



# SCREENING THE FORMATION OF THE POLYCYCLIC AROMATIC HYDROCARBONS DURING COMBUSTION OF COMMON DOMESTIC FUELS

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The use of biomass and other solid material as a source of energy is associated with some deleterious effects consequent to incomplete combustion associated with poor ventilation leading to production of a number of chemical compounds that are known or suspected to be a health threat. This study reports the screening of the formation of the polycyclic hydrocarbons during pyrolysis of the fuel materials, namely, coal, dung and wood, commonly used as fuel in rural areas in Lesotho, under poor aeration using a simple in-house pyrolysis unit. The method demonstrated sufficient linearity for the standards with correlation coefficient,  $R^2 \geq 0.9884$  and repeatability (%RSD  $\leq 15$  %) of the real samples used, coal demonstrated production of naphthalene and pyrene, while from the cake dung formation of naphthalene was detected. Despite not being extensive, the results form a basis for a more rigorous study including employing more identification tools, such as mass spectrometry that enables identification and a better detection of low levels of the analytes.

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## INTRODUCTION

Solid biomass fuel is one of earliest energy sources since the medieval times, and it is still the most easily accessible and affordable source of energy particularly in rural areas.<sup>1,2</sup> Literally any combustible material can be used as fuel to produce heat or power. However these sources of energy are not devoid of setbacks such as producing some hazardous chemical compounds associated with the fumes they produce during combustion especially in poorly ventilated rooms,<sup>3</sup> as well as reducing the amount that is recycled back into agricultural practices as manure.<sup>4</sup> Solid fuels typically are difficult to burn in simple combustion devices such as household cooking and heating stoves without substantial emissions of hazardous chemicals, principally because of the difficulty of completely pre-mixing the fuel and air during burning, which is done easily with liquid and gaseous fuels.

Consequently, a substantial fraction of the fuel carbon is converted to by-products of incomplete combustion, namely, fine particulates which are reportedly highly oxidising<sup>2</sup> and other obnoxious gases containing principally carbon monoxide, carbon dioxide and polycyclic aromatic hydrocarbons (PAHs).<sup>5</sup> Of these chemicals carbon monoxide is the most dangerous as it can cause fatality within minutes if inhaled, consequently, highly sensitive detectors have been developed for detection and monitoring of carbon monoxide in places that are likely to produce them. On the other hand, PAHs, a series of six-membered ring compounds, are suspected to be carcinogenic<sup>6</sup> and/or to have some endocrine activity.<sup>7</sup>

The major source of indoor air pollution in rural areas around the world is the burning of traditional biomass fuel such as wood, dung and agricultural wastes.<sup>8</sup> Due to their poor aeration solid fuels are characterized by incomplete combustion. A study reported that household coal and biomass cooking stoves in China (similar to those in households of developing countries) diverted between 10% and 38 % of their fuel carbon into by-products of incomplete combustion.<sup>9</sup> Due to this incomplete combustion, solid fuels are associated with respiratory ailments. Another study in India on 897 women, 615 of whom used biomass exclusively, demonstrated a correlation of the effect of biomass burning to prevalence of respiratory ailments, 71 % of these women presented respiratory symptoms as opposed to only 28 % of the 282 who used LPG gas exclusively.

These ailments included chest tightness or chest discomfort (43.3 % vs. 7.3 %), sore throat, cough, recurring headache, eye irritation, eye watering, dizziness, muscle pain, tingling and numbness in the extremities. Like the adults, children from biomass using families had 2-times more respiratory symptoms than age- and sex-matched children from LPG gas using families (70.3 vs. 35.9 %). The prevalence of respiratory symptoms both in adults and children was positively correlated with particulate pollutant level in indoor air.<sup>10</sup>

A different study showed that chronic exposures to biomass smoke were associated with impaired lung function. Lung function decrement was most prevalent in women who cook predominantly with dung cake and in kitchen adjacent to living areas.<sup>11</sup> Reduction of lung function was positively associated with years of exposure to biomass smoke and low socio-economic status.<sup>12</sup> Women who used to cook with biomass fuels had greater prevalence of metaplasia and dysplasia of airway epithelial cells, which are recognized as early cellular changes towards development of cancer, several-fold rise in micronucleus frequency in buccal and airway epithelial cells that suggest chromosomal damage in these cells.

Taken together, these findings indicate greater risk of cancer in the lungs and the airways in rural women who are inhaling smoke from burning biomass during daily household cooking. According to Zhang and Smith,<sup>9</sup> global meta-analyses of epidemiologic studies indicate that indoor air pollution from solid fuel use in many developing countries is responsible for approximately 420,000 premature deaths annually, more than the approximately 300,000 attributed to urban outdoor air pollution in cities with populations of more than 100,000.<sup>13</sup> Household use of solid fuels is thus estimated to be the largest single environmental risk factor and ranks sixth among all risk factors examined for ill-health.

As a typical least developed country, Lesotho, a small mountainous country wholly landlocked within South Africa still relies heavily on burning of biomass for provision of energy for domestic purposes with about 67 % usage.<sup>14</sup> Although, there is considerable urbanisation, about 85 % of Lesotho's population of about 2.2 million, still reside in rural areas,<sup>15</sup> while also a considerable fraction of poor urban residents still rely almost exclusively to the use solid fuels (biomass and coal) for household cooking and/or heating. Among the most widely used solid fuel in Lesotho are wood (70 %), animal dung in all its forms (25 %) and the remaining 5 % ascribed to crops residues as well as any other combustible materials,<sup>14</sup> with coal being accessible to middle class, usually for heating rather than cooking. Of the used solid materials used for fuel, coal is the widely studied and well-documented fuel globally in terms of its benefit and disadvantages while the other materials are not as widely studied.

Usually dung is used in two forms after natural air and sun drying, normal droppings and the cake dung (compacted dung) which is usually dug in the kraals after a number of years of using that kraal to secure the animals. Due to its compactness, cake dung hardly burns into a flame. It is however preferred as it is believed to provide more heat per unit volume as compared to wood and normal dropping. Despite this benefit, cake dung is associated with obnoxious smell and produces a lot of smoke leading to soot formation on the roof and the top part of the walls of the room in which it is burned. This is possibly due to the lower porosity than the other form (normal dropping). Consequently, it is believed that this cake dung should be liable to producing more PAHs as well as other xenobiotic compounds than the other solid materials used as fuel.

PAHs are usually analysed using chromatographic techniques coupled to different detectors depending on their concentration levels.<sup>16,17</sup> Being such conjugated systems PAHs have relatively high molar absorptivity as such they can easily be detected using either molecular absorption or fluorescence spectrophotometry.<sup>18</sup> However, this still requires some sample preparation and extraction of these compounds from the matrices they are occurring in. Some of the extraction and sample preparation methods employed include the purge and trap,<sup>19</sup> solid- and liquid-based with the solid-based techniques the most preferred for gaseous samples.<sup>20</sup> In this study we describe an application of a simple in-house built pyrolysis unit coupled to hollow-fibre supported liquid-liquid micro-extraction and gas chromatography for screening of production of PAHs during

pyrolysis of some solid materials like coal, wood, cow dung (both normal droppings and cake dung), which are commonly used as fuel source in Lesotho.

## EXPERIMENTAL

All the chemicals were of analytical grade and obtained from Merck South Africa. Toluene, xylene and dodecane were used as extracting solvents, while trichlorobenzene was used as internal standard for the real samples, the choice of which was based on the lack of possibility of neither being present nor produced during pyrolysis of these materials. Different PAHs, namely, naphthalene and pyrene were used as standards for the extraction. A sample of activated charcoal was used as reference virgin sample on which the preliminary experiments were carried out. A coal sample was obtained from a local coal supplier while the cow dung samples - dry dropping sample and the compacted cake dung were collected from one small-holder farmer in a village just outside the NUL – Roma campus. All the solid samples were ground to a fine powder and were weighed appropriately before the sampling.

### Apparatus

Samples were collected in a cock-stoppered Schlenk® tube leaving only the side-arm open to release the pyrolysis gases. A gas tight 100  $\mu$ L Hamilton® syringe was fitted with a 1 cm long hollow-fibre membrane (HFM) filled with sufficient organic solvent. The extracts were analysed using a Saturn 3800 gas chromatograph (Varian, USA) fitted with a 30 m x 0.53 mm x 0.25  $\mu$ m SGE-BP5 (5 % phenyl-95 % dimethyl-polysiloxane) fused glass capillary column (Texas, USA) connected to the flame ionisation detector. Grade 5.0 nitrogen was used as a carrier gas at a constant flow rate of 5 mL min<sup>-1</sup>. The temperature program started with the 80 °C held 3 min, followed by 10 °C min<sup>-1</sup> ramping to 300 °C and held for 3 min. The split-splitless injection port was kept on split at the ratio of 1:10 and set at 250 °C while the detector temperature was also set at 250 °C.

### Preparation of the solid samples and the sampling procedure

About 100 g of a fine activated charcoal powder was heated in the oven at a temperature of 250 °C for 30 minutes to get rid of any organic compounds that it may have adsorbed. This activated charcoal sample was spiked with a mixture of naphthalene and pyrene and mixed thoroughly to obtain a surrogate sample with the composition of about 0.1 g the PAH in 100 g of activated charcoal. Working samples were prepared from this surrogate and were used in portions of about 1 g in all the experiment except where the variation of mass was necessary, in which case the actual mass will be stated.

To test whether the experiment could succeed, about 1 g of the surrogate sample was poured gently (to reduce the amount of sample attaching on the walls) into the Schlenk tube mounted on the retort stand. Thereafter, an organic solvent-filled hollow fibre membrane was introduced through the syringe into the pyrolysis unit through the side-arm to about 1.5 cm deep so that it gets into contact with the

plum of gases from the sample as it is heated/pyrolysed. Thereafter a flame was introduced using the Bunsen burner to heat the test tube gently. After the sampling time has elapsed, the extract (2  $\mu\text{L}$  of the remaining sampling organic solvent) was injected into the gas chromatograph for analysis repeated in triplicates for determination of repeatability. The pyrolysis assembly can be visualised in Supplementary material (Figure S1).

Following the success thereof, different parameters were tried for experiment to optimise the extraction of the spiked PAHs virgin charcoal samples. Only a few parameters were studied following a univariate approach, namely, the choice of solvent for the HF-LPME, effect of distance of the flame from the test tube base, the effect of varying sample size (linearity) and repeatability. Following the optimisation, the charcoal samples were replaced by the real fuel samples, coal, wood, normal and compacted (cake) dung respectively. Trichlorobenzene was spiked into the extracting solvent as an internal standard at a concentration of  $0.01 \text{ g } 100 \text{ g}^{-1}$  which was later reduced accordingly so that the responses were in the same order of magnitude as the analytes from the real samples.

## RESULTS AND DISCUSSIONS

### Demonstration of the assembly and proof of concept

A home-made pyrolysis and sampling unit using a Schlenk tube, a Bunsen burner and a Hamilton® syringe fitted a hollow fibre membrane containing an organic solvent was used. Since the membrane gets colourless when it is impregnated with the solvent, sampling was stopped at the first sight of white colouration appearing at the tip as the solvents start to evaporate due to the hot gas coming from the heated sample.

The experiment initially suffered a lot of inconsistencies as a few times, the extracting solvent evaporated to dryness before the importance of controlled the heating rate was noted. Different trials were made moving the flame back and forth until a perfect distance was achieved both by height of the test tube relative to the flame and the distance from the flame. These were, however, not measured accurately except that the test tube should about 5 cm from the end of the visible part of the flame to ensure slow heating. A summary of the chromatographic information is summarised in Table 1. The method was further refined for the choice of solvent used for extraction, variation of sample size and composition the results of which are presented in the following sections of this report.

### Effect of solvent choice on the extraction efficiency

Only three solvents with sufficient purity and high boiling temperatures were available as such solvent choice was limited to these three. Figure 1 shows the effect of different solvents on the extraction efficiency of the analytes from the spiked charcoal sample.

As can be seen, dodecane demonstrated better extraction efficiency although this was coupled with a limitation that dodecane and naphthalene were significantly overlapping leading to sometimes difficulty in integrating the naphthalene peak. On the other hand, xylene was a bit old and contaminated, consequently toluene was chosen as a best solvent. The efficiency with dodecane could be attributable to a relatively higher boiling point, hence lower volatility than the other two solvents, as such it would sample for a slightly longer period than toluene.

### Investigation of the effect of varying sample size on the amount of PAHs recovered

To assess the effect of the sample size, different amounts of the charcoal sample were introduced and treated as explained. The results presented in Figure 2 demonstrated an expected increase with the increase in sample size although as the sample mass increases, there is a slight drop in extraction efficiency with an compromised precision as evidenced by an increased standard deviation denoted by the error bars. However, it seems that the extraction reaches a somewhat saturation beyond 1.5 g. This could be due to the uneven distribution of heat throughout the sample leading to different times of the analytes pyrolysis from the matrix, hence the increased variation between the analytes. Moreover, as the extracting solvent kept evaporating from the hot fumes, it could be that as the late analytes pyrolysed, the solvent was already too limited in the membrane to efficiently extract it.

### Effect of varying the concentration of the analytes in the charcoal sample

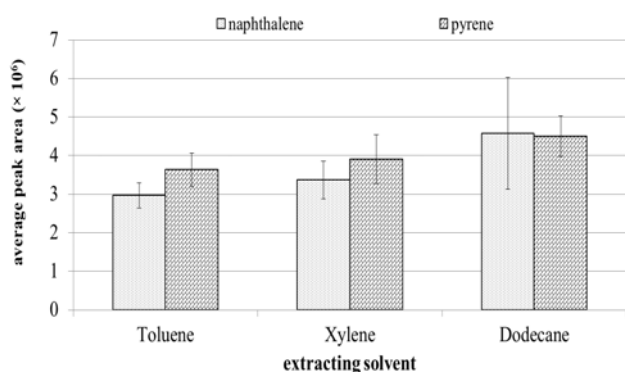
To investigate the effect of varying initial concentration of the analytes in sample, the pre-spiked 'stock' sample was diluted by mixing it different amounts of the virgin charcoal sample to obtain different concentrations/compositions. Table 1 depicts the effect of varying the initial concentration on the extraction efficiency.

**Table 1.** Some analytical calibration data obtained using the variation of analyte composition

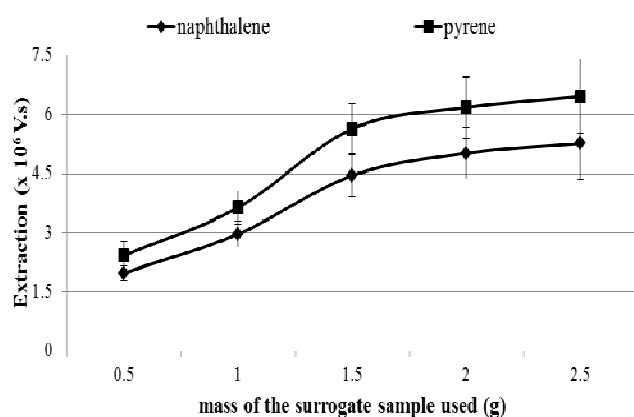
Parameter	Naphthalene	Pyrene
Retention time	11.583	16.002
Repeatability (% RSD)	11.3	13.9
Regression eqn.	$y = 7147x + 97$	$y = 10085x + 104$
Linearity, $R^2$	0.9986	0.9884
Calibration error	57	63
Error of the intercept	29	47
Est. LOD* ( $\text{mg } 100 \text{ g}^{-1}$ )	0.016	0.014
Est. LOD ( $\mu\text{g } \text{g}^{-1}$ )	0.16	0.14

\*Estimated LOD calculated using equation  $\text{LOD} = 3\sigma/m$  where  $\sigma$  represents the standard error and  $m$  represents the slope of the calibration data from varying the analyte composition.

Clearly this approach yields similar trend to the one using different mass of sample except that the linearity is more improved ( $R^2 \geq 0.9884$  from 0.9132).



**Figure 1.** The effect of different organic solvents on extraction efficiency.



**Figure 2.** The effect of increasing the sample size on the recovery of the analytes.

This is possibly due to uneven distribution of heat as the sample increases, while in the latter approach, there is always the same sample mass, hence the problem of non-uniform heat distribution is minimised.

Due to the inevitable analytes loss with the fumes through the side-arm opening, the method demonstrated relatively high limits of detection ( $0.14$  and  $0.16 \mu\text{g g}^{-1}$  of sample). However, these are gratifying considering the method is yet to be fully validated. Moreover, these can be improved by using an online pyrolysis, which is not a very common instrument in resource-constrained laboratories.

#### Analysis of real samples

To determine the amount and presence of the PAHs in the real samples, an external standard calibration approach with 1-g samples was used whereby the intensities of the signals were read off and corresponding concentrations for the 1 g real samples calculated from the regression equations in Table 2. As can be seen from Table 2, no analyte was detectable in the normal dropping but naphthalene was detectable in both the coal and compacted dung samples. The considerably high % RSD could be attributable to poor validation of the method, which will be improved in the next

phase of the experiment as well as the fact that the amounts of the detectable analytes are at the same level as the limits of detection.

The normal droppings did not show any detectable levels of the PAHs, possibly due to the fact that droppings are highly porous which enables effective aeration during combustion, hence burning of droppings was more complete than that of the compacted dung.

**Table 2.** Determination of the production of the PAHs from the different fuel samples.

Sample	Amount of analyte in the sample*	
	Naphthalene	Pyrene
Coal	8.31 (11 <sup>#</sup> )	0.67 (14 <sup>#</sup> )
Wood	n.d.	n.d.
Cow dung dropping	n.d.	n.d.
Cake cow dung	0.78 (18)	n.d.

\*  $\mu\text{g g}^{-1}$  of sample; <sup>#</sup> % RSD for  $n = 3$

Besides naphthalene, the coal sample demonstrated a production of some compounds with retention times between 12 and 14 minutes. These could be lower order PAHs such as anthracene and phenanthrene (3-membered ring) since pyrene is a 4-membered ring structure. There was another dominant peak whose peak area was about 20 times that of pyrene at the retention time of 6.988 minutes. Unfortunately this peak could not be attributed to any PAHs since the lowest in the PAHs family and hence the most volatile is naphthalene with the retention time of 11.583 minutes. However, since there were no standards against which to compare with, these compounds were not identified nor quantified.

## CONCLUSION

The presence of naphthalene in the compacted sample confirms what the researchers had apprehended i.e., the potential production of PAHs during burning these materials in poorly ventilated areas. Although the levels are low, this is still a concern given that the materials are usually burnt in poorly ventilated rooms sometimes with no windows thus exposing the occupants to these compounds. Although this is only at the preliminary level, the results are gratifying since they can point towards the need of further research in the safe use of these materials, since not all households can afford the other fuel materials. Unfortunately, no similar work is available for comparison.

However, it can be concluded that the in-house constructed technique can be usable for the detection of the PAHs, with the only limitation being the detection limit of the detector used. Only one PAH – naphthalene was detected and tentatively identified in coal ( $8.31 \mu\text{g g}^{-1} = 0.831 \text{ mg } 100 \text{ g}^{-1}$ ) and compacted cake dung ( $0.78 \mu\text{g g}^{-1} = 0.078 \text{ mg } 100 \text{ g}^{-1}$ ) of sample. The method demonstrated sufficient linearity ( $R^2 \geq 0.9884$ ) and a relatively low repeatability with an average standard deviation between 11 and 18 %. Since Lesotho cannot afford to electrify every household and neither can every household afford the

electricity as a sole domestic fuel source it is recommended that introduction of overhead chimneys or chulhas should be considered for proper ventilation for kitchens.

## REFERENCES

- <sup>1</sup>Balakrishnan, K., Sankar, S., Parikh, J., Padmavathi, R., Srividya, K., Venugopal, V., Prasad, S., Pandey, V. L., *Environ. Health Perspect.*, **2002**, *110*(11), 1069.
- <sup>2</sup>Barnes, D. F., Openshaw, K., Smith, K. R., van der Plas, R. *World Bank Techn. Paper 242*, World Bank, **1994**, 1.
- <sup>3</sup>Mudway, I. S., Duggan, S. T., Venkataraman, C., Habib, G., Kelly, F.J., Grigg, J. *Part. Fibre Toxicol.*, **2005**, *2*(1), 6.
- <sup>4</sup>Pant, K. P. *A Report to the South Asia Network of Economic Res. Inst.*, **2010**, 1.
- <sup>5</sup>Raiyani C. V., Jani J. P., Desai, N. M., Shah, S. H., Shah, P. G., Kashyap, S. K. *Bull. Environ. Contam. Toxicol.*, **1993**, *50*(5), 757.
- <sup>6</sup>Mastrangelo, G., Fadda, E., Marzia, V. *Environ. Health Perspect.* **1996**, *104*(11), 1166.
- <sup>7</sup>Kummer, V., Mašková, J., Zralý, Z., Neča, J., Šimečková, P., Vondráček J., Machala, M. *Toxicol. Lett.*, **2008**, *180*(3), 212.
- <sup>8</sup>Nigel, B., Perez-Padilla, R., Albalak, R. *Bull. World Health Organ.*, **2000**, *78* (9), 1078.
- <sup>9</sup>Zhang, J., Smith, K. R. *Environ. Health Perspect.*, **2007**, *115*(6), 848.
- <sup>10</sup>Albalak, R., Frisancho, A. R., Keeler, G. J. *Thorax*, **1999**, *54*(11), 1004.
- <sup>11</sup>Ki-Hyun, K., Jahan, S. A., Kabir, E. *J. Hazard. Mater.*, **2011**, *192*(2), 425.
- <sup>12</sup>Anderson, H. R. A Chapter in *The Rising Trends in Asthma*, Wiley, Chichester, **1997**, *206*, 190.
- <sup>13</sup>Cohen, A. J., Anderson, H. R., Ostro, B., Pandey, K. D., Krzyzanowski, M., Künzli, N., Gutschmidt, K., Pope III, C. A., Romieu, I., Samet, J. M., Smith, K. R., *Comp. Quantif. Health Risks*, **2004**, *2*, 1353.
- <sup>14</sup>Tsehlo, T. B. *A Report to the United Nations Commission on Africa (UNECA)*, United Nations, Washington DC, USA, 2012.
- <sup>15</sup>*United Nations Development Programme Lesotho*, **2006**, pp1-72. Maseru, Lesotho. Retrieved on 21 May 2016 from [http://www.undp.org/content/dam/undp/documents/projects/LSO/00042547\\_LREBRE\\_00049143\\_Prodoc.pdf](http://www.undp.org/content/dam/undp/documents/projects/LSO/00042547_LREBRE_00049143_Prodoc.pdf).
- <sup>16</sup>Poster, D. L., Schantz, M. M., Sander, L. C., Wise, S. A. *Anal. Bioanal. Chem.*, **2006**, *386*(4), 859.
- <sup>17</sup>Pandey, S. K., Kim, K. H., Brown, R. J. *Trends Anal. Chem.*, **2011**, *30*(11), 1716.
- <sup>18</sup>Ghasemi, J. B., Zolfonoun, E. *Environ. Monit. Assess.*, **2013**, *185*(3), 2297.
- <sup>19</sup>Wang, M., Zhang, S., Zhang, X., Zhang, J. *Anal. Lett.*, **2013**, *46*(12), 1951.
- <sup>20</sup>Hüffer, T., Osorio, X. L., Jochmann, M. A., Schilling, B., Schmidt, T. C. *Anal. Bioanal. Chem.*, **2013**, *405*(26), 8387.

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