

## MORPHOLOGY AND ENVIRONMENTALLY PERSISTENT FREE RADICALS ON BIOCHARS: A REVIEW

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### Abstract

This study sought to investigate the need for alternative renewable, clean and sustainable energy resource arise. Biomass-derived fuels offer the best alternative to fossil fuels. Pyrolysis is one of the techniques used to produce biofuel from biomass. However, the thermal decomposition of biomass in a limited supply of oxygen leads to emissions of complex matrices that affect biofuel utilisation and stability. The major by-products from biomass pyrolysis include liquid oil, biochar and gases depending on operating conditions such as temperature, particle size, heating rate and reactor configuration. Biochars generated tend to find their use majorly in industry, agriculture and cleaning of industrial waste. Nonetheless, biochars may contain organic compounds such as furans, aldehydes, polyaromatic hydrocarbons (PAHS) and environmentally persistent free radicals, which are toxic, carcinogenic, cause oxidative stress and mutagenic. This review, therefore, focuses on the characteristics of biochar in terms of morphology and the nature of persistent free radicals embedded on the surface of the biochar. Notably, the information on optimum conditions for producing biochars free of persistent free radicals is scanty, if any. This review recommends further research on the effects of EPFRs on biological systems and optimum conditions for the formation of biochars with almost nil radicals.

**Key Terms:** Biodiesel, morphology, environmentally persistent free radicals, particulate matter, and pyrolysis.

## 1.0 INTRODUCTION

Biomass is a renewable energy resource that comes from plants and animals. Major Biomass feed stocks which have been used over decades include agricultural crop residues, forestry residues, algae, wood processing residues, municipal waste, and wet waste (Demirbas, 2011; Demirbaş, 2001; Duku, Gu, & Hagan, 2011; Ghosh, 2016; Perlack & Stokes, 2011; Yu et al., 2021). Thermal biomass degradation in the absence or limited supply of air results in the formation of biochars, as well as other by-products such as organic volatiles, liquid oil, tar and non-condensable gases such as CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub> (Ranzi et al., 2014; Sfakiotakis & Vamvuka, 2018; Tripathi et al., 2016). Biochar is a porous carbonaceous solid with embedded molecular functional groups that have a high degree of aromaticity and are resistant to decomposition (Akhil et al., 2021; Dey & Adhikary, 2020; Richard et al., 2016).

Biochar has piqued the researchers' interest due to its widespread use in agriculture, the environment, and industry ((Lehmann et al., 2006; Rehman et al., 2021; Sutar et al., 2022). The major properties investigated in the use of biochars in various sectors are adsorption power, char morphology (porosity and surface area), and surface functional groups (Suliman et al., 2016; Zhao, Ta, & Wang, 2017). For example, biochars' adsorption capacity in soil improves soil pH, hydrological properties, and soil nutrients (thereby increasing crop yield)(Ahmed et al., 2016; Alkharabsheh et al., 2021; Ding et al., 2016; El-Naggar et al., 2019; Meng et al., 2021). Furthermore, functional and charged groups on the surface of biochars are used in the remediation of greenhouse gases, as pollutant sorbent for polycyclic aromatic hydrocarbons (PAHs) and heavy metals ((Mandal et al., 2016; Qadeer et al., 2017; Qambrani et al., 2017; Shrestha et al., 2010; Singh et al., 2020). Biochars can also be used as industrial catalysts (Bolan et al., 2021; Cheng & Li, 2018; Lee et al., 2017; Velusamy et al., 2021). Regardless of its many benefits, biochars may contain organic compounds such as furans, aldehydes, polyaromatic hydrocarbons (PAHS) and environmentally persistent free radicals, which are great environmental pollutants (Godlewska et al., 2021; Tao et al., 2020; Zheng et al., 2019). This review, therefore, discusses the recent research developments on the morphology, persistent free radicals, functional groups and particulate matter embedded on the surface of biochar.

## 2.0 LITERATURE REVIEW

Because of the presence of these volatile organic compounds and stable free radicals, biochar is unsuitable for agricultural use and other applications (Hussain et al., 2017; Nidheesh et al., 2021; Wu et al., 2021). As a result, elemental analysis and characterisation are required. The particle size of the biochars varies, ranging from ultrafine to coarse particulates (Maienza et al., 2017). The ultrafine and fine particulates with aerodynamic diameters ranging from 1nm to 100 um are hazardous to human health and are known to be among the precursors of respiratory illnesses and cancer (Camatini et al., 2017; Dubey et al., 2018). When compared to coarse (10 m) particulates, ultrafine (0.01 m) and fine (2.5 m) particulates are known to travel deep into respiratory tissues and are difficult to clear (Li et al., 2016).

## 3.0 METHODOLOGY

The procedure were adopted from Mosonik et al. (2018). In order to determine the surface radical immobilization on biochar, approximately 5 mg sample of biochar particulates were analyzed using a Bruker EMX-20/2.7 X-band EPR spectrometer comprising of dual cavities, modulation and microwave frequencies of 100 kHz and 9.298 GHz respectively (Khachatryan et al., 2010). The typical parameters were: sweep width of 200 G, EPR microwave power of 1–20 mW, and modulation amplitude of  $\leq 6$  G. The time constant was set at 16 sec while the sweep time was set at 30 sec. The g-factor was computed using Bruker's WINEPR program, which is a comprehensive line of software allowing control of the Bruker EPR

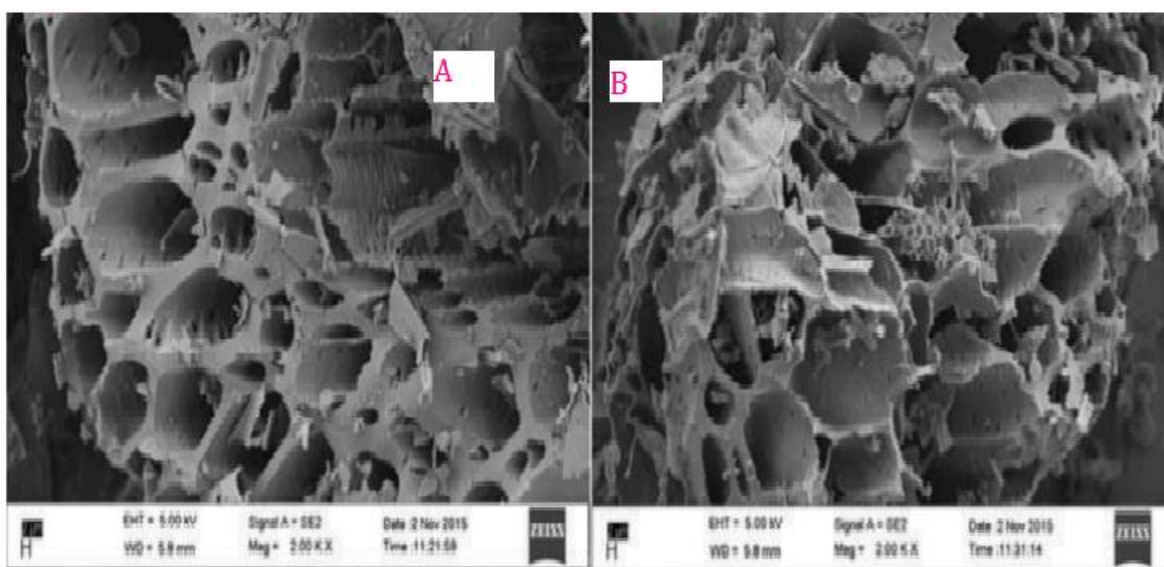
spectrometer, data-acquisition, automation routines, tuning, and calibration programs on a Windows-based PC (Eaton et al., 2010; Kibet et al., 2012). The exact g-value for the key spectrum was determined by comparison with a 2,2-diphenyl-1-picrylhydrazyl (DPPH) standard (Adoukpe et al., 2008). The EPR runs were conducted in 3 replicates.

## 4.0 RESULTS AND DISCUSSION

### Morphology of Biochar

Scanning electron microscopy (SEM) and Energy Dispersive X-ray Analysis (EDX) are techniques used to generate biochars' surface morphology and elemental analysis. Thermal degradation of biomass at very high temperatures in the absence of limited oxygen produces biochar as one by-product (Crombie et al., 2013). Biochar is an acronym for biomass charcoal. Biochars are known to be highly carbonaceous, porous surfaces (figure 1) and have high adsorption properties, therefore, making them be used in soil ameliorate and catalyst in industries (Ahmed & Najmi, 2018; Khorram et al., 2016; Weber & Quicker, 2018). Biochars are perfect in Soil amelioration, not in adding carbon, but its porous structure allows retention of water in the soil hence increasing the water holding capacity of the soil (Sun & Lu, 2014). Additionally, biochar morphology has active negative sites (functional groups) which bind nutrients such magnesium, calcium and potassium (Archanjo et al., 2017; Tong et al., 2011). This leads to improvement of soil pH, which is favourable to most plants (Oliveira et al., 2017). Further, biochar is used as a bio-sorbent in the remediation of inorganic and organic water contaminants (Awad et al., 2017).

A study on characteristics of biochar produced from rapeseed straws and poplar tree shavings at a temperature ranging from 300 degrees Celsius to 800 degrees Celsius indicated that an increase in temperature increased the porosity of the biochar (Gheorghe-Bulmau et al., 2021). In addition, biochar characterisation from wooden biomass (soft and hard) showed that surface morphology had a highly distinctive honeycomb structure with a very small pore diameter (Bamdad & Hawboldt, 2016). This is a significant feature of biochars that can be applied in the gas sorption process.



**Fig 1:** FE-SEM image of (A) Sugarcane bagasse (B) Wheat husks adapted (Suman, Panwar, & Gautam, 2017)

## Chemical Composition of Pyrolytic Biochars

Biochars being by-products of biomass pyrolysis at very high temperatures is majorly carbonaceous with the absence of polyaromatic compounds (PAHs); hence, it is safe for use (Agarwal et al., 2015). On the other hand, biochars are known to have high carbon content that depends on the biomass used and low content of hydrogen and oxygen (Cha et al., 2016). The levels of these elements, in particular biochar, are majorly dependent on the pyrolysis temperatures, the type of pyrolysis, whether slow or fast and biomass feed used (Dhyani and Bhaskar, 2018).

Biochar mainly contains C, H, N, S, O and other trace elements depending on the feedstock used and pyrolysis conditions (Lehmann et al., 2011; Kim et al., 2013; Kwak et al., 2019). The elemental quantification of carbon, hydrogen and nitrogen in biochars helps in understanding its quality (Yuan et al., 2022). The elemental analysis is determined from their corresponding oxides, CO<sub>2</sub>, H<sub>2</sub>O and NO<sub>2</sub>, respectively (Enders et al., 2017). The carbon content for most biochars is quite (> 80%), while hydrogen is found to be almost constant at 1.4 per cent, and nitrogen and other organic materials are in trace amounts (Kim et al., 2013). For example, a study carried out of various biomass-derived char (wood maize and meadow grass) showed that nitrogen content is below 2 per cent by wt, the hydrogen content is more or less 2 per cent. In contrast, oxygen content varies between 13 per cent and 23 per cent and carbon content varies between 44 per cent and 64 per cent (Břendová et al., 2012).

Biochars are very stable in the soil environment and can remain unbleached for very many years (Chen et al., 2019). This property of biochars has been explored for use in soil sequestration. Additionally, the level of metals such as K, Na, Ca, Mg, and Al in biochar vary with the type of biomass used (Nanda et al., 2013; Tong et al., 2011). The composition of biomass and pyrolysis temperatures tend to affect the morphology and Physiochemical properties of biochars-table 1. Biochars formed at high temperatures above 600 °C have been shown to have higher Cation exchange capacity, surface area, and micro porosity and stronger buffering capacity, and thus are more promising to improve soil fertility remediation heavy metals in the environment (Antonangelo et al., 2021; Yuan et al., 2022)) and as industrial adsorbents. In addition, previous research has biochar can be a promising bio fertiliser as it contains macronutrients (Suman et al., 2017; Tong et al., 2011;, 2021).

**Table 1. Composition of Biomass-Derived Biochar**

Author/year	feedstock	Thermal procedure	Operating temp. °C	Surface functionality of biochar
Tong et al., 2011	straws of peanut, soybean and canola	pyrolysis	400	Cations of Ca <sup>2+</sup> , Mg <sup>2+</sup> , K <sup>+</sup> , and Na <sup>+</sup> and non-metals total P, N and C were found in biochars
Bamdad & Hawboldt,	rapeseed straws and poplar tree	Fast pyrolysis	450	High carbon content and aromatic functional groups in biochar than a metal-organic framework. Porous

2016	shavings			carbonaceous
(Suman et al., 2017)	Sugarcane bagasse and wheat husk	pyrolysis	800	Minerals K, Mg, Si, and P with rich micropores
Mara et al., 2018	Olive mill waste	pyrolysis	300-1000	Highly porous with complete absence of organic compounds at temperatures > 500 °C
Antonangelo et al., 2019	Switch grass & poultry litter	pyrolysis	350 & 700	Presence of hydroxyl groups, aromatic rings, phosphate-containing functional groups, organic azides, ketenes
Qin et al., 2020	pine nutshells	pyrolysis	400-700	Phenols, alcohols, carboxylic groups, basic acidic and lactonic compounds
Vilakazi, 2021	Potato peels, cull potato & pine bark	pyrolysis	350 & 650	Alkaline with P and K

Biomass decomposition starts at temperatures slightly above 200 °C, subject to the nature of char and gaseous pathways in the reactor (Hoang et al., 2021).

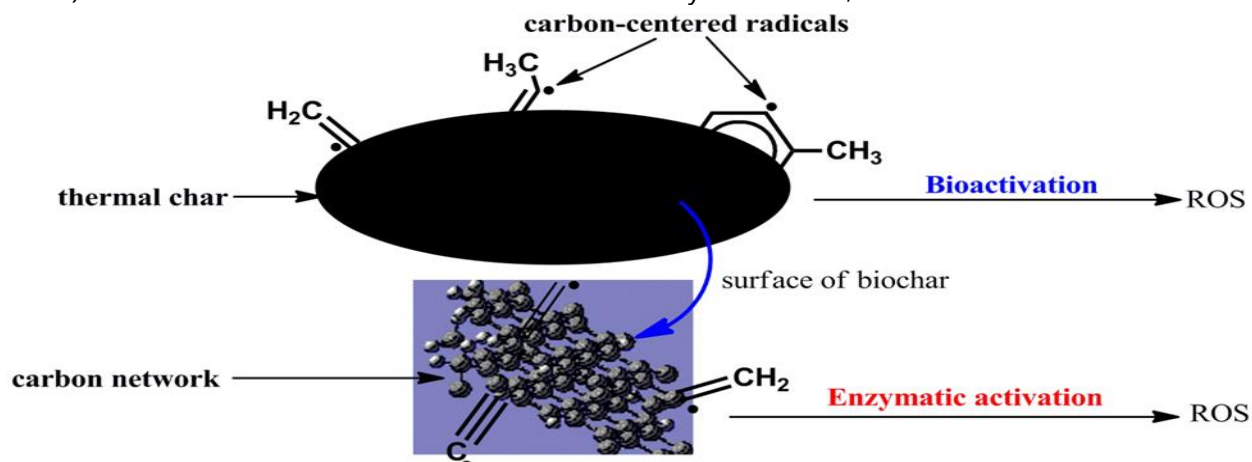
## Environmental Persistent Free Radicals (EPFRs) on Biochars

The availability and environmental compatibility of biochar have made it to be utilised in the remediation of environmental pollutants and soil sequestration. Recent advances in biochar chemistry have shown the presence of environmentally persistent free radicals on its surface structure (Zhao et al., 2018; Yuan et al., 2022). The presence of EPFRs on biochars' surfaces is one of the chemical properties that give them cation exchange capacity and can be used to remediation of heavy metals in soil and water (Yuan et al., 2022). Past research has demonstrated that free radicals have caused inhibition of germination and damage of plasma membrane in plants (Liao et al., 2014).

Thermochemical transformation of biomass generates free radical intermediates in the gas phase (Melkior et al., 2012). However, stable radicals are usually immobilised on the solid matter – thermal char and/or particulate emissions (Chelangat, 2020). This review aimed at establishing the type of free radicals emitted during the pyrolysis production of biochar. This is of great significance as it determines the safety in their diverse applications.

Free radicals are the main precursors of reactive oxygen species (ROS) production in biological systems (Dellinger et al., 2001; Shi et al., 2021; Zhao et al., 2022). Reactive oxygen species, including lipids, proteins, and deoxyribonucleic acid (DNA), can contribute to severe oxidative stress within cells through the formation of oxidised cellular macromolecules (Moridani et al., 2004). For example, EPR studies on rice husks biochar showed the presence of hydroquinone-Quinone moieties on biochar (Zhang et al., 2018).

The generation of stable free radicals is initiated by primary thermal cracking reactions. The organic matter is further broken down into small unstable radical fragments that reside on carbon char surfaces (Tian et al., 2009). A model of radical immobilisation was done by Kibet et al., 2018 –scheme 1.



**Scheme 1:** A model of free radicals immobilised on the surface of croton char particulate and possible channels in the generation of reactive oxygen species (ROS) in bio systems (Mosonik et al., 2018).

## Electron Spin Resonance Spectroscopy and Radical Characteristics

The electron paramagnetic resonance refers to the resonance absorption of the electromagnetic radiation by electronic systems that possess permanent magnetic moments due to the orbital as well as the spin angular momentum of electrons, which are paramagnetic ( Dellinger, 2015; Weil & Bolton, 2007; Lancaster, 1967). The stability of EPFRs embedded in biochar has indicated that the radicals' decay rate is very low because of the presence of resonance stabilised Pi systems in their structures. Consequently, they tend to be available in the environment for longer periods causing a lot of harm in the end. This fact has attracted the researcher's attention as opposed to short-lived radicals such as hydroxyl and oxygen.

Electron spin resonance spectroscopy (EPR) study was conducted on original wood, herbaceous biomass, holocelluloses, lignin and their chars, prepared at high temperatures up to 1400 °C showed high radical concentrations in the decay stage (  $7.1 \times 10^{16}$  and  $1.5 \times 10^{18}$  spins/g) (Trubetskaya et al., 2016) and there was no correlation existing between the nature of feedstock and concentration of radicals. Biochars generated from the combustion of *Croton megalocarpus* biofuel indicated high concentrations of radicals after 80 days of generation, as in Table 2.

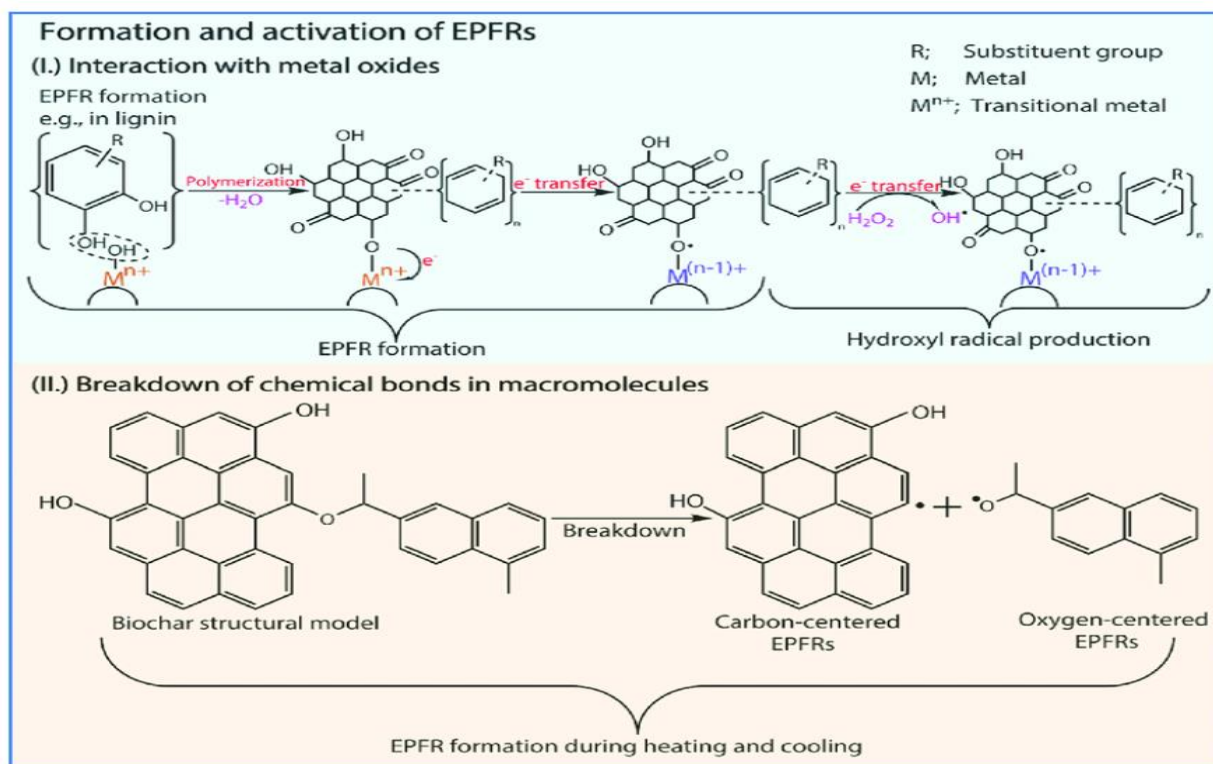
**Table 2: The EPR Parameters for the Thermal char Formed from the Co-pyrolysis of the Binary Mixture of Biodiesel and Conventional Diesel.**

Char/Run	Time (days)	g/cm	spins/cm	spins/g
BCD (1)	20	0.0022	$3.84 \times 10^{17}$	$9.18 \times 10^{19}$
BCD (2)	50	0.0022	$3.63 \times 10^{17}$	$8.03 \times 10^{19}$
BCD (3)	60	0.0022	$3.55 \times 10^{17}$	$7.88 \times 10^{19}$

BCD (4)	80	0.0022	$3.34 \times 10^{17}$	$7.81 \times 10^{19}$
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**Legend:** BCD- Binary mixture of biodiesel and conventional diesel (Kibet et al., 2018)

EPFRs are stable and relatively unreactive radicals due to the presence of resonance stability. Radicals have been classified according to g-factor; Carbon-centred has g-factors similar to the ones of free electron ( $g < 2.003$ ), carbon centred radicals with an adjacent oxygen atom ( $g = 2.003-2.004$ ) and oxygen centred ( $g > 2.004$ ) radicals (Dellinger et al., 2007) -scheme 2.



Scheme 2: EPFR formation and free radical generation mechanisms on biochar (adapted from (Odinga et al., 2020).

The oxygen-centred radicals are more stable in an atmospheric environment less reactive, whereas carbon-centred radicals are prone to oxidation in the atmosphere (Wan et al., 2020) due to conjugation via pi systems in the aromatic compound. For instance, semi Quinone radicals has g-factor  $> 2.0045$  indicating oxygen-centred, while cyclopentadienyls are carbon centred radicals ( $g < 2.003$ ) (Wan et al., 2020).

## 5.0 CONCLUSIONS AND RECOMMENDATIONS

**Conclusion:** Biochar being a highly porous and carbonaceous material has found its use in various sectors globally, ranging from the agriculture sector to environmental remediation of pollutants. However, its boast myriad applications, it suffers from immobilised persistent free radicals that threaten human health and plants. EPFRs has been seen to induce the formation of reactive oxygen species, which are known to cause oxidative stress on biological systems.

**Recommendation:** This review recommends further research on the effects of EPFRs on biological systems and optimum conditions for the formation of biochars with almost nil radicals.

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