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ORIGINAL PAPER

Analysis of emission profiles from charcoal produced from selected tree species by different pyrolysis methods

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Abstract

The use of charcoal is associated with indoor air pollution where users are continually exposed to combustion pollutants with detrimental effects to their health. This study analyzed the emission profiles of selected domestically used charcoal produced by different pyrolysis methods. Charcoal samples from three tree species *Acacia polyacantha*, *Acacia xanthophloea* and *Eucalyptus grandis*, produced by both efficient and traditional pyrolysis were collected from charcoal producers in rural Kenya. The volatile organic compounds were collected using a fabricated chimney placed on clay cook stove such that smoke was vented to a glass cannula and condensed. Extracted volatiles were analyzed by gas chromatography-linked mass spectrometry. Twenty-two polycyclic aromatic hydrocarbons were identified together with other hydrocarbons. Polycyclic aromatic hydrocarbons found in the smoke extracts with known health effects included naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, fluorene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, benzo(a)anthracene and chrysene. There were significant differences in the concentrations of fluorine, naphthalene and pyrene emitted from *Acacia polyacantha* and *Acacia xanthophloea* prepared by traditional pyrolysis. From *Acacia polyacantha*, concentrations were naphthalene (110 µg/g), fluorine (72 µg/g) and pyrene (60 µg/g), while from *Acacia xanthophloea*, concentrations were naphthalene (140.42 µg/g), fluorene (97.35 µg/g) and pyrene (71.82 µg/g). Charcoal prepared by traditional pyrolysis emitted the highest number of polycyclic aromatic hydrocarbons and also had higher concentration of polycyclic aromatic hydrocarbons relative to the accepted 0.1–0.2 mg/m^3 levels, while those prepared by efficient pyrolysis produced the lowest concentration. Therefore, there is need to use efficient pyrolysis methods of charcoal production.

Keywords Volatile emissions · Polycyclic aromatic hydrocarbons · Gas chromatography–mass spectrometry · Combustion pollutants · Human health

Introduction

Charcoal is a wood-based secondary form of fuel produced by the pyrolysis of wood with limited air supply (McQueeen and Korhaliller 2011). This is achieved by cutting wood into pieces and burning them in a kiln where the flow of air is controlled. Charcoal is widely used as a fuel by approximately 80% of Kenyan households and will continue being an important fuel for many years to come (Mugo and Gathui 2010). In small-scale charcoal production, wood is commonly pyrolyzed using an earth mound or steel drum kilns, while in large-scale production, brick kilns are used (Kammen and Lew 2005). The pyrolysis takes a few hours to weeks to complete with half of the primary energy lost through the process (Bailis 2005). The energy efficiency of the process is influenced by the kiln, moisture content of the wood, wood species, wood arrangement and the experience of the charcoal producer (Kammen

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and Lew 2005). Complete combustion of charcoal produces mainly carbon dioxide and water. However, it is difficult to achieve such efficiency in the cook stoves commonly used in rural and urban areas (Smith 2006). Incomplete combustion of charcoal thus leads to the emission of organic compounds such as carbon monoxide, formaldehyde, polycyclic aromatic hydrocarbons (PAHs) and other compounds that are detrimental to human health (Chakraborty et al. 2014). Impurities contained in biomass fuels eventually lead to formation of inorganic compounds including sulfur dioxide, nitric oxide and ammonia and a myriad of other compounds, which have been identified (International Agency for Research on Cancer 2010; Lim and Seow 2011). Worldwide, over 4 million annual deaths are caused by indoor air pollution resulting from cooking fuel. Studies show that children are the most susceptible group to pollutant cooking fuels with harmful health outcome (Opiyo et al. 2017).

The emissions produced during the combustion of charcoal may depend on the method used to carbonize the wood and the type of plant species from which the charcoal is being produced (Hindi 2012). The chemical make-up of wood, which is mainly lignin, hemicelluloses, cellulose and organics, varies from one tree species to the other (Pattersen 1984). It is reported that thermal decomposition of wood begins at 100 °C, while hemicelluloses, cellulose and lignin are degraded from 200–260 °C, 240–350 °C to 280–500 °C, respectively (Hindi 2012). Thus, the conditions under which the charcoal was produced affect the chemical composition of the charcoal produced and hence emitted compounds when the same charcoal is burnt on a cook stove.

Carbon monoxide and carbon dioxide from biomass fuels are well known to cause suffocation in poorly ventilated rooms. However, other pollutants in charcoal smoke known as products of incomplete combustion, for example, PAHs, have shown the ability to be injurious to human health especially due to their chronic effects. PAHs have been classified as priority pollutants owing to the carcinogenic potential of several individual PAH compounds and PAH mixtures (International Agency for Research on Cancer 2017). Indoor air is contaminated by PAHs, which come not only from infiltration or intrusion of outdoor air but also from indoor emission sources such as smoking, cooking and domestic heating with fuel stoves and open fireplaces, as well as from incense and candle emissions (Baek et al. 1991; Zhang and Tao 2009). A study by Gachanja et al. (1992) showed the presence of benzo[a]pyrene (1) (BaP) in charcoal smoke from the *Acacia mearnsii* species. BaP has been a subject for numerous studies that have sought to determine its presence, for example, in food cooked by various methods. Research by Akpambang et al. (2009) found that charcoal smoked fish and meat contained BaP. High concentrations of PAHs are also reported to be contained in food cooked over open flames, for example, roasted meat with concentrations of BaP present at 30 parts per billion (El-Badry 2010). In Kenya, charcoal production and consumption continue resulting to deforestation and air pollution posing health risk to human life. Therefore, the current study aimed at finding out the emission of chemical profiles of three *Acacia* tree species (*A. polyacantha*, *A. xanthophloea* and *Eucalyptus grandis*) commonly used for charcoal production and to compare the emission profiles of charcoal produced by efficient pyrolysis methods and by traditional pyrolysis methods.

Materials and methods

Plant materials

Wood samples were collected from three plant species, namely *A. polyacantha*, *A. xanthophloea* and *E. grandis*, from selected charcoal producers using purposive sampling method. The wood samples of 6-year-old *Acacia* species were collected from farmers' fields in Kajiado (1°28′50.1″S 36°57′35.7″E—Kitengela Wood Energy Arboretum) and Machakos (1°24′59.5″S 37°19′56.9″E) Counties, while 8-year-old *E. grandis* were obtained from Kakuzi Limited, Thika, Kiambu County, Kenya (0°49′14.9″S, 37°13′47.6″E). The stems of woods from each tree species were cut between 0.5 or below 1 m from the ground to allow for regrowth and diameter within the range of 10–15 cm. The wood from each separate plant species was dried in the sun for 5 days and then carbonated into charcoal by using a traditional or efficient pyrolysis. The moisture content for *E. grandis*, *A. polyacantha* and *A. xanthophloea* ranged from 5–8%, 3–6% to 3–5%, respectively. Measurements were taken using a portable wood moisture meter GM620. Charcoal was produced from the three plant species using the traditional earth mound kiln by two farmers in Machakos,Kenya. For efficient pyrolysis, farmer's 'Cookswell Jikos' (Kitengela, Kenya) and a dome-shaped brick kiln (Kakuzi Limited,Thika, Kenya) were employed to produce charcoal from the two *Acacia* plant species and *E. grandis*, respectively. About 1.5 kg of each sample was randomly collected from the yields after pyrolysis and stored in labeled high-density polythene bags in a dry cabinet before further analysis.

Extraction and collection of volatiles

A tailor-made chimney (Fig. 1) with two joined conical-shaped metal casings and clay between them to facilitate cooling of the emitted smoke from the clay Jiko was used to collect aliquot samples from the different types of charcoal under study. The length between the smoke inlet and outlet was made as thin as possible to ease smoke movement. The clay Jiko used was fabricated in a way that its edges were the same size as the chimney to minimize smoke losses. The chimney was placed on top of the cook stove to allow the smoke to flow in one

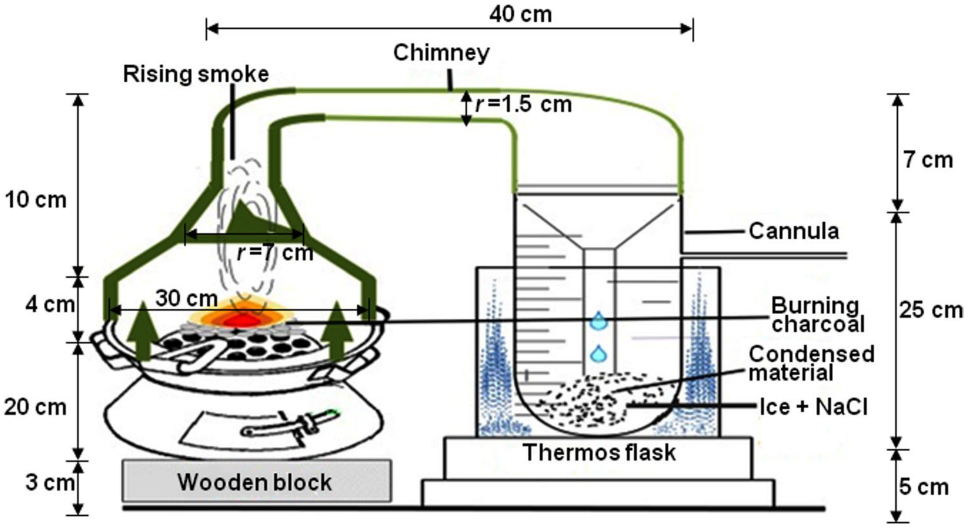

Fig. 1 A schematic diagram of the experimental set up for collection of volatiles

direction into the collecting cannula where the volatiles were condensed (Fig. 1). To collect volatiles, each charcoal sample weighing 300 g was separately combusted in clay cook Jiko and the smoke condensed in a cannula tube held in a Thermos flask containing ice and sodium chloride maintained between − 8 °C and 10 °C. This was repeated three times for each sample such that there were 18 extracted volatile samples.

The condensed volatiles were extracted in 30 mL of dichloromethane (DCM) (99.6% AR grade—Sigma-Aldrich) in a separating funnel and mixed vigorously for 5 min. The mixture was then allowed to settle forming two layers that were then separated. This was repeated three times, and the resulting DCM fractions were pooled together. A scoopful of anhydrous sodium sulfate (Na_2SO_4) granules dried in the oven at 105 °C for 2 h was added to the extract in a conical flask and then swirled gently. More Na_2SO_4 were gradually added to the extract with swirling of the flask until all the water was removed completely. The dried extract was then filtered using Macherey-Nagel filter papers (0.7 µm) to remove the Na_2SO_4, and the process was repeated for all the other extracts. The dried extracts were then transferred into a round-bottomed flask and concentrated with a rotary evaporator at a temperature of 30 °C to dryness.

Chemical analysis

The extracted volatiles from charcoals from the selected plant species were analyzed using a Hewlett Packard (HP) 5890 series II gas chromatography (GC) machine (Agilent Technologies Company Limited, Santa Clara, CA, USA) linked to a mass spectrometry (MS) machine (AG, Autospec; Fisons instruments, Manchester, UK). The GC machine was fitted with a split-less capillary injector system (30 × 0.25 mm i.d., and a film thickness of 0.25 µm cross-linked methylsilicone capillary column (Phenomenex Inc) and a flame ionization detector (FID) coupled to Hewlett Packard HP 3393A series II integrator. One µL of each of the extracted volatile samples was injected into the injector port of the GC machine, and helium was used as the carrier gas at a determined flow rate. The oven temperature was maintained at 90 °C for 2 min and then programmed to work at 5 °C/min to 320 °C.

The flow rate of helium gas was 3 mL/min, while the flow rates for air and hydrogen were set at 400 and 30.5 mL/min, respectively. Ionization by MS was performed by electron impact 70 eV at 230 °C. The mass range was set at 45–450 m/z, the event time at 0.3 s and the solvent delay at 3.5 min. The interface and ion source temperatures were 300 °C and 230 °C, respectively. The constituents were characterized by their fragmentation patterns and compared with those in the National Institute of Standards and Technology database library (https://www.nist.gov) and their relative amounts determined. Co-injection with an authentic sample of naphthalene was used to confirm its identity. Quantification of key compounds emitted by charcoal from the plant species was done by comparing MS peak areas of the eluted compounds to the peak area of a 100 ng/µL of naphthalene standard. This was done by injecting 2.0 µL of the prepared naphthalene standard that contained 100 ng of naphthalene prepared in Analar hexane. The peak area was recorded, and the concentration of eluted compounds calculated using the equation below

$$\frac{A_x}{C_x} = Fx\frac{A_s}{C_s}$$

where A_x peak area of analyte; C_x concentration of analyte; A_s peak area of standard; C_s concentration of standard; and F is the response factor calculated as below

$$F = \frac{A_s}{C_s}.$$

Data analysis

The concentrations of different PAH compounds obtained were subjected to statistical analysis using Statistical Package for Social Sciences (SPSS) Version 17 (SPSS Inc. Chicago, USA). The SPSS version was used to analyze significant differences in the mean concentrations of emitted compounds and one-way analysis of variance (ANOVA) test performed with the level of significance set at 0.05. Once a P value of less than 0.05 was obtained, further analysis, separation of means, using SAS (version 9.1.3) software was undertaken to determine which specific concentrations were different. Duncan's multiple range test was used to separate the means. An independent *t* test was performed to establish whether there were significant differences between the concentrations of identical PAHs emitted from two different tree species.

Results and discussion

Results

Emissions from charcoal prepared from the plant species

The GC–MS characterization of emissions obtained from *A. polyacantha* charcoal prepared by traditional pyrolysis revealed a total of 84 compounds. With 42% of all volatile organic compounds (VOCs) emitted, phenols were the most compounds produced in *A. polyacantha* followed by benzene derivatives (15%), ketones (12%), alkenes (9%), PAHs (6%), alkanes (4%), esters (2%) and phthalates, aldehydes and carboxylic acids each with 1%. Volatile chemicals emitted from charcoals obtained from *A. polyacantha* prepared by efficient pyrolysis revealed a total of 51 chemical compounds including 37% phenols, 22% ketones, 11% benzene derivatives, 9% alkenes, 8% PAHs, alkanes, alcohols and esters each with 4% and 1% phthalates. GC–MS analysis of emissions obtained from charcoal prepared from *A. xanthophloea* by efficient and traditional pyrolysis revealed a total of 61 and 62 compounds, respectively. With 33% of all compounds emitted, phenols were the most chemical compounds produced using traditional earth mound kiln followed by PAHs and alkanes each with 12%, alkenes with 10%, carboxylic acids with 8%, benzene derivatives with 7%, phthalates and esters each with 6%, alcohols (4%) and ketones with 2%. Volatile chemicals emitted obtained from *A. xanthophloea* charcoal prepared by efficient pyrolysis included 45% phenols, followed by benzene derivatives (16%), ketones (9%), alkenes (8%), esters (7%), aldehydes and alkanes each with 5%, PAHs (4%) and phthalates (1%). Seventy-four VOCs including 45% phenols, 19% benzene derivatives, 9% ketones, 7% PAHs, 6% alcohols, 5% alkanes, 4% alkenes, 3% aldehydes and phthalates and esters with 1% each were obtained from charcoal from *E. grandis* prepared by traditional earth mound kiln. However, the number of chemical compounds produced from charcoal prepared from *E. grandis* reduced from 74 to 69 when the dome-shaped brick kiln was used. The VOCs emitted included 23% benzene derivatives, 21% phenols, 17% alkenes, 10% alkanes, 9% esters, PAHs and ketones each with 6%, 5% alcohols, 2% phthalates and 1% aldehydes.

Polycyclic aromatic hydrocarbons emitted by charcoal from the plant species

In this study, a total of 22 parent and alkyl-PAHs and one oxygenated (O-PAH) PAHs were identified and quantified in the plant species. The emissions of PAHs varied considerably between biofuels and combustion appliances. The total PAHs for the biofuels extracted using traditional earth mound kiln ranged from 25.67 µg/g in *E. grandis* to 201.54 µg/g in *A. polyacantha*. Eleven PAHs (Fig. 2) were identified from emissions obtained from *A. polyacantha* charcoal prepared by traditional earth mound kiln, and their concentrations differed significantly ($P < 0.05$; Table 1). The concentrations of naphthalene, 2,6-diisopropylnaphthalene and anthracene were significantly different, while the concentrations of 2-methylnaphthalene, 9H-fluoren-9-one, fluoranthene and pyrene did not differ significantly. The concentrations of benzo (a) anthracene and phenanthrene as well as chrysene and fluorene were also not significantly different ($P < 0.05$; Table 1).

There were significant differences ($P < 0.05$) in the amounts of nine PAHs (Fig. 3) emitted from *A. xanthophloea* charcoal prepared by traditional pyrolysis. 2,6-diisopropylnaphthalene was the VOC with the highest concentration emitted (201.54×10^{-3}µg/g), and 1,5-dimethyl-1,2,3,4-tetrahydronaphthalene (54.23×10^{-3}µg/g) was the least emitted (Table 1).

There were 10 PAHs (Fig. 4; Table 1) including three parental, three alkylated, one nitrogenized and three oxygenated emitted by charcoal from *E. grandis* prepared by traditional pyrolysis. The quantities of the emitted PAHs varied significantly ($P < 0.05$) with 1,4,5-trimethylnaphthalene having the highest amount produced (94.00×10^{-3} µg/g) and fluoranthene with the least amount (25.67×10^{-3} µg/g).

Only four PAHs including three parental PAHs and one alkylated PAH were emitted from charcoal obtained from *A. polyacantha* prepared by efficient pyrolysis (Fig. 5; Table 2). The quantities of these VOCs differed significantly ranging from 48.33×10^{-3} µg/g in fluorene to 86×10^{-3} µg/g in naphthalene ($P < 0.05$; Table 2).

When wood samples from *A. xanthophloea* were subjected to pyrolysis using a dome-shaped brick kiln (efficient pyrolysis), only two PAHs (Fig. 6) were identified from the resulting smoke emission extracts. These were

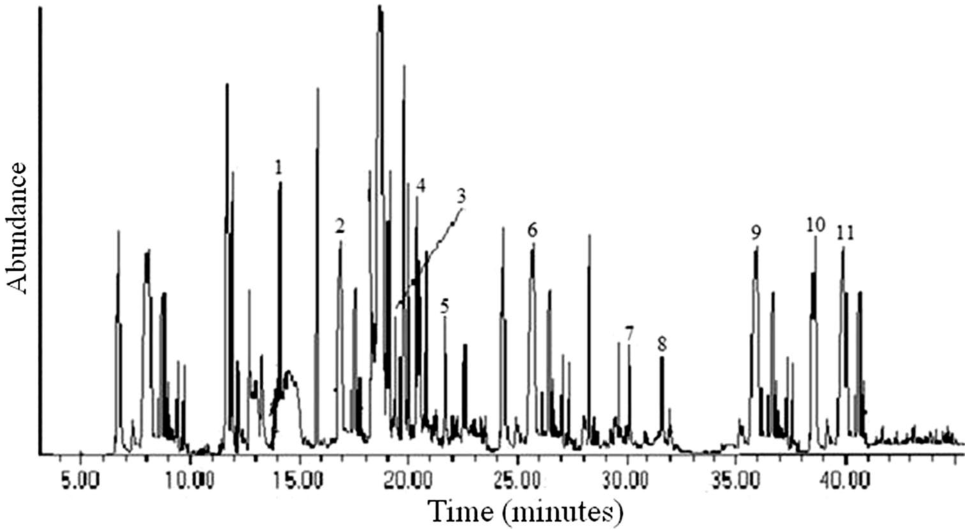

Fig. 2 Total ion chromatogram of smoke emitted by charcoal prepared from *Acacia polyacantha* by traditional pyrolysis. A total of 11 PAHs were identified, namely naphthalene (1), 2-methylnaphthalene (2), fluorene (3), 2,6-diisopropylnaphthalene (4), 9H-fluoren-9-one (5), phenanthrene (6), fluoranthene (7), anthracene (8), pyrene (9), benzo(a)anthracene (10) and chrysene (11)

Table 1 PAHs from charcoal from tree plants prepared by traditional pyrolysis

PAHs	*A. polyacantha* ($\times 10^{-3}$ µg/g)*	*A. xanthophloea* ($\times 10^{-3}$ µg/g)*	*E. grandis* ($\times 10^{-3}$ µg/g)*	NIOSH exposure limit ($\times 10^{-3}$ µg/g)*
Naphthalene	110.00 ± 4.93^{a}	140.42 ± 2.08^{b}	nd	38.15
Benzo(a)anthracene	91.67 ± 10.82^{ba}	nd	nd	16.96
Phenanthrene	91.00 ± 2.08^{ba}	nd	59.00 ± 5.51^{a}	35.67
Anthracene	80.33 ± 10.04^{bc}	84.80 ± 2.12^{cde}	67.33 ± 2.60^{d}	35.67
Chrysene	74.67 ± 14.24^{bcd}	nd	nd	22.05
Fluorene	72.00 ± 4.58^{bcd}	97.35 ± 5.90^{cd}	nd	31.43
Fluoranthene	66.67 ± 4.70^{cd}	nd	25.67 ± 2.85^{f}	38.24
2-Methylnaphthalene	64.00 ± 7.23^{cd}	nd	nd	33.06
Pyrene	60.00 ± 3.79^{cd}	71.82 ± 1.78^{cde}	nd	31.43
9H-fluoren-9-one	58.33 ± 6.36^{cd}	nd	32.47 ± 6.26^{f}	27.00
2,6-Diisopropylnaphthalene	53.67 ± 1.76^{d}	201.54 ± 37.26^{a}	nd	30.00
2,7-Dimethylnaphthalene	nd	109.96 ± 3.07^{cb}	nd	31.30
1-Methylnaphthalene	nd	70.11 ± 1.60^{cde}	nd	34.39
1,4-Dimethylnaphthalene	nd	65.64 ± 1.97^{de}	nd	31.30
1,5-Dimethyl-1,2,3,4-tetrahydronaphthalene	nd	54.23 ± 3.38^{e}	nd	30.51
1,4-Dimethyl-9,10-anthracenedione	nd	nd	31.00 ± 4.04^{f}	21.00
1-Methylphenanthrene	nd	nd	48.00 ± 4.36^{e}	38.22
4-Methylphenanthrene	nd	nd	35.33 ± 4.67^{f}	38.22
1,4,5-Trimethylnaphthalene	nd	nd	94.00 ± 2.65^{b}	29.00
Fluorene-9-methanol	nd	nd	92.00 ± 4.62^{b}	25.00
9H-fluoren-9-one, Hydrazone	nd	nd	79.33 ± 2.03^{c}	25.00

Means of concentrations separated using Duncan's multiple range test by the same letters are not significantly different ($P > 0.05$) from each other

Asterisk indicates means of concentrations $\times 10^{-3}$µg/g

nd not detected, *NIOSH* is the abbreviation for The National Institute for Occupational Safety and Health (https://www.nist.gov)

1-methylnaphthalene (55.67×10^{-3}µg/g) and fluorene (60.67×10^{-3}µg/g). There were no significant differences ($P > 0.05$) in the concentrations of emitted 1-methylnaphthalene and (55.67×10^{-3}µg/g) fluorine (60.67×10^{-3}µg/g) from *A. xanthophloea* charcoal prepared by efficient pyrolysis.

From the analysis of *E. grandis* using efficient pyrolysis, five PAHs were identified and are shown (Fig. 7). These were naphthalene, 2-naphthalenecarbonitrile, 2,6-diisopropylnaphthalene, 9H-fluoren-9-one and anthracene. There was significant difference ($P < 0.05$) in the concentration of

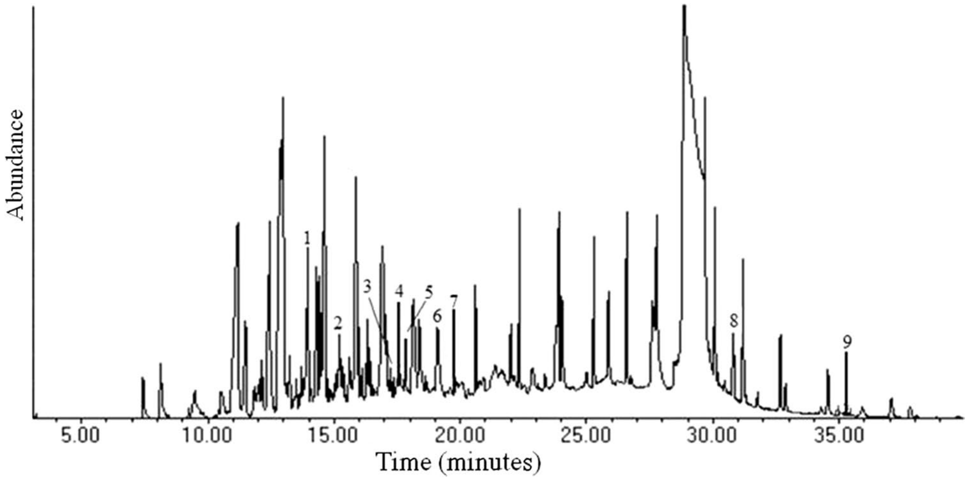

Fig. 3 Total ion chromatogram of smoke emitted by charcoal prepared from *Acacia xanthophloea* by traditional pyrolysis. Nine volatile organic compounds were emitted including naphthalene (1), 1-methylnaphthalene (2), 1,5-dimethyl-1,2,3,4-tetrahydronaphthalene (3), 2,7-dimethylnaphthalene (4), 1,4-dimethylnaphthalene (5), fluorene (7), 2,6-diisopropylnaphthalene (6), anthracene (8) and pyrene (9)

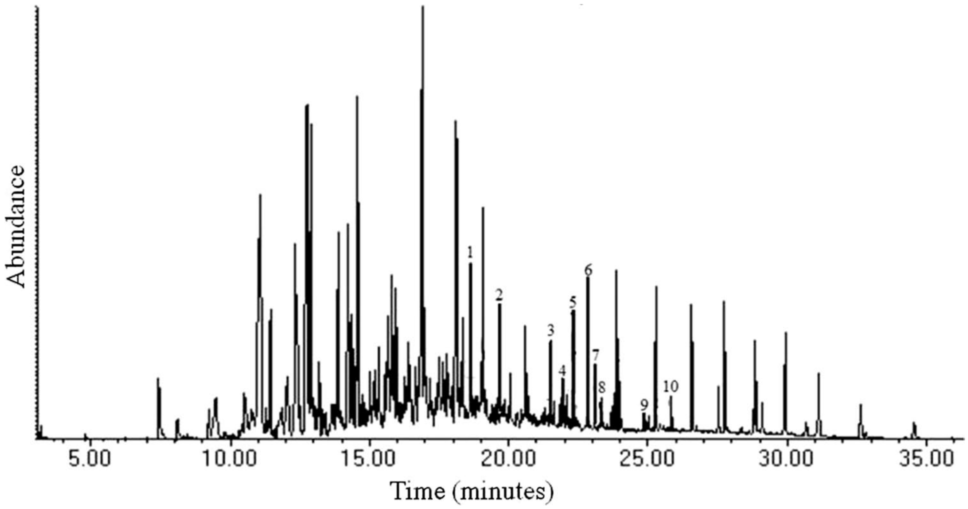

Fig. 4 Total ion chromatogram of smoke emitted by charcoal prepared from *Eucalyptus grandis* by traditional pyrolysis. Ten PAHs were identified and indicated on the chromatogram. These were 1,4,5-trimethylnaphthalene (1), fluorene-9-methanol (2), phenanthrene (3), anthracene (4), 9*H*-fluorene-9-one (5), 9*H*-fluoren-9-one, hydrazone (6), 1-methylphenanthrene (7), 4-methylphenanthrene (8), fluoranthene (9) and 1,4-dimethyl-9,10-anthracenedione (10)

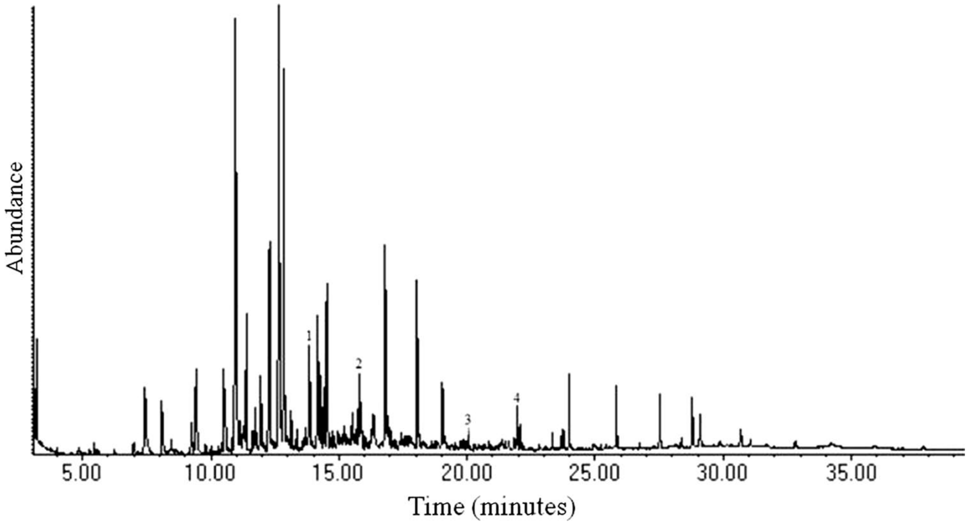

Fig. 5 Total ion chromatogram of smoke emitted by charcoal prepared from *Acacia polyacantha* by efficient pyrolysis. Four PAHs were identified and are indicated on the chromatogram. These were naphthalene (1), 2-methylnaphthalene (2), fluorene (3) and phenanthrene (4)

the emitted PAHs from *E. grandis* charcoal prepared by efficient pyrolysis. There was also significant difference in the concentration of anthracene (35.67×10^{-3} μg/g). However, there was no significant difference in the concentration of emitted naphthalene (69.00×10^{-3} μg/g) and 2-naphthalenecarbonitrile (64.67×10^{-3} μg/g). Similarly, there was

Table 2 PAHs from charcoal from tree plants prepared by efficient pyrolysis

PAHs	*A. polyacantha* ($\times 10^{-3}$ µg/g)*	*A. xanthophloea* ($\times 10^{-3}$ µg/g)*	*E. grandis* ($\times 10^{-3}$ µg/g)*	NIOSH exposure limit ($\times 10^{-3}$ µg/g)
2,6-Diisopropylnaphthalene	nd	nd	101.33 ± 22.45^{a}	30.00
9*H*-fluoren-9-one	nd	nd	96.67 ± 10.48^{a}	27.00
Naphthalene	86 ± 3.06^{a}	nd	69.00 ± 4.726^{ba}	38.50
2-Naphthalenecarbonitrile	nd	nd	64.67 ± 3.28^{ba}	31.00
Anthracene	nd	nd	35.67 ± 2.91^{b}	35.67
1-Methylnaphthalene	nd	55.67 ± 1.20	nd	34.39
Fluorene	48.3 ± 1.67^{b}	60.67 ± 3.73	nd	31.43
Phenanthrene	71.33 ± 0.88^{ab}	nd	nd	35.67
2-Methylnaphthalene	$54.\ 7 \pm 9.14^{b}$	nd	nd	33.06

Means of concentrations separated using Duncan's multiple range test by the same letters are not significantly different ($P > 0.05$) from each other

Asterisk indicates means of concentrations $\times 10^{-3}$µg/g

nd not detected, *NIOSH* is the abbreviation for The National Institute for Occupational Safety and Health (https://www.nist.gov)

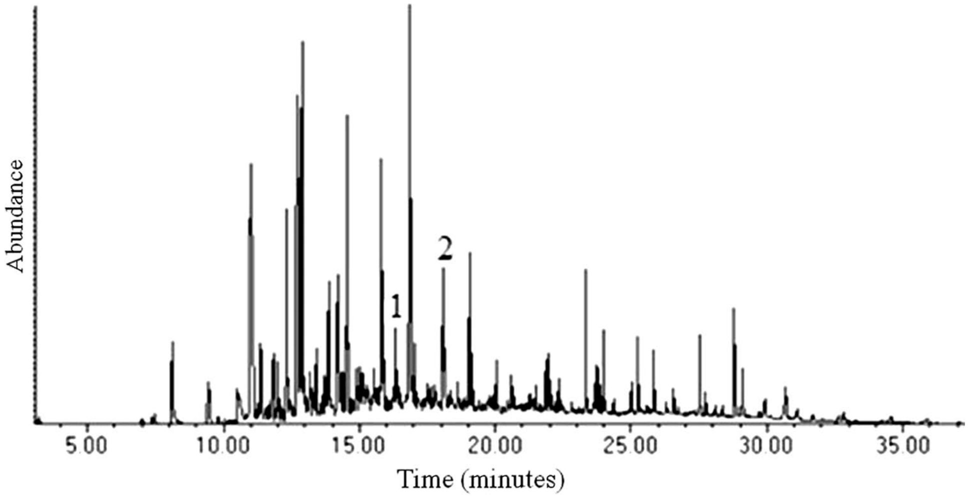

Fig. 6 Total ion chromatogram of smoke emitted by charcoal prepared from *A. xanthophloea* by efficient pyrolysis. From the analysis, only two PAHs: 1-methylnaphthalene (1) and fluorene (2), were identified

also no notable significant difference in the concentration of 2,6-diisopropylnaphthalene (101.33×10^{-3} µg/g) and 9H-fluoren-9-one (96.67×10^{-3} µg/g).

Comparison of concentrations of PAH emissions from *A. polyacantha* charcoal smoke prepared by traditional and efficient pyrolysis

Paired *t* tests showed that there were significant differences ($P < 0.05$; Table 3) in fluorene, naphthalene and phenanthrene emitted between charcoal obtained from *A. polyacantha* prepared by traditional and efficient pyrolysis. Thus, the quantities of fluorene, naphthalene and phenanthrene obtained were higher in charcoals prepared by traditional earth mound kiln than those obtained using 'Cookswell Jikos' or dome-shaped brick kiln. However, there was no significant difference in the concentrations between 2-methylnaphthalene emitted from *A. polyacantha* charcoal prepared by both traditional and efficient pyrolysis ($P > 0.05$; Table 3). There were also significant differences ($P = 0.013$; Table 3) between 1-methylnaphthalene and fluorene emitted by charcoal from *A. xanthophloea* prepared by traditional and efficient pyrolysis.

Discussion

Charcoal is used by majority of households in sub-Saharan Africa including Kenya, and its use is projected to increase or remain the same for many years to come (Mugo and Gathui 2010). This major source of biofuel for many homes, however, presents many challenges posing risk to human health and contributing to environmental pollution (International Agency for Research on Cancer 2010; Lim and Seow 2011). Therefore, we identified the specific contaminants in different types of charcoal derived from three tree species prepared using two different methods of pyrolysis. The study identified 22 PAHs

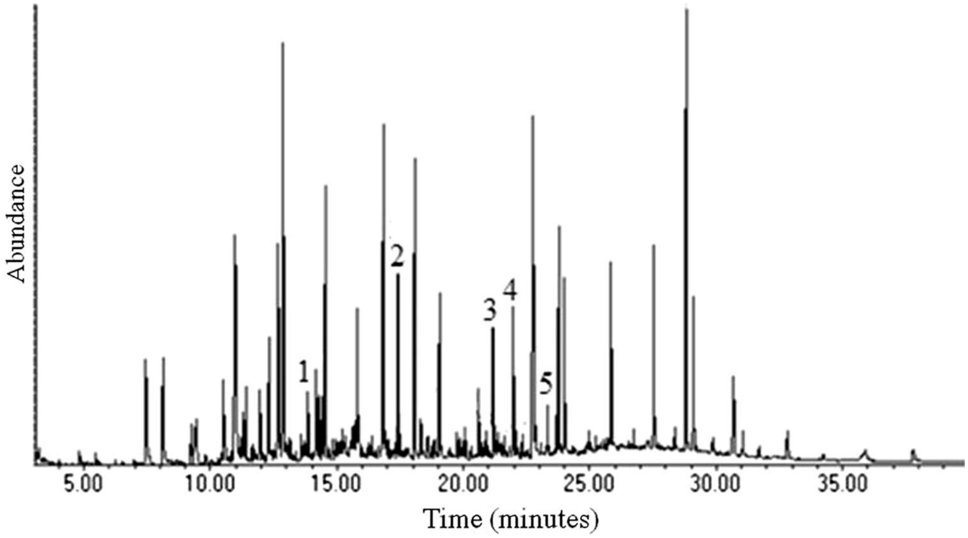

Fig. 7 Total ion chromatogram of smoke emitted by charcoal prepared from *E. grandis* by efficient pyrolysis. From the analysis, five PAHs were identified and are indicated on the chromatogram. These are naphthalene (1), 2-naphthalenecarbonitrile (2), 2,6-diisopropylnaphthalene (3), 9H-fluoren-9-one (4) and anthracene (5)

Table 3 Comparison of concentrations of PAH emissions from plants charcoal smoke prepared by traditional and efficient pyrolysis

PAHs	Plant species	Traditional ($\times 10^{-3}$ µg/g)	Efficient ($\times 10^{-3}$ µg/g)	*t*	*P* value
Naphthalene	*A. polyacantha*	110 ± 4.93	86 ± 3.06a	− 11.53	0.007
Phenanthrene	*A. polyacantha*	91 ± 2.08	71.33 ± 0.88	− 14.75	0.005
2-Methylnaphthalene	*A. polyacantha*	64 ± 7.23	54. 7 ± 9.14	− 1.26	0.336
Fluorene	*A. polyacantha*	72 ± 4.58	48.3 ± 1.67	− 6.38	0.024
	A. xanthophloea	97.35 ± 5.9	60.67 ± 32	− 8.59	0.013
1-Methylnaphthalene	*A. xanthophloea*	70.11 ± 1.60	55.67 ± 06	− 8.84	0.013

Means of concentrations separated using Duncan's multiple range test by the same letters are not significantly different ($P^{>}$ 0.05) from each other

Asterisk indicates means of concentrations $\times 10^{-3}$µg/g

nd not detected, *NIOSH* is the abbreviation for The National Institute for Occupational Safety and Health (https://www.nist.gov)

comprising parental, oxygenated, nitrogenated and alkylated groups. The study showed that most of the emitted PAHs from the six different types of charcoal had concentrations higher than the permissible levels of between 0.1 and 0.2 mg/m^3. However, few concentrations were slightly close to the recommended levels, for example, fluoranthene (0.26 mg/m^3) emitted by charcoal from *E. grandis* prepared by traditional pyrolysis. The National Institute for Occupational Safety and Health (NIOSH) has recommended that the workplace exposure limit for PAHs should be set at the lowest detectable concentration with a recommended exposure limit (REL) of 0.1 mg/m^3 for coal tar pitch volatile agents for a 10-h workday (National Institute for Occupational Safety and Health 2007). In addition, World Health Organization (2010) recommends a permissible exposure limit (PEL) of 0.2 mg/m^3. Thus, continuous chronic exposure to smoke from charcoal may have detrimental effects to users.

The identification of PAHs in the six charcoal smoke extracts indicates that the smoke extracts from charcoals prepared by traditional pyrolysis yielded a greater number of PAHs as compared to those identified in charcoals prepared by efficient pyrolysis. For example, 10 PAHs were detected in *A. polyacantha* extracts from traditional pyrolysis compared to four PAHs from charcoal prepared by efficient pyrolysis. Furthermore, nine PAHs were identified from the *A. xanthophloea* charcoal smoke extracts prepared by traditional pyrolysis compared to two PAHs from the same species but prepared by efficient pyrolysis. On the other hand, 10 PAHs were identified from *E. grandis* charcoal smoke extracts prepared by traditional pyrolysis compared to four PAHs from the same species but prepared by efficient pyrolysis.

These PAHs also differed in the quantities emitted. The differences in the concentrations of emitted PAHs can be attributed to the different concentrations of the precursor compounds from which PAHs were formed (Britt et al. 2003). In pyrolysis, PAHs are proposed to be formed by pyro-synthesis, in which radicals undergo a series of bimolecular reactions with alkenes, alkynes and aromatics to form larger ring structures (Britt et al. 2004). The pyro-synthesis of individual PAHs is also linked to phytochemicals present in biomass fuels (Britt et al. 2004). For example, it is reported that the native structure of steroids was maintained to form PAHs such as phenanthrene and chrysene structures, and the yield of PAHs was dependent on the steroid structure (Britt et al. 2004). Hence, phenanthrene, a pyrosynthesis product of steroids in biomass, was found in higher concentrations in *A. polyacantha* than in *E. grandis* but was not detected in *A. xanthophloea*. Steroids together with tannins, saponins, phenolic compounds and flavonoids are present in eucalyptus species (Vasantharaj et al. 2013). Accordingly, the concentration of steroids, as a precursor for pyro-synthesis of phenanthrene, could have been higher in *A. polyacantha* than other precursors leading to more emissions of phenanthrene than other PAHs. Phytochemical screening of *A. polyacantha* stem bark has revealed the presence of flavonoids, steroids, carbohydrates, tannins, anthraquinones, cardiac glycosides, alkaloids, triterpenoids and saponins (Okpanachi et al. 2012). Thus, it may be plausible to conclude that since PAHs are formed from different phytochemicals present in biomass, their resulting concentrations are different owing to the quantity of phytochemicals in the plant. Similar results have been reported where naphthalene, 2-methylnaphthalene, phenanthrene and fluoranthene were the most abundant in burning charcoal from water-pipe smoking (Nguyen et al. 2013).

The differences in the concentrations of other emitted PAHs can be attributed to the differences in the chemical composition of the three tree species from which the charcoals were obtained. The building blocks of wood are mainly cellulose, hemicellulose, lignin, extractives and mineral materials also called ash (Klass 1998). The difference in concentration of PAHs produced during combustion may be ascribed to the difference in concentration of chemical compounds present in the charcoal. In addition, the inorganic ashes are reported to catalyze biomass thermal decomposition of cellulose, hemicellulose, lignin and phytochemicals in the charcoal resulting in the formation of different volatiles (Agblevor et al. 1994). Ash in biomass is mainly composed of carbonates, sulfates and phosphates of silica and metals from the first and second group of the periodic table (Garcia-Perez et al. 2008). Two mechanisms have been postulated for the formation of PAHs during combustion: one initiated and catalyzed by the ash and the other due to the non-catalytic condensation of combustion products (Agblevor et al. 1994). It is reported that removal of potassium and sodium from lignin during combustion decreases formation of PAHs (Sharma and Hajaligol 2003). The ash content and minerals may vary from one tree species to another and consequently from one charcoal type to another. Thus, the minerals in the ash may have influenced the emission of different PAHs at different concentrations when traditionally *A. xanthophloea* and *A. polyacantha* charcoal were burned on a cook stove.

The PAHs emitted by both traditional and efficient pyrolysis were compared. The traditional pyrolysis yielded higher amounts of PAHs compared to the same PAHs emitted by efficient pyrolysis. The differences in the concentrations of the same PAHs emitted by different pyrolysis methods can be attributed to the differences in oxygen circulation during pyrolysis (Antal and Morten 2003). Pyrolysis by traditional earth mound kilns leads to excess flow of oxygen into the carbonizing wood through openings in the covering soil and leaves. This results in non-uniform carbonized charcoal, which produces high concentrations of volatiles when burned on a cook stove (Adam 2009). On the other hand, charcoal production by efficient pyrolysis (brick kiln) results in uniformly carbonized charcoal (Kammen and Lew 2005). The brick walls of the kiln prevent entry of oxygen from the surroundings resulting in charcoal that produces low concentration of volatiles when burned on a cook stove. In addition, the double brick walls in a brick kiln ensure that most of the heat is retained inside the pyrolysis chamber allowing carbonization to take place at high temperatures as compared to earth mound kilns. It is reported that pyrolysis of wood into charcoal at low temperatures yields charcoal with a high content of volatile material which produces poisonous fumes when combusted, while charcoal produced at high temperatures emits low content of volatiles (Seidel 2008).

Conclusion

In this study, we have demonstrated that type and concentration of emissions from combusted charcoal are dependent on the pyrolysis method and the type of tree species that was used in preparation of the charcoal. Charcoal produced by traditional pyrolysis yielded the highest concentration of PAHs as compared to charcoal produced by efficient pyrolysis. The total concentration of PAHs from *A. polyacantha*, *A. xanthophloea* and *E. grandis* charcoal prepared by traditional pyrolysis was 6.18 mg/m^3, 6.25 mg/m^3 and 5.18 mg/m^3, respectively, while the total concentration of PAHs from the same wood species charcoal prepared by efficient pyrolysis was 1.62 mg/m^3, 0.73 mg/m^3 and 2.62 mg/m^3, respectively. The health effects of pollutants such as PAHs largely depend on the dose and amount of time an individual is exposed to the pollutant. Thus, individuals exposed to smoke from charcoal prepared by traditional pyrolysis are at a higher risk of suffering from health effects associated with PAHs such as cataracts, mutagenic, genotoxic and carcinogenic effects.

All the charcoal from the three tree species under study emitted similar types of PAHs but at significantly different concentrations. *A. xanthophloea* charcoal prepared by efficient pyrolysis emitted the least concentration of PAHs. Thus, according to this study, using charcoal produced from *A. xanthophloea* by efficient pyrolysis presents a better opportunity to reducing exposure from PAHs emitted from biomass fuels. The toxic effects of some of the group of compounds identified in this study, especially the PAHs, have been studied, and their effects are documented. Moreover, eight PAHs identified here, that is, naphthalene, benzo(a)anthracene, phenanthrene, anthracene, chrysene, fluorine, fluoranthene and pyrene have been classified are part of the 16 PAHs on the environment protection agency priority pollutants list (United States Environmental Protection Agency 1996). The study highlights existent of potent pollutants in biomass fuels, apart from CO_2 and CO, that the scientific community could focus on. Further study of emission of these pollutants and the pyrolysis and combustion conditions under which they are produced could help inform charcoal producers of the best methods and species from which to produce less harmful charcoal.

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