed by the rapid cooling in the reactors.

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