



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 $\sigma\text{-CH}_2$ -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] |

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