

Polycyclic Aromatic Hydrocarbons In Smokes Of Two Biomasses Used For Domestic Cooking In Nigeria

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ABSTRACT

Domestic cooking of foods is predominantly carried out in Nigeria through the burning of different types of biomass. Smoke resulting from such burning in most cases is been inhaled by people in the immediate environment where the cooking exercise is taking place. Where incomplete combustion occurs, the smoke may carry some products of incomplete combustion; prominent among these are polycyclic aromatic hydrocarbons (PAHs). Some of these PAHs have been implicated for various health challenges such as cancer. Incomplete combustion of fuels is known to generate PAHs. Smokes from some biomasses have also been established to contain some PAHs. This group of organic compounds is of global environment concern. The composition and concentration of PAHs in the smokes of two biomasses used in domestic cooking in Nigeria were determined. For this purpose, a pyrolytic unit was fabricated and used for the pyrolysis of Wood Charcoal (WC) and Palm Kernel Shell (PKS). Gases resulting from their pyrolysis were collected and analyzed using Gas Chromatography (GC). The results of GC analysis showed that the composition and concentration of PAHs in gas obtained from the pyrolysis of WC were; Acenaphthene ($0.218 \mu\text{g}/\text{cm}^3$), Fluorene ($0.573 \mu\text{g}/\text{cm}^3$), Phenanthrene ($13.305 \mu\text{g}/\text{cm}^3$), Anthracene ($0.552 \mu\text{g}/\text{cm}^3$), Fluoranthene ($9.069 \mu\text{g}/\text{cm}^3$), Pyrene ($8.677 \mu\text{g}/\text{cm}^3$), Benzo(a)anthracene ($0.660 \mu\text{g}/\text{cm}^3$), Chrysene ($0.660 \mu\text{g}/\text{cm}^3$), Benzo(b)Fluorene ($0.593 \mu\text{g}/\text{cm}^3$) and Benzo(k)fluoranthene ($0.853 \mu\text{g}/\text{cm}^3$). While the composition and concentration of PAHs in gas obtained from the pyrolysis of PKS were; Acenaphthene ($0.208 \mu\text{g}/\text{cm}^3$), Fluorene ($0.567 \mu\text{g}/\text{cm}^3$), Phenanthrene ($14.190 \mu\text{g}/\text{cm}^3$), Anthracene ($0.527 \mu\text{g}/\text{cm}^3$), Fluoranthene ($11.808 \mu\text{g}/\text{cm}^3$), Pyrene ($9.794 \mu\text{g}/\text{cm}^3$), Benzo(a)anthracene ($0.448 \mu\text{g}/\text{cm}^3$), Chrysene ($0.415 \mu\text{g}/\text{cm}^3$), Benzo(b)Fluoranthene ($0.346 \mu\text{g}/\text{cm}^3$) and Benzo(k)fluoranthene ($0.215 \mu\text{g}/\text{cm}^3$). Source diagnostic ratios calculated for the PAHs found in the pyrolytic gases of the biomasses showed that these PAHs were of pyrogenic origin, thus confirming that they were generated from the pyrolysis of WC and PKS

Key words: Biomass, pyrolysis, GC, Smoke and PAHs

INTRODUCTION

The burning of biomass to generate thermal energy for domestic cooking is very common in Nigeria and some other developing countries of the world. Poverty is the major reason for this practice. The cost of other sources of energy such as gas and kerosene is relatively expensive hence the dependence of people in lower and middle classes in developing countries on biomass for their domestic cooking. Where, houses are not well ventilated, a large proportion of smoke resulting from burning of such biomass is inhaled by the occupants of such houses. Such smoke and soot from burning of biomass may contain polycyclic Aromatic Hydrocarbons (PAHs) as established by some studies (Freeman and Cattel 1990; Naeluer et al., 2007; Pintes et al., 1998; Zou et al., 2003; Fine et al., 2004; Bergautt et al., 2008; Ravindra et al., 2008). In fact, incomplete combustion of fossil fuel and biomass is one of the main sources of PAHs in our environment (Zhang and Tao, 2009; Baek et al., 1991; Fisher et al., 2002; Ding et al., 2007). PAHs are hazardous organic chemicals which contain two or more benzene rings (Marce and Borull, 2000). They are recalcitrant organic compounds and some of them have also been linked with various different types of health challenges such as cancer (Menzie et al., 1992). Some others PAHs have been linked to impacting deleterious effects on both animals and humans such as respiratory, immunological, neurological, genotoxic and reproductive defects (Gupta et al., 1999; Mumford et al., 1993; Szczeklik et al., 1994).

In view of the link of generation of PAHs with incomplete combustion and wide use of charcoal and other biomasses for cooking in the rural areas and urban centers in Nigeria, it was decided to carry out a qualitative and quantitative determination of PAHs in the smokes produced during the pyrolysis of palm kernel shell and wood charcoal. The objective of the study was to enlighten the general public on the likely health hazards the practice of burning biomass for domestic cooking may cause.

MATERIALS AND METHODS

PYROLYSIS OF WC AND PKS

In order to stimulate the smokes produced when WC and PKS were being burnt, the two biomasses were separately pyrolysed in a locally fabricated pyrolytic unit. The gases produced from this process were collected and analysed for PAHs. The materials for the development of the pyrolytic equipment used for this work were sourced locally. The pyrolytic equipment consists of retort, brick furnace, condensation, receiver and gas collection unit. Other auxiliary units are: Measuring Cylinder, Valve of 12.7mm made of Zinc material, flange coupling, galvanized iron pipes, rubber hoses of 25mm external diameter, two rubber gaskets each of 280mm diameter, asbestos gasket of 200mm diameter. The pyrolytic unit is as shown in Figure 1.

The PKS and WC used for this work were obtained from Palm Kernel Oil Factory and Wood Charcoal Retail Shop respectively, in Ogbomoso, Nigeria. The Palm-Kernel shell was oven dried and milled. 0.9Kg of each of the milled samples were separately transferred into the retort and the inlet of the retort sealed with a cap that had asbestos on it, to make it air-tight. The retort was fixed into the brick-furnace and covered with 1.5kg of air-dried fuel wood billets. The fuel wood billets were then sprinkled with small quantity of Kerosene and ignited to generate the heat needed for the pyrolysis process. Gas produced from the process was collected into the gas cylinder (I), as shown in figure 1. The gas collected was subsequently analysed for PAHs using Gas Chromatograph coupled with flame ionization detector (GC-FID).

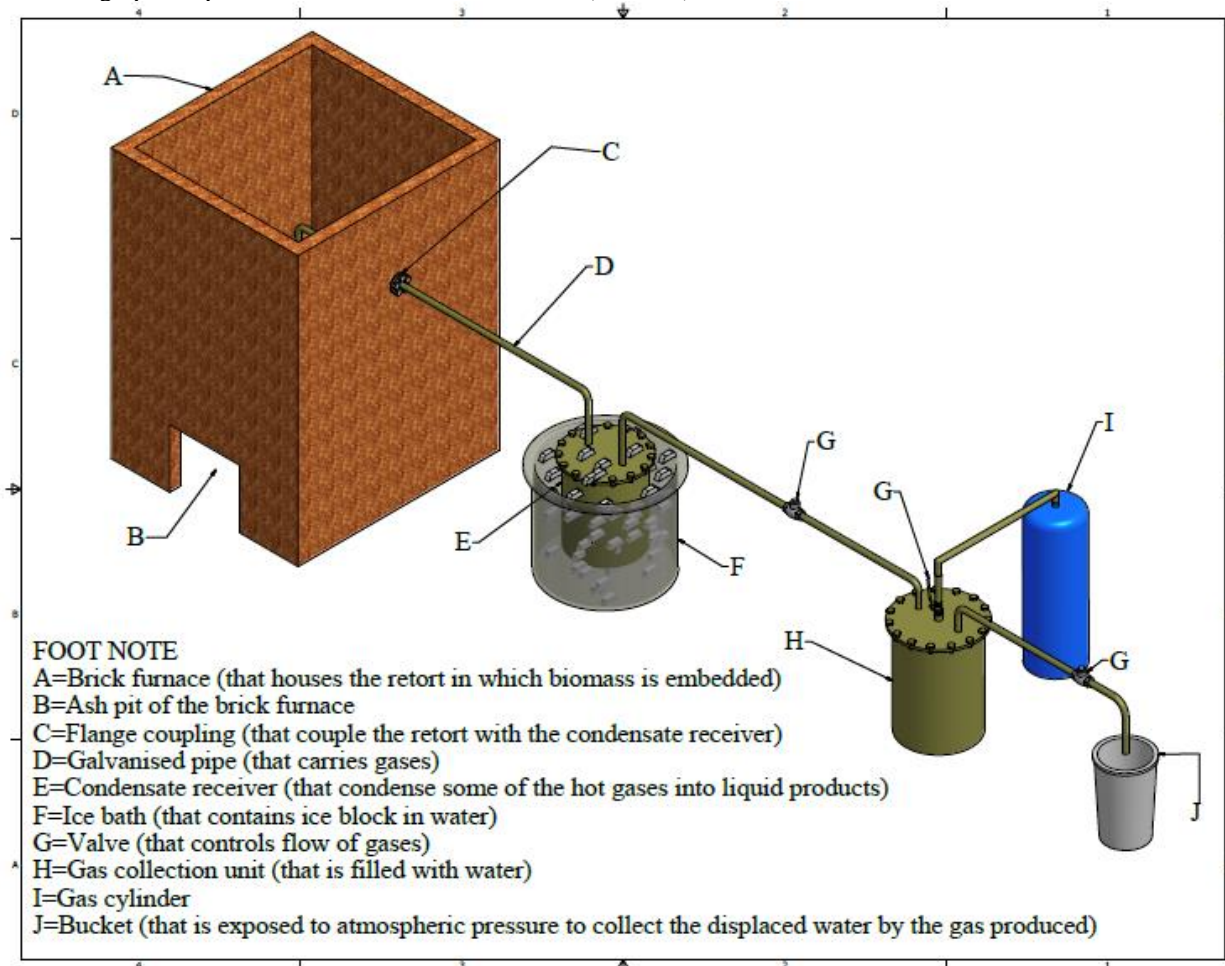


Figure 1 : Flow diagram for the pyrolysis of PKS and WC

GC ANALYSIS OF PAHs IN PYROLYTIC GASES

The PAHs analysis was performed on a Hewlett Packard (HP) GC Model 5890. The system consists of a gas chromatography (GC) equipped with a flame ionization detector (FID) and a data processor (Hewlett Packard, Wilmington, DE, USA). Loading of the sample into the GC was carried out using a micro syringe. The micro syringe was inserted into the rubber tubing of the gas tap of the cylinder that contained the pyrolysis gas. The gas was drawn into the syringe and content flushed out and process repeated twice. Thereafter, sample for the analysis (1 μ l) was taken and immediately and carefully loaded at the injection port of the GC-FID. The PAHs contained in the sample were automatically detected as they emerged from the column by the FID. The identification of PAHs was based on comparison of the retention times of the peaks with those obtained from standard mixture of PAHs (standards supplied by instrument manufacturer). Quantification was based on external calibrations curves prepared from the standard solution of each of the PAHs. The operation conditions for the GC analysis were as described by Olabemiwo et al. (Olabemiwo et al., 2010).

RESULTS AND DISCUSSION

The PAHs profile of gas from the pyrolysis of wood charcoal (WC) is as contained in Table 1. Ten different PAHs were found in the gas and their concentration varied from 0.218 to 13.305 μ g/cm³. Similarly, the PAHs profile of the gas from the palm kernel shell charcoal is as shown in Table 1. The gas contained ten PAHs, and their concentration varied from 0.208 to 13.305 μ g/cm³. The total concentrations of all PAHs in gases collected from the pyrolysis of WC and PKS were 35.190 μ g/cm³ and 38.518 μ g/cm³ respectively. It can be seen from Table 1 that the PAH profiles of the gases from the pyrolysis of the two biomasses are the same qualitatively. However, there was quantitative difference between the two gases which may be ascribed to difference in the type of the biomasses.

The sources of the PAHs found in the gases obtained from the pyrolysis of the biomasses studied were authenticated using some diagnostic ratios for source identification as earlier used by some authors. (Bhupander et al., 2012; Hwang et al., 2003; Fadzil et al., 2008; Yunker et al., 2002; Lee et al., 1995) Table 2 shows these ratios. The values of Flt/(Flt + Pyr) ratio for CW and PKS are 0.51 and 0.55 respectively (Table 2). The values are greater than 0.5 which indicate that the sources of the PAHs are from biomass or coal combustion as earlier established by Fadzil et al.(2008). The BaA/ (BaA + Chr) ratio for PAHs produced from combustion of biomass and coal should be greater than 0.35, according to Hwang et al.(2003). The values obtained for this ratio for the two biomasses are 0.51 and 0.52, showing that the PAHs obtained in this study are combustion products of the two biomasses. Furthermore, the values of flt / (Pyr) ratio for WC and PKS are 1.05 and 1.21 respectively, proving that the PAHs obtained from this study are from pyrolytic sources. This is in agreement with the findings of Lee et al.(1982) which gave a range of 1.0 – 1.4 for PAHs generated from combustion of biomass and charcoal.

PAHs having up to four benzene rings are classified as low molecular weight PAHs (LMW-PAHs) and those having more than four are classified as high molecular weight PAHs (HMW-PAHs). Igwo Ezikpe et al., (2010) Based on this classification, the PAHs found in the smoke or pyrolytic gases of WC and PKS were classified and summed (Table 1). The percentages of LMW-PAHs and HMW-PAHs in pyrolytic gas of WC were 41.63 and 58.37 respectively. In case of PKS, the percentages of LMW-PAHs and HMW-PAHs were 40.22 and 59.78 respectively. This implies that the smokes of WC and PKSC are predominated with HMW-PAHs. The detection of PAHs in the smoke of the two biomasses studied is in agreement with the findings of some other authors. These authors (Liu et al., 2001; Naumova et al., 2002; Ohura et al., 2004) attributed the presence of PAHs in outdoor environment to automotive and industrial sources but linked PAHs in indoor environment with human activities such as domestic heating, smoking and age of the building. Recently, a study by Gustafson et al. (Gustafson et al., 2008) showed elevated levels of several of the 4- and 5- ring PAHs in homes that used wood stoves.

The implication of the presence of PAHs in the smokes of these biomasses is that people who use them as sources of energy for domestic cooking are prone to inhalation of PAHs in the smokes. Some authors, using animals and humans in their studies have established the fact that exposure to wood smoke poses a risk to human health (Naeher et al., 2007; Stone 1995; Maria et al., 2009). Thus, health wise, the presence of PAHs in wood smoke is not good. The fact that the PAHs profiles of the smokes of these biomasses are dominated by HMW-PAHs makes the inhalation of these smokes even more worrisome. HMW-PAHs are been established to be more stable and toxic than LMW-PAHs. (Kondybach 1999). Apart from this, some of the medium and high molecular PAHs have been implicated in lung, colon and breast cancers in humans (Alonge, 1998, Simko, 2002). Thus, the non desirability of PAHs in our environment cannot be contested. Even some PAHs that have not yet been established to exhibit carcinogenic effect in humans have been reported to act as synergists (Ramesh et al.,

2004). Other health challenges that have been linked with PAHs in humans and laboratory animals are: renal, cardio, immuno, reproductive and developmental toxicities.(Alonge,1998).

Therefore, a precautionary measure needs to be taken, if it becomes impossible to avoid the use of biomass for heating in indoor environment. This is necessary because in such environment, inhalation of smoke generated from such burning is of very high probability. Inhalation of such smoke implies exposure to PAHs because smoke from burning of biomass is likely to contain PAHs as established in this study and others.

Table1: Composition and Concentrations of PAHs ($\mu\text{g}/\text{cm}^3$) in WC and PKS Smokes

| PAH | *Concentration of PAHs ($\mu\text{g}/\text{cm}^3$) in | |
|-------------------|---|--------|
| | WC | PKS |
| A _{Ne} | 0.218 | 0.208 |
| F _{le} | 0.573 | 0.567 |
| P _{he} | 13.305 | 14.190 |
| A _{nt} | 0.552 | 0.527 |
| F _{lt} | 9.069 | 11.808 |
| P _{yr} | 8.677 | 9.794 |
| B(a) _A | 0.690 | 0.448 |
| C _{hr} | 0.660 | 0.415 |
| B(b) _F | 0.593 | 0.346 |
| B(k) _F | 0.853 | 0.215 |
| Σ PAHs | 35.190 | 38.518 |
| Σ LMW PAHs | 14.648 | 15.492 |
| Σ HMW PAHs | 20.542 | 23.026 |

*Average of three readings

Acenaphthene (A_{Ne}), Fluorene (F_{le}), Anthracene (A_{nt}), Phenanthrene (P_{he}), Fluoranthene (F_{lt}), Pyrene (p_{yr}), Benzo(a)anthracene (B(a)_A), Chrysene (C_{hr}), Benzo(b)Fluoranthene (B(b)_F), Benzo(k)fluoranthene (B(k)_F).

PAHs = Polycyclic Aromatic Hydrocarbons

LMW PAHs = Low Molecular Weight PAHs

HMW PAHs = High Molecular Weight PAHs

WC = Wood Charcoal

PKS = Palm Kernel Shell

Table 2: Source Diagnostic Ratios of PAHs in WC and PKS Smokes

| PAH ratio | Value of ratio | Indication | Reference | Present study | |
|-----------------|----------------|--------------------------|-----------------------|---------------|------|
| | | | | CW | PKS |
| Ant/(Ant + Phe) | <0.1 | Petrogenic | (Hwang et al., 2003) | | |
| | >0.1 | Pyrogenic | | 0.04 | 0.04 |
| Flt/(Flt + Pyr) | <0.4 | Petrogenic | (Hwang et al., 2003) | | |
| | ≥0.4 – 0.5 | Pyrogenic | (Hwang et al., 2003) | | |
| | >0.5 | Biomass, coal combustion | (Fadzil et al., 2008) | 0.51 | 0.55 |
| BaA/(BaA+ Chr) | <0.2 | Petrogenic | | | |
| | 0.2 – 0.35 | Petroleum combustion | (Hwang et al 2003) | | |
| | >0.35 | Biomass, coal combustion | (Yunker et al., 2002) | 50.51 | 0.52 |
| Flt / Pyr | <1.0 | Gasoline, diesel | | | |
| | 1.0 – 1.4 | Biomass, coal combustion | (Lee et al., 1982) | 1.05 | 1.21 |

CONCLUSION

Analysis of smokes produced from pyrolysis of WC and PKS showed the presence of ten different PAHs in varying concentrations in each of the smokes. Thus, people who use these biomasses for cooking are at the risk of inhaling some of the PAHs contained in their smokes.

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