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# Biocarbon Emissions and Risks Assessment in Pyrolysis and Combustion

Bénit Bouesso, Ronan Pelé, María González Martínez, Morgane Poser, and Ange Nzihou*

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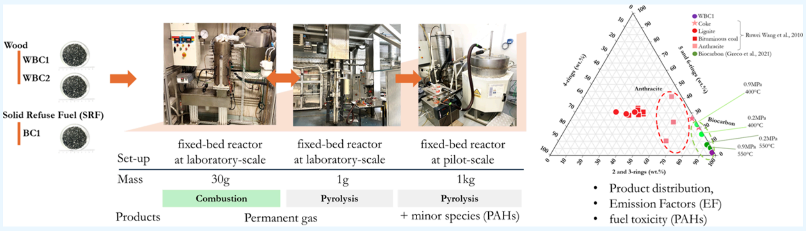

**ABSTRACT:** Decarbonization of society requires industry to urgently reduce carbon-based and toxic gas emissions, such as polycyclic aromatic hydrocarbons (PAH), to mitigate their environmental impact and associated health risks. Biocarbon (Biochar), due to its properties closer to those of coal and the biogenic nature of its emissions, is a renewable alternative to replace fossil fuels in industrial processes. In this context, the objective of this work is to determine gaseous emissions fate and toxicity in pyrolysis and combustion for biocarbon from solid refuse fuels (SRF, named BC1) and 2 biocarbons from wood with different H/C ratios and volatile matter (VM) content (WBC1, WBC2). The obtained results were correlated to resource characteristics and compared with standard values reported for fossil fuels. Emission factors (EF, $g_{gas}/g_{fuel}$) were calculated for the main permanent gases (CO, $CO_2$, $H_2$, $CH_4$), as well as for PAH. Biocarbons EF were directly related to their physicochemical characteristics, namely their VM content and, to a lesser extent, their inorganic composition, catalyzing or inhibiting thermochemical conversion reactions. High VM content biocarbon (WBC1, 18.5 wt%) was associated with higher EF values (i.e., 3696 $g_{CO2}/kg_{fuel}$). However, EF($CH_4$+$H_2$) values at pilot scale met EN ISO 562 standard (<4 wt%) both in pyrolysis (2.8 wt% yield for WBC1) and combustion (0.07 and 0.3 wt% for WBC2 and BC1, respectively). Although PAH released by high VM content biocarbon (WBC1) were less toxic due to their lower number of aromatic rings (<3), they presented a higher EF (46.3 $mg_{PAH}/kg_{fuel}$) than that reported for fossil fuels (0.002−64.0 $mg_{PAH}/kg_{fuel}$). As a result, the toxicity equivalent factor (TEQ), associated with the carcinogenic potential of a PAH and its yield, was higher for biocarbon (WBC1, 0.132) compared with fossil fuels (0.005−0.03). Most importantly, reduce condensable species production, and, consequently, lower EF values for permanent gases were measured (2000−2980 $g_{CO2}/kg_{fuel}$) in combustion, and no PAH was detected, resulting in a lower TEQ.

## 1. INTRODUCTION

For decades, high-ranking fossil fuels have been the main energy source in many industrial processes. They are associated with high calorific performance, which depends on their degree of maturity.[1] Hard coal, namely, anthracite, has been used for this purpose at an industrial scale. About 75% of global $CO_2$ emissions (38.8Gt, in 2022) come from the combustion of fossil fuels.[2] In the short term, there is an urgent need to replace fossil fuels with coal fuels derived from renewable resources, such as biomass and waste, due to their low cost and abundance.

Pyrolysis is used to produce biosourced fuels from biomass, with thermal and processing properties close to those of coal. This process implies heating biomass (300 °C < $T$ < 1000 °C) under an inert atmosphere. During pyrolysis, devolatilization occurs through depolymerization, fragmentation, and cross-linking of biomass macromolecules. As the temperature rises, aldehydes and ketones will be formed at 100 °C; thus, from 300 to 350 °C, the decomposition of the cellulose chain occurs, as well as the decarboxylation reaction of hemicellulose.[3] Above 550 °C, there is a fusion of biocarbon ring structures, making biocarbon more aliphatic and less aromatic.[4]

Combustion and pyrolysis of carbon-based fuels are associated with emissions, including particle matter (PM), permanent gases (CO, $CO_2$, $H_2$, $CH_4$), sulfur oxides (SOx), nitrogen oxides (NOx), and condensable species ($C_2H_2$, $C_2H_4$, $C_2H_6$, $C_6H_6$, etc.). The distribution of these products is directly related to fuel composition and characteristics, as well

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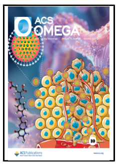

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Table 1. Elemental Composition of Biocarbon Samples

| sample | C | H | O[a] | N | $A_{550}$ | VM | H/C | AAEM (Na, K, Mg, Ca) | Si+Al | AAEM/(Si+Al) |
|---|---|---|---|---|---|---|---|---|---|---|
| | wt%, daf | | | | | | | g/kg (ash), db | | |
| BC1 | 70.2 | 2.5 | 16.4 | 2.87 | 8.04 | 12.9 | 0.43 | 1.37 | 1.13 | 1.2 |
| WBC1 | 81.8 | 3.02 | 12.5 | <0.01 | 2.7 | 18.5 | 0.44 | 0.21 | 0.07 | 3 |
| WBC2 | 90 | 1.01 | 6.96 | <0.01 | 2.01 | 4.7 | 0.13 | 0.12 | 0.02 | 6 |

[a] By difference, $S < 0.01$ wt%, daf: dry ash-free basis; db: dry basis.

as to process operating conditions. For example, hydrocarbons were reported as precursors of gas and condensable species.[5] Pyrolysis promotes the highest production of condensable species, such as phenolic compounds from lignin and anhydrosaccharides and furans from cellulose and hemicellulose, together with other small molecules such as acetic acid, methanol, and water.[6,7] Combustion can enhance the oxidation of some of these released species and thus result in lower emissions, mostly composed of small gases such as CO, $CO_2$, and water.[8] The distribution of these products is directly related to fuel composition and characteristics as well as to process operating conditions. For example, hydrocarbons were reported as precursors of gas and condensable species.[5] These two situations constitute extreme conditions for thermal conversion.

Emissions related to a given species (i.e., $CO_2$) can be evaluated through the emission factor (EF), which represents the quantity of a given gaseous compound produced in pyrolysis or combustion by units of fuel mass. Bituminous coal EF values reported for $CO_2$ (1800 mg/$kg_{fuel}$) and CO (87 mg/$kg_{fuel}$) were higher than those for anthracite (1100 and 56 mg/$kg_{fuel}$, respectively).[9] The increase in pyrolysis temperature showed a decrease in CO production.[10] However, at an equivalent pyrolysis temperature (300 °C), peanut shell biocarbon produces 5% higher $CO_2$ compared to wheat straw biocarbon (13.5 wt%).[8]

Among thermochemical conversion products, polycyclic aromatic hydrocarbons (PAH) require particular monitoring due to their high toxicity. These organic pollutants, which contain two or more condensed benzene rings in their structure, were demonstrated to be carcinogens and teratogens.[11] PAH are formed during biomass pyrolysis due to the combination of aromatic rings already present in the raw resource or formed because of the dehydrogenation, polymerization, cyclization, and aromatization of biomass polysaccharides or of its decomposition products.[12] At high pyrolysis temperatures (>400 °C), PAH mostly result from the rupture of the main carbon chain of the carbon residue, followed by condensation and repolymerization reactions.[13] PAH are present in the pyrolysis gas phase to a higher extent than in the solid phase (biochar), but they can recondense on its surface depending on the reactor configuration and operating conditions.[14] In terms of toxicity risk assessment, the U.S. Environmental Agency selected 16 PAH to be monitored as priority pollutants due to their toxicity and representativeness of this chemical family.[15] The number of rings of an aromatic compound, such as PAH, which is directly related to pyrolysis operating conditions, may be an indicator of its carcinogenic potential and thus its toxicity.[16] Indeed, small PAH (2 and 3 rings), produced at low pyrolysis temperatures (around 400 °C), present a lower toxicity than larger PAH, which were reported to be mostly released above 500 °C.[17] In the case of PAH, toxic equivalent factors (TEQ) can be calculated to indicate the carcinogenic potential of a PAH by considering benzo[a]pyrene as a reference and ponderating by the production yield of each PAH.[18] Furthermore, the fuel grade is also directly related to its emissions.[10] PAH EFs were reduced by 75 and 80% when using semicoke and 90 and 97% when using upgraded coke.[10]

In this context, the objective of this work is to determine gas EFs and associated toxicity from biocarbon pyrolysis and combustion. The results were correlated with the bioresource characteristics. A comparison was made with standard values reported for fossil fuels, as biocarbon is considered an alternative to replace fossil fuels in industrial processes. To this end, product yields were determined for three biocarbon samples (one from solid refuse fuel (SRF) and two from wood) in pyrolysis and combustion. EFs related to permanent gases (CO, $CO_2$, $CH_4$, $H_2$) and PAH were calculated. Toxic equivalent factors were also determined for PAH due to its high toxicity and restrictive environmental regulations. The results were compared to those reported for fossil fuels and with environmental thresholds.

## 2. MATERIALS AND METHODS

### 2.1. Selected Materials.

Biocarbon samples were produced through pyrolysis at 600 °C. The influence of the resource was studied by comparing a biocarbon sample derived from solid waste fuel (SRF, named BC1) and a biocarbon sample derived from wood (WBC1). In parallel, the influence of post-treating the wood-derived biocarbon according to a confidential industrial process, which led to a lower hydrogen to carbon (H/C) ratio and lower volatile matter content (WBC2), was also assessed. The tests were performed with 2−5 mm particle size samples, which were previously dried for 24 h at 105 °C in an oven.

Elemental analysis (EN ISO 16948) was carried out for biocarbon samples (Table 1). Ash content was determined at 550 °C ($A_{550}$, EN ISO 21656), and ash inorganic composition was quantified by ICP-OES (EN ISO 16967). Inorganic elements were regrouped according to their reported catalytic or inhibitor effect in thermochemical conversion, namely, Alkaline and Alkaline-Earth Metals (AAEM) and Silicon + Aluminum (Si + Al), respectively, as well as the ratio between them (AAEM/(Si + Al)). Volatile matter (VM) content determination was carried out at 900 °C for 7 min in an oven (EN ISO 18123).

The carbon content of wood biocarbons (81.8−90.0 wt%, Table 1) was higher than that reported in the literature (51.2−75.6 wt%), due to the relatively low pyrolysis temperature for biocarbon production (600 °C).[19] The H/C ratio decreased for biocarbons with a lower VM content (i.e., 0.44 for WBC1 and 0.13 for WBC2). Wood biocarbons presented the lowest ash content (2.01−2.70 wt%). These values were lower than those reported for fossil solid fuels such as anthracite (3.80−57.1 wt%).[20,21] VM content was the main difference in the proximate analysis for biocarbon samples from the same resource. BC1 and WBC1 exhibited higher VM content (12.9 and 18.5 wt%, respectively) compared to WBC2 (7.53 wt%, Table 1).

In general, the AAEM content measured for wood biocarbons was lower (0.12−0.21 g/$kg_{ash}$, Table 1) than that measured for biocarbon (1.37 g/$kg_{ash}$, Table 1). This was also the case for Si+Al (0.02 and 0.07 g/$kg_{ash}$, for wood biocarbons, and 1.13 g/$kg_{ash}$ for SRF biocarbon). AAEM were reported to enhance combustion as promoters of the catalysts in oxidation reactions,[22] while silicon (Si) and aluminum (Al) were pointed to be inhibitor metals.[23] The effect of these elements on the thermal behavior of biocarbon samples was demonstrated by thermogravimetric analysis in a previous study.[24] The ratio between catalytic (AAEM) and inhibitor (Si+Al) metals (AAEM/(Si+Al)) was calculated. The obtained values indicated that promoters are predominant for wood biocarbons compared to inhibitor metals. In the case of SRF biocarbon, the AAEM/(Si+Al) ratio close to 1 suggested a compensation effect between both types of metals, which may result in a mitigated catalytic or inhibitor impact on thermochemical conversion. The recombination of Si with O to form silicate ($SiO_2$) may decrease the reactivity of fuel mixtures in cocombustion.[25] Potassium may enhance the formation of silicon−aluminum ($Al_2SiO_5$), which is responsible for fusion and sintering in ash content.[26]

**2.2. Methodology.** *2.2.1. Experimental Setup.* Fuel emissions were assessed from laboratory scale to pilot scale in different setups. This includes 2 fixed-bed reactors at laboratory scale for pyrolysis (1 g) and combustion (30 g), and 1 fixed-bed reactor at pilot scale for pyrolysis tests (1 kg). At the lab scale, the chemical regime and thus the control of heat transfer limitations allowed a direct correlation of emission release with pyrolysis and combustion operating conditions, as well as with the characteristics of the biocarbon samples (resource, composition in terms of H/C ratio, and VM content). At the pilot scale, minor compounds such as PAH could be detected thanks to the higher sample mass. Each experiment was carried out twice to check results repeatability.

*2.2.1.1. Pyrolysis in Fixed-Bed Reactor at Laboratory Scale.* A downdraft fixed-bed reactor was used for pyrolysis tests at the laboratory scale (Figure 1). It allowed emission quantification at a given temperature for a given sample mass (around 1 g). The furnace was heated from ambient temperature to 800 °C at 20 °C/min under a $N_2$ flow rate of 0.85 N $m^3$/h. Once this temperature was reached, the crucible was lifted and placed in the center of the furnace. The exhaust gases were collected since the crucible was introduced in the reactor, and for the whole duration of the test. A cold condensable trap (−20 °C, tar protocol) was used to trap condensable species into isopropyl alcohol, and silica gel was used to remove moisture. After the tar protocol, clean exhaust gas was collected using four 10 L Tedlar bags. The experiment ended when the $CO_2$ concentration tended to zero.

*2.2.1.2. Pyrolysis in Fixed-Bed Reactor at Pilot Scale.* A fixed-bed reactor was used at the pilot scale to enhance the capture of condensable species in pyrolysis, especially minor ones such as PAH. 1 kg of sample was introduced in the reactor under a 15Nl/h flow of $N_2$ (Figure 2). The sample was then heated from ambient temperature to 800 °C at 20 °C/min. The temperature was maintained at 800 °C until no $CO_2$ production was observed, indicating that the transformation ended. The exhaust gas was cleaned by passing it through two condensers at 0 °C, and then moisture was removed using silica gel. An online monitoring of cleaned permanent gases through micro-GC was carried out. A derivation of 1 Nl/h of the exhaust gases produced was connected to a cold condensable trap (−20 °C, tar protocol) for a fine condensable species determination. The cold condensable trap was composed of two isopropanol impinger bottles (room temperature and −20 °C, respectively) and then a silica gel trap to remove moisture.

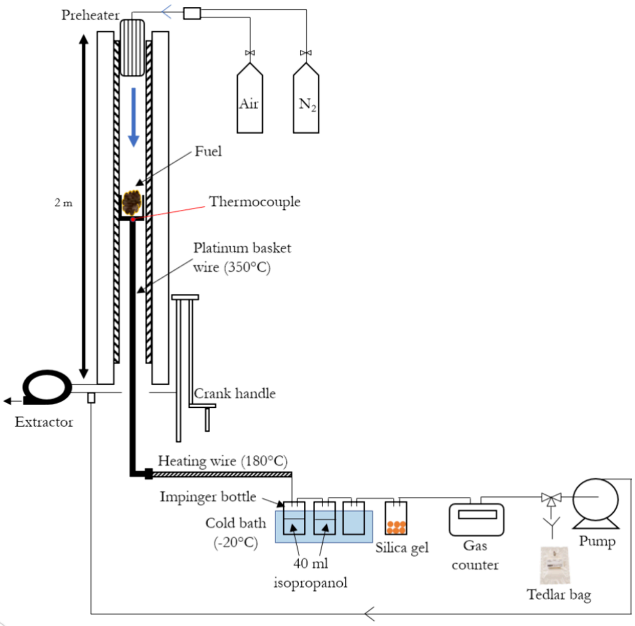

**Figure 1.** Schematic diagram of the fixed-bed reactor for pyrolysis experiments at laboratory scale.

*2.2.1.3. Combustion in Fixed-Bed Reactor at Laboratory Scale.* Combustion was carried out in a fixed-bed reactor at a laboratory scale to monitor permanent gas production and to enhance volatile species trapping for a given mass sample (30 g, Figure 3). The sample was introduced and heated in a stainless-steel tubular reactor from room temperature to 105 °C for 30 min to remove moisture. Then the temperature was increased up to 800 °C at a rate of 20 °C/min and held for 2h to ensure total combustion. A gas flow rate of 0.12 $m^3$/h was used, and the bed temperature was monitored during the test. A condensable trap with two impinger bottles with 2-propanol at −20 °C was used in the gas exhaust. Cleaned permanent gases were then collected using 0.5 L bags at each 100 °C.

*2.2.2. Analytical Protocols. 2.2.2.1. Permanent Gas Analysis.* Permanent gases ($CO_2$, CO, $CH_4$, and $H_2$) were quantitatively analyzed using an A3000 Agilent Micro GC, by considering the average of five measurements. The injection duration was 70 ms, and the total duration of analysis was 200 s. The online quantification in the pilot-scale fixed-bed reactor consisted of one measurement every 3 min.

*2.2.2.2. Condensable Species Analysis.* 1 $\mu$L of the condensable species collected into isopropanol, thanks to the cold trap, was injected into a gas chromatography−mass spectrometer (Shimadzu GC/MS-TQ8030) at a split ratio of 10. A Rxi-5Sil MS column with a length of 30 m, an inner diameter of 0.25 mm, and a film thickness of 25 $\mu$m was used with a flow rate of 3 mL/min of helium. The GC temperature program was 40 °C for 5 min, then increased to 280 °C at 5 °C/min, held for 20 min, and finally increased to 300 °C and

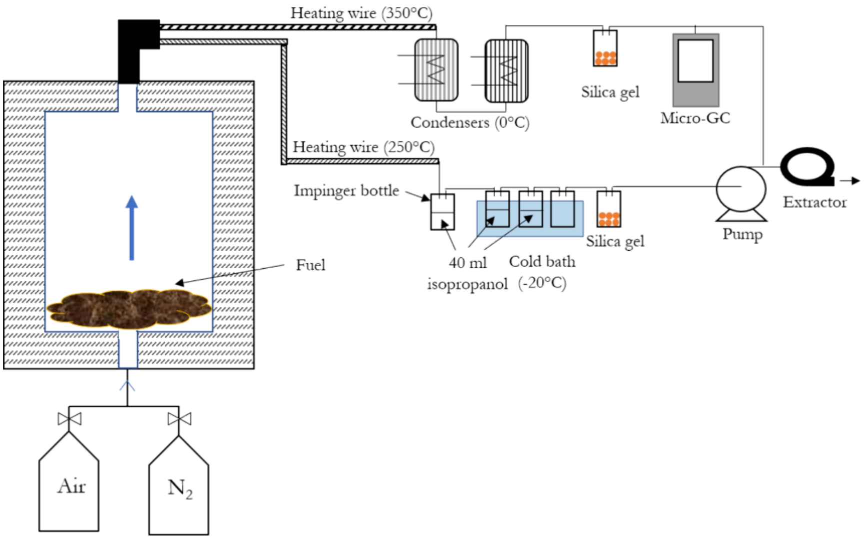

**Figure 2.** Schematic diagram of the fixed-bed reactor for pyrolysis experiments at pilot scale.

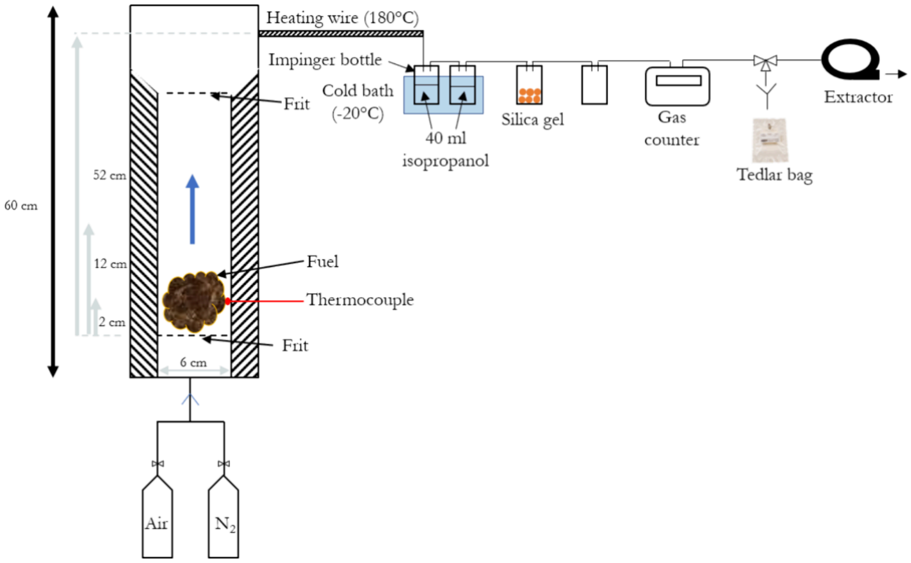

**Figure 3.** Schematic diagram of the fixed-bed reactor for combustion experiments at the laboratory scale.

held for 10 min. The analysis lasted 70 min. The chemical compounds identified were in the $m/z$ range of 40−600.

Among condensable species, PAH was quantified by setting a custom single ion monitoring (SIM) mode to focus the MS on the corresponding $m/z$. The temperature program of the GC has been updated to evaluate the 16 PAH according to EN 17503 standard:[27] GC started at 60 °C, then temperature was increased to 120 °C at 20 °C/min and held for 1 min before being increased to 180 °C at 5 °C/min, then increased to 200 at 20 °C/min, then increased to 270 at 2 °C/min and finally increased to 300 °C at 30 °C/min and held for 3 min. The analysis duration was 56 min. An ionization energy of 70 eV operated the mass-selective detector in electron impact ionization mode. The temperatures of the transfer line and ion source were 280 and 250 °C, respectively. Calibration was performed using standards based on the correlation of area peaks and concentrations (calibration curves in Supporting Information, Figure S1).

Water content in condensable species was determined using the Karl Fischer method using a V30 Mettler Toledo volumetric titrator. Hydranal composite was used as a titrant of about 0.5 g of isopropanol solvent for the blank and analysis.

#### 2.2.3. Data Treatment. 2.2.3.1. Product Yield.

Product yield ($Y_i$) was determined as the ratio between the product mass and the initial mass of fuel (eq 1). In the case of the solid residue, it corresponded to the difference in the fuel mass before and after the test.

$$Y_i\ (\text{wt. \%}) = {}^{m_i}\!/_{m_{\text{fuel,t0}}} \times 100 \tag{1}$$

where $m_i$ is the mass of the product and $m_{\text{fuel,t0}}$ is the initial mass of fuel.

In combustion, the product yield was determined after removing the excess air (eq 2) based on the balance of $N_2$ (inert).

$$Y_{i,\text{combustion}}\ (\text{wt. \%}) = \{[{}^{m_i}\!/_{m_f}(m_{\text{total}} - m_{N_2})] - e_{\text{air}}\} \times 100 \tag{2}$$

where $e_{air}$ is the excess of air (%), and $m_{total}$ and $m_{N2}$ correspond to the mass (mg) of total gas produced and of nitrogen, respectively.

*2.2.3.2. Emission Factor.* The emission factor ($EF_i$) corresponds to the quantity of a given gaseous species produced in pyrolysis or combustion by unit of fuel mass (eq 3). It corresponds to the product yield in pyrolysis when it is not expressed as a percentage.

$$EF_i = m_i/\Delta m_f \tag{3}$$

where $m_i$ is the mass of a gaseous species (g), $\Delta m_f$ represents the change in fuel mass during combustion or pyrolysis (g).

*2.2.3.3. Toxic Equivalent Factor.* The toxic equivalent factor (TEQ) was determined based on PAH emissions and the toxicity of PAH, which was related to its ring number. Toxic equivalent factors (TEF) correspond to the carcinogenic potential of a PAH. Benzo[a]pyrene was taken as a reference, and a weight of one was assigned to it (Table 2). Sixteen PAH were analyzed following the EN ISO 17503 standard.[27] The toxicity of a fuel ($TEQ_{fuel}$) was calculated by considering the TEF of each HAP emitted weighted by its associated yield ($Y_i$, eq 4).

**Table 2. TEQ Values Attributed to the Common PAH Species[18a]**

| PAH species | number of rings | TEF |
|---|---|---|
| naphthalene | 2 | 0.001 |
| acenaphthylene | 3 | 0.001 |
| acenaphthene | 3 | 0.001 |
| fluorene | 3 | 0.001 |
| phenanthrene | 3 | 0.001 |
| anthracene | 3 | 0.01 |
| fluoranthene | 4 | 0.001 |
| pyrene | 4 | 0.001 |
| benz[a]anthracene | 4 | 0.1 |
| chrysene | 4 | 0.01 |
| benz[e]acephenanthrylene | 5 | 0.1 |
| benzo[k]fluoranthene | 5 | 0.1 |
| **benzo[a]pyrene** | **5** | **1** |
| indeno[1,2,3-cd]pyrene | 6 | 0.1 |
| dibenz[a,h]anthracene | 5 | 1 |
| benzo[ghi]perylene | 6 | 0.01 |

[a] Reprinted with permission from I.C.T. Nisbet and P.K. LaGoy, Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). Copyright 1992 Regulatory Toxicology and Pharmacology.

$$TEQ_{fuel} = \sum_{i}^{16} TEF_i.\ Y_i \tag{4}$$

## 3. RESULTS AND DISCUSSION

**3.1. Emissions in Pyrolysis.** Fuel emissions in pyrolysis were assessed in terms of permanent gases (CO, $CO_2$, $H_2$, $CH_4$, and hydrocarbons) and condensable species, including water and, at pilot scale, HAP.

*3.1.1. Pyrolysis in Fixed-Bed Reactor at Laboratory Scale.* A fixed-bed reactor was used for pyrolysis experiments at laboratory scale (800 °C, around 1 g) to provide the analysis of the pyrolysis products under isothermal conditions, with a focus on permanent gases.

*3.1.1.1. Product Distribution.* The distribution of biocarbon pyrolysis products was determined at 800 °C. A higher mass of solid residue was obtained for low VM content biocarbon (WBC2, 92.2 wt%) compared to high VM content ones (80.8−84.0 wt%, for BC1 and WBC1, respectively), which may be related to enhanced C−H bond cleavage.[28] Furthermore, high temperature (800 °C) and long residence time (2 h) favored carbon conversion and interaction with oxygen, leading to a higher production of gas and condensates.[29] Low VM content biochars presented lower condensate yield, as observed for WBC2 (5.26 wt%) compared to WBC1 (10.5 wt %). Furthermore, WBC2 showed lower permanent gas emissions (2.54 wt%) compared to WBC1 (5.53 wt%) and BC1 (5.72 wt%), which may be related to VM content, while the slight difference between these last two samples will be related to the resource.

*3.1.1.2. Emission Factors.* Emission factors ($EF_i$) of biocarbons were calculated for the total production of permanent gases (CO, $CO_2$, $CH_4$, and $H_2$) in 2 h-pyrolysis tests (Table 3).

**Table 3. Emission Factors of Permanent Gases on Pyrolysis Tests in the Fixed-Bed Reactor at Laboratory Scale[a]**

| | EF | | | | | |
|---|---|---|---|---|---|---|
| samples | $CO_2$ | CO | $H_2$ | $CH_4$ | $H_2/CO_2$ | $CO/CO_2$ |
| | $g/kg_{fuel}$ | | | | | |
| BC1 | 4149 | 1014 | 221 | 332 | 0.053 | 0.24 |
| WBC1 | 3696 | 1260 | 249 | 546 | 0.067 | 0.34 |
| WBC2 | 2435 | ND | 7.51 | ND | 0.003 | <0.02 |

[a] ND: detection limit: <50 $g/kg_{fuel}$.

The lowest EF was observed for low VM content biocarbon (WBC2). The EFs were comparable for biocarbons, except for $H_2$, where the WBC2 EF is an order of magnitude lower (7.51 $g/kg_{fuel}$) than that of WBC1 (249 $g/kg_{fuel}$). In general, high VM content biocarbons showed higher $CO_2$ EF (BC1:4149 $g/kg_{fuel}$, WBC1:3696 $g/kg_{fuel}$). All EF values of WBC2 were lower than those of other biocarbons, which may indicate the impact of a low VM content in decreasing biocarbon-associated emissions.

$H_2/CO_2$ ratio was calculated as an indicator of the competition between the water−gas shift reaction (WGS, eq 5) and Boudouard reaction (eq 6), and thus $H_2$ production.[30] In this case, WBC1 presented the highest $H_2/CO_2$ ratio (0.067), comparable to that of BC1 (0.053). Lower values were found for low VM content biocarbon (0.003), directly associated with their lower $H_2$ production. This could be explained by the hydrogasification reaction related to $CH_4$ production with the consumption of carbon and $H_2$ (eq 7). On the other hand, $CH_4$ oxidation may lead to the production of $H_2$ via steam methane reforming (eq 8).[31] However, no correlation could be established between $CH_4$ and $H_2$ production in this study.

$$\begin{aligned}&\text{Water Gas Shift (WGS): } CO + H_2O\\ &\quad \leftrightarrow CO_2 + H_2,\ \Delta Hr\\ &\quad = -41 kJ/mol\end{aligned} \tag{5}$$

$$\text{Boudouard: } C + CO_2 \rightarrow 2CO,\ \Delta Hr = +172 kJ/mol \tag{6}$$

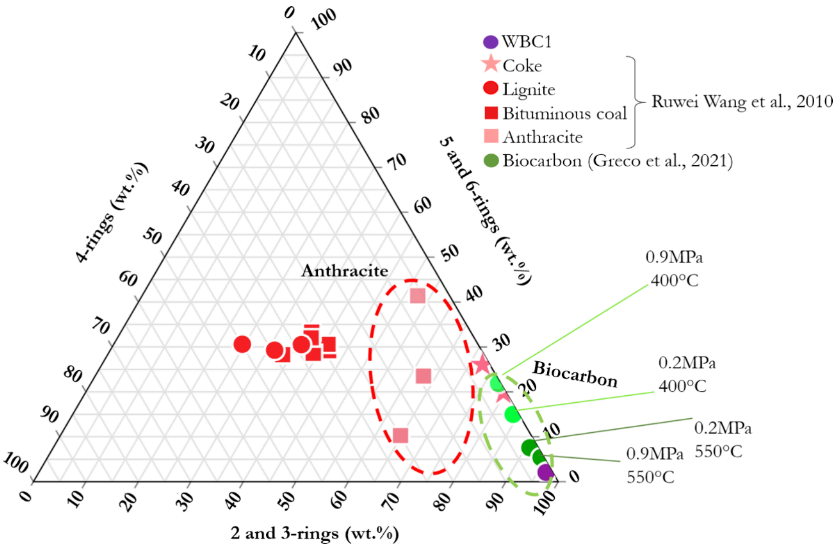

**Figure 4.** PAH ring distribution as a function of the coal type[38] (Adapted with permission from R. Wang et al., Abundances of Polycyclic Aromatic Hydrocarbons (PAHs) in 14 Chinese and American Coals and Their Relation to Coal Rank and Weathering, Copyright 2010 Energy Fuel), biocarbon[37] (Adapted with permission from G. Greco et al., Importance of pyrolysis temperature and pressure in the concentration of polycyclic aromatic hydrocarbons in wood waste-derived biochars, Copyright 2021 Journal of Analytical and Applied Pyrolysis), and investigated fuels such as woody biocarbon, anthracite, and woody biocarbon/anthracite mixture.

$$\text{Hydrogasification: } C + 2H_2 \rightarrow CH_4,\ \Delta Hr = -73\text{kJ/mol} \quad (7)$$

$$\text{Steam methane reforming: } CH_4 + 2H_2O \rightarrow CO + 3H_2,\ \Delta Hr = +206\text{kJ/mol} \quad (8)$$

The inorganic composition of the fuel may affect the balance between water–gas shift (WGS) reaction and other reactions in the gas phase, thus explaining the differences between biocarbons in terms of $CO/CO_2$ ratio.[32] As a result, a high $CO/CO_2$ ratio may suggest that $CO_2$ is consumed to produce CO via the Boudouard reaction. In this study, WBC1 showed the highest $CO/CO_2$ ratio (0.34), which was in agreement with its higher AAEM/(Si+Al) ratio (6.0) and thus with the strong role of catalytic promoters in enhancing gas production according to eqs 5–8. However, biocarbon samples with comparable VM content but different AAEM/(Si+Al) content showed a comparable $CO/CO_2$ ratio (0.24 for BC1 and 0.34 for WBC1), while WBC2, with the lowest VM content, showed a $CO/CO_2$ ratio 2 orders of magnitude lower (<0.02). These results suggested that the role of the VM content was predominant in enhancing gas production compared to that of catalytic and inhibitor metals for the biocarbons of this study.

#### 3.1.2. Pyrolysis in Fixed-Bed Reactor at Pilot Scale.

A fixed-bed reactor (around 1 kg) was used for the detection and quantification of minor species, more precisely PAH, in the condensates in pyrolysis at pilot scale, from room temperature to 800 °C. Wood biocarbon with the highest VM content (WBC1) was considered for this experiment. Product distribution

The distribution of pyrolysis products of WBC1 was determined from room temperature to 800 °C and compared to previous results at 800 °C in the fixed-bed reactor at laboratory scale. WBC1 solid yield was 81 wt%, which was consistent with previous experiments. In this case, a higher permanent gas yield (13 wt%) and thus a lower condensate yield (6 wt%) were obtained.

The condensable species collected in the cold condensable trap (tar protocol) were qualitatively analyzed by GC/MS (Supporting Information, Table S1). Some Volatile Organic Compounds (VOCs) reported in the literature as released by anthracite, such as benzene and toluene, were found for WBC1. However, other VOCs, such as 3-hexadecene and styrene, reported for anthracite, were not found for biocarbon.[33] This suggested that long-chain fragmentation may occur in the anthracite matrix rather than in biocarbon.

##### 3.1.2.1. Emission Factors.

The emission factors ($EF_i$) were calculated for permanent gases and PAH.

EF(CO) and $EF(CO_2)$ for WBC1 were comparable (50.5 and 52.3 $g/kg_{fuel}$), respectively, as WGS (eq 5) and Boudouard (eq 6) reactions may be promoted by the high AAEM/(Si+Al) ratio for WBC1 (3.0). $EF(H_2)$ and $EF(CH_4)$ are comparable (14.1 and 14.4 $g/kg_{fuel}$, respectively). Hence, WBC1 had a significant $H_2/CO_2$ ratio (2.79), which is favorable for $H_2$ generation. $EF(CH_4+H_2)$ corresponded to 2.8 wt% in terms of product yield, which remains below the 4 wt% recommendation according to EN ISO 562 standard.

According to the EN ISO 562 standard, 16 PAH were quantified among the condensable species (Supporting Information, Table S2). Naphthalene was the major PAH emitted (37.402 $mg/kg_{fuel}$), which would be derived from fused benzene rings.[34] It represented around 81% of the total PAH for WBC1. The dominant PAH in minor species were acenaphthylene, fluorene, and phenanthrene, which constitute 14% of the total PAH. EF(PAH) of biocarbon was 46.3 $mg/kg_{fuel}$. AAEM content in biocarbons may favor volatile species release, increasing EF(PAH), due to the promoting role of these metals in catalytic thermochemical conversion reactions.[35] By comparison, EF(PAH) for WBC1 (46.3 $mg/kg_{fuel}$) was similar to that of a demolition woody biocarbon (carbonized at 750 °C, 48.1 $mg/kg_{fuel}$). Pyrolysis temperature may affect PAH emissions.[36] Other coal samples, such as bituminous coal, showed PAH emissions of up to 1,435 mg/$kg_{fuel}$.

*3.1.2.2. Fuel Toxicity.* Fuel toxicity was assessed by comparing the PAH yield and their ring number, which is directly associated with their toxicity. A diagram representing the number of PAH rings of WBC1 and several fuels reported in the literature was proposed (Figure 4). It includes PAH ring distribution of biocarbon derived from wood waste (sawdust/sawmill mixture) and wood (from pallets and crates) produced from 400 to 550 °C using a moderate pressure (0.2−0.9 MPa),[37] as well as values for several coals (i.e., lignite, bituminous coal, anthracite, and coke).[38]

Pyrolysis operating conditions, as well as a resource type (wood or waste), directly impact biocarbon toxicity.[13] Biocarbon emits typically a higher PAH yield of 2 and 3-rings (77.5−97.0%) compared to 4 rings (<1.65%). In contrast, its PAH range of 5 and 6 rings is large (2.35−22.0%), which may be related to the use of an intermediate pyrolysis temperature (600 °C).[17] The yield of 5 and 6-rings biocarbons produced at 550 °C was 63% lower than that produced at 400 °C. At equivalent carbonization temperatures (400 or 550 °C), increasing pressure may not show a clear trend. It can be assumed that temperature is the main parameter affecting the PAH distribution.[36] The trend of biocarbon with a high VM content (WBC1) seems to be coherent, also supported by a predominance of AAEM metals compared to inhibitors in this case (AAEM/(Si+Al) ratio of 3.0 for WBC1).

Anthracite emits typically moderate PAH yields of 2 and 3-rings (52.7−64.7%) and 4-rings (6.15−24.9%). Its yield for 5 and 6-rings may be higher than that of biocarbon (10.3−41.5%). Low coal ranks, such as bituminous coal and lignite, are in the middle of the diagram. Bituminous coal and lignite emit moderate yields of 2 and 3-rings (24.3−42.0%), lower than those for anthracite and biocarbon. However, they exhibit a yield of 4 rings (28.6−31.3%) higher than anthracite and biocarbon. These coals may produce 5 and 6-ring PAH in moderate yield (28.2−34.1%). As coke is mainly derived from bituminous coal, its PAH yield of 2 and 3 rings can be in a high range (74.5−79.3%). Indeed, the cooking process could reduce 4-ring PAH to a low range (<1.80%), as so far 5 and 6-rings (<25.0%). Anthracite yield for 5 and 6-rings is also higher than other coals (bituminous coal, lignite) and coke.

Biocarbon PAH emissions were also investigated in terms of toxicity, which is directly related to the number of rings of the PAH compounds. The results showed that biocarbon produced a large percentage of 2-ring PAH (81%), and it mainly produced PAH up to 4 rings. In comparison, anthracite was reported to emit PAH with ring numbers higher than 2 and up to 6 rings, principally.[37] This may be due to the lower thermal stability of biocarbon, making its degradation into smaller molecules (with fewer rings) easier than that of anthracite.

*3.1.2.3. Toxic Equivalent Factor and EF for PAH.* The toxic equivalent factor (TEQ) calculated for WBC1 (0.132) was comparable to that reported for some biocarbons, such as miscanthus biocarbon (0.432) and softwood biocarbon (0.284). However, TEQ values for biocarbon (0.284−6.011) are within a wide range, as they are strongly dependent on the production temperature and the feedstock. In all cases, WBC1 and reported TEQ values for biocarbons are 2−3 orders of magnitude higher than those for anthracite in pyrolysis (0.005−0.030). This may be directly related to their different physicochemical and inorganic composition, as well as their different reactivity.[38] Natural Coke had the lowest value of TEQ (0.0004).

TEQ and EF(PAH) values were compared for WBC1 and several biosourced and fossil fuels from the literature (Figure 5). Biocarbons showed, in general, higher values of EF (>10 mg/$kg_{fuel}$) and TEQ (>0.1) in pyrolysis compared to fossil fuels such as anthracite (EF < 0.01 mg/$kg_{fuel}$ and TEQ < 0.01). However, higher emissions are not directly associated with a higher health risk, as PAH toxicity is strongly related to the number of aromatic rings. Anthracite typically releases PAH with a larger distribution in terms of the number of aromatic rings (from 2 to 6 rings), while biocarbons emit more PAH with a low number of aromatic rings and are potentially less toxic.

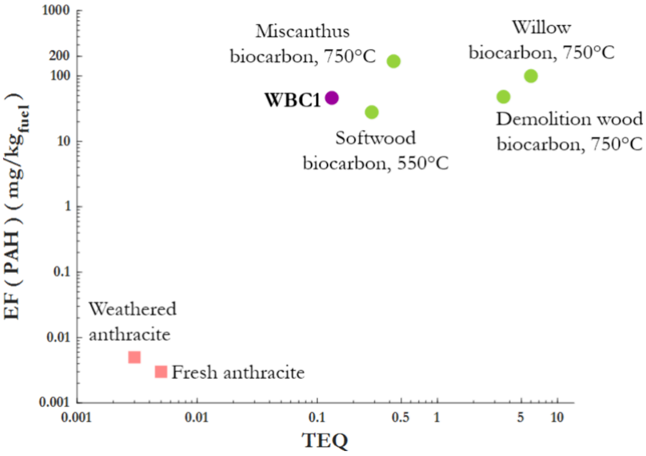

**Figure 5.** Comparison of EF(PAH) and TEQ for biocarbons and fossil fuels in pyrolysis.

**3.2. Emissions in Combustion.** Fuel emissions in combustion were assessed in terms of permanent gases (CO, $CO_2$, $H_2$, and $CH_4$) and main condensable species, including water. Combustion tests on a fixed-bed reactor at a laboratory scale (30 g) allowed the determination of detailed product distribution and gas production profiles as a function of time, as well as EFs. The selected samples for these tests were BC1 and WBC2, to complement the analysis carried out in Section 3.1.2.

*3.2.1. Product Distribution.* A similar product distribution was observed for both samples in pyrolysis. A lower solid yield was observed for BC1 (10.0 wt%) compared to that of WBC2 (2.0 wt%), which presented a higher gas yield (79 wt% for WBC2 compared to 71 wt% for BC1). Condensate yield (around 12 wt%) and water production (around 7.0 wt%) were similar for both samples.

The trapped condensable species were qualitatively analyzed by GC/MS (Supporting Information, Table S1). Acids, alcohols, aldehydes, and ketones were detected, with carbon chains ranging from C5 to C11. A total of 15 VOCs were identified for BC1 compared to 5 VOCs for WBC2. Benzene was a common VOC produced by all fuels considered. Its presence may be related to the cleavage of C−C bonds in aliphatic compounds.[39] Pyridine, its derivative (i.e., 2-Ethynyl pyridine), as well as pyrrole, were associated with N content in biocarbons.[40] Of particular interest was azulene ($C_{10}H_8$) because of its potential conversion to naphthalene ($C_{10}H_8$), a PAH.[41] However, PAH were under the detection limit for the

Table 4. Emission Factors of Permanent Gases on Combustion Tests in the Fixed-Bed Reactor at Laboratory Scale

| samples | EF(CO) | EF($CO_2$) | CO/$CO_2$ | EF($H_2$) | EF($CH_4$) | Y($CH_4$+$H_2$) |
|---|---|---|---|---|---|---|
| | g/$kg_{fuel}$ | | | g/$kg_{fuel}$ | | wt% |
| BC1 | 680 | 2000 | 0.34 | 11.3 | 9.46 | 0.53 |
| WBC2 | 496 | 2980 | 0.17 | 2.67 | 0.62 | 0.07 |

operating conditions and scale considered, most likely because of the oxidative conditions in pyrolysis that may destroy the aromatic rings.[13]

*3.2.2. Emission Factors.* EFs of biocarbons were calculated for CO, $CO_2$, $CH_4$, and $H_2$ as the main permanent gases observed in combustion (Table 4).

According to the results, an increase in CO and $CO_2$ production was observed, which was correlated with an increase in the AAEM/(Si+Al) ratio and a decrease in the VM content of biocarbons. As a result, the lowest CO/$CO_2$ value (0.17) was found for WBC2. Biocarbon with a lower VM content (WBC2) presented lower $CH_4$ and $H_2$ production. This suggested again that the presence of catalytic promoters, abundant in WBC2 (with an AAEM/(Si+Al) of 6.0), influences gas production to a lower extent than biocarbons' VM content, which is low for WBC2 (4.7 wt%). At the same time, EF($CH_4$) and EF($H_2$) were related to the hydrogen content and energy potential of the fuels (Table 1). WBC2 had the lowest hydrogen content (1.03 wt%), then the lowest associated EF (11.3 $g_{H2}/kg_{fuel}$ and 9.46 $g_{CH4}/kg_{fuel}$). Both $CH_4$ and $H_2$ enhance spontaneous fuel combustion as well as release hydrocarbons ($C_2H_4$, $C_2H_6$, etc.), increasing explosion risk conditions.[42,43] When expressing $CH_4$ and $H_2$ in terms of product mass yield, Y($CH_4$+$H_2$) was below 4wt% both for BC1 (0.53 wt%) and WBC2 (0.07 wt%), which complies with the QHSE criterion of the fuel combustion (EN ISO 562 standard).[44]

## 4. CONCLUSIONS

In this study, gas emission fate and toxicity were quantified in biocarbon pyrolysis and combustion, leading to the highest and the lowest associated emissions, respectively. The results obtained were linked to biocarbon characteristics and compared to standards for fossil fuels, as biocarbon is considered to be an alternative to replace fossil fuels in industrial processes.

In pyrolysis, wood biocarbon (WBC1) exhibited the highest $CO_2$ production with an EF($CO_2$) of 3696 g/$kg_{fuel}$. The impact of the VM content on the gas emissions was demonstrated to be predominant compared to that of catalytic and inhibitor metals, such as AAEM and Si+Al, respectively. Biocarbon with a high VM content (WBC1, 18.5 wt%) emits PAH with a smaller number of rings (<3) and thus with a lower toxicity than PAH emissions reported for fossil fuels. However, its higher production yield and thus EF values lead to a higher TEQ than the values obtained for fossil fuels, despite the biogenic nature of its emissions.

In combustion, wood biocarbon (WBC2) showed a higher EF for $CO_2$ (2980 g/$kg_{fuel}$) compared to SRF biocarbon (BC1, 2000 g/$kg_{fuel}$), which is related to its higher AAEM/(Si+Al) ratio and lower VM content. $CO_2$ EFs of biocarbons were 10−33% higher compared to values reported for hard coal (2010−2230 g/$kg_{fuel}$). The presence of oxygen guarantees a reduction of condensable species production and, consequently, PAH emissions, translating into a lower TEQ of the related emissions.

To sum up, the fate and toxicity of gas emissions from biocarbon both in pyrolysis and combustion are directly related to biocarbon characteristics, namely its VM content, which impacts not only the amount (EF) but also the toxicity (TEQ) of the compounds released (CO, $CO_2$, $CH_4$, PAH). These results provide insights into the assessment of emission fate and toxicity of renewable fuels, which concerns fossil fuel replacement in industrial processes. The larger scale of these processes compared to the laboratory and pilot scale carried out in this work needs to be considered. In fact, on an industrial scale, the dilution rate of the emitted gas should be considered, as this impacts the pollutants' fate.

B.B.: Methodology, Formal analysis, Investigation, Writing—Original Draft, and Visualization. R.P.: Methodology, Formal analysis, Investigation, Writing—Review & Editing, Visualization. M.G.M.: Validation, Resources, Writing—Review & Editing, Visualization, Supervision. M.P.: Methodology, Formal analysis, Investigation, Writing—Review & Editing, Visualization. A.N.: Conceptualization, Validation, Resources, Writing—Review & Editing, Supervision, Project administration, Funding acquisition.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.5c05555.

> HAP calibration curves; Qualitative analysis of condensable species in pyrolysis tests in a fixed-bed reactor at pilot-scale; HAP quantification in pyrolysis tests in a fixed-bed reactor at pilot-scale; Condensable species produced in combustion tests in the fixed bed reactor at laboratory-scale (PDF)

## ■ AUTHOR INFORMATION

### Corresponding Author

**Ange Nzihou** − *Université de Toulouse, IMT Mines Albi, F.81013 Albi Cedex 09, France; Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey 08544, United States;* orcid.org/0000-0002-1547-2567; Email: ange.nzihou@mines-albi.fr, ange.nzihou@princeton.edu

### Authors

**Bénit Bouesso** − *Université de Toulouse, IMT Mines Albi, F.81013 Albi Cedex 09, France*
**Ronan Pelé** − *Université de Toulouse, IMT Mines Albi, F.81013 Albi Cedex 09, France*
**María González Martínez** − *Université de Toulouse, IMT Mines Albi, F.81013 Albi Cedex 09, France*
**Morgane Poser** − *Université de Toulouse, IMT Mines Albi, F.81013 Albi Cedex 09, France*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.5c05555

## Notes

The authors declare no competing financial interest.

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