

Volatile Organic Compounds (VOCs) Emitted from the Point of Combustion of Charcoals Produced from Three Potentially Toxic Tree Plants in Nigeria



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Submission: March 15, 2021; **Published:** April 08, 2021

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Abstract

In order to have empirical insight into the toxicity linked to indoor exposure to charcoal products used for commercial and domestic heating in indigenous Nigerian communities, three potentially toxic tree plants widely used for making charcoals, which includes 'Gwaska' (*Erythrophleum sauevolens*), 'Kwalbiya' (*Prosopis* spp) and 'Tukpoku' (African tulip: *Spathodea campanulata*), were identified from their natural habitats. They were processed into charcoals using indigenous kiln by the experts under the supervision of the research team. The processed charcoals were subjected to control combustion in a 21cm x 21cm x 15cm furnace from where the VOCs and other essential air quality parameters were detected from the venting outlet (chimney) with diameter 6.6cm, using calibrated indoor air detector (Air Master). The air quality parameters detected were VOCs, formaldehyde (HCHO), PM_{2.5}, PM₁₀, and % relative humidity (RH). Various VOCs were detected after characterizing them from the hot smoke emitted from each of the charcoal samples using Gas Chromatography Mass Spectrometry (GC-MS). Some of the VOCs such as toluene and carbonyl derivatives were potentially toxic, due to this, the work recommends that charcoals should not be produced from any of these tree plants under the conditions adopted in this research.

Keywords: Profile, VOCs, Charcoal

Introduction

Use of charcoal and wood products have become almost unavoidable as it is the widely used source of energy for heating purposes in most developing nations. Because of the varieties of the sources of the charcoal products from different tree plants, some toxic chemical substances are often emitted during the burning processes. Among such substances are the volatile organic compounds (VOCs), full of uncertainties as the fate of these class of compounds cannot be clearly defined. Apart from being directly injurious to human and other living beings, they also affect the environment. For instance, VOCs containing halogens are potential green house and ozone depleting substances [1]. They are widely released from burning fuel such as, gasoline, wood, coal, or natural gas. They are also emitted from oil and gas field and diesel exhaust. Their sources can also be traced to releases from solvents, paints, glues, and other products that are used and stored at home and at work place. The effect of these substances when inhaled ranges from dry mucous membrane and skin; irritation of eyes nose and

throat, chest tightness, headache; and mental fatigue [2]. Common examples of volatile organic compounds are: gasoline, benzene, formaldehyde, carboxylic acid derivatives, solvents such as toluene and xylene, styrene and perchloroethylene (tetrachloroethylene)-the main solvent used in dry cleaning [3]. Charcoal is a widely used household energy source used as the most predominant source of energy for heating in most households in developing nations and is fast becoming the source of most unintended VOCs in the environment. This study on VOCs is very important because apart from the health implication due to direct exposure to them, they also play strategic roles on atmospheric chemistry as they affect the formation of photochemical smog which dwindle the air quality and further threatens human health and the ecosystem [4]. An earlier study has indicated that VOCs enters the bloodstream through inhalation, ingestion and the skin [5]. This work detects and characterise the VOCs in potentially toxic tree plants being used in some places in Nigeria for making charcoals.

Materials and Methods

Study area

The study was carried out in Jos North and Bassa LGA Metropolis of Plateau State (Figure 1), North Central Nigeria. Jos North is located in the North-West part of the State, which is situated on latitude 7° and 11°N and longitude 7° and 25° E

and at an average altitude of about 1200m above sea level; with a population of about 873,943 at the Census, 2006 (although quite a lot more now). Jos North and Bassa are Local Government Areas in the northern part of Plateau State, Nigeria, bordering Kaduna and Bauchi States. The topography of the area is undulating grassland with scattered trees.

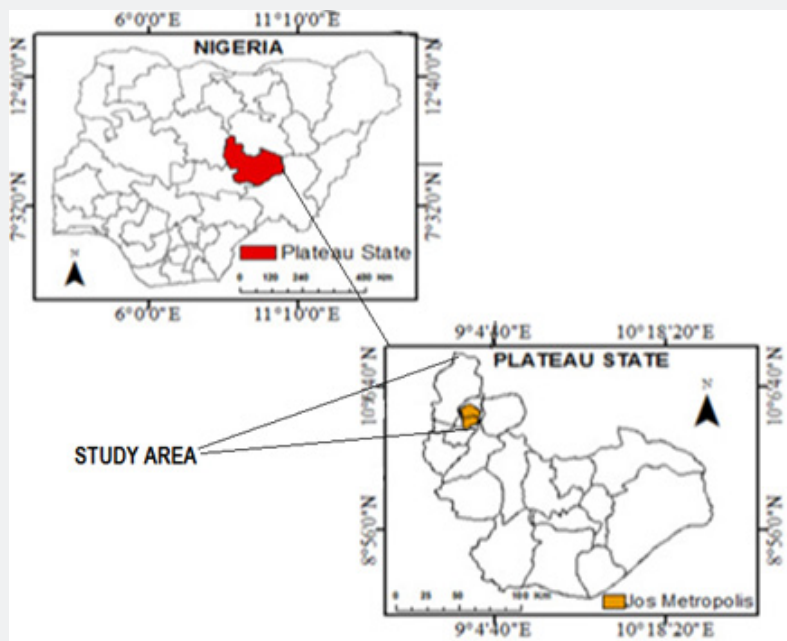


Figure 1: Map of Jos North and Bassa LGA, Plateau State, Nigeria.

Samples collection and preparation

The samples used for this research were collected at Jengre, Bassa LGA and Mazah, Jos North LGA, Plateau state, Nigeria. Various grades of the charcoal were collected in polythene bag, after which they were transported to the research area at the Chemical Sciences Laboratories of University of Jos, Nigeria.

Detection of VOCs emissions on combustion of charcoals

A combustion chamber made up of 21cm x 21cm x 15cm flat sheet iron constructed furnace with a fume head (chimney) of 6.6cm diameter was used to carry out a controlled combustion of the prepared charcoal samples. A calibrated indoor air detector (Air Master) was used to detect the VOCs and other essential quality parameters such as: HCHO, PM_{2.5}, PM₁₀, and % relative humidity (RH) from the smoke emitted through the chimney.

Analytical methods & characterization

Sampling device and collection of VOCs for characterization

The smoke fumes produced from a combustion chamber

were collected in a sampler which comprises glass sampling tube (sorbet tubes) open at both ends and filled with activated charcoal (Figure 2). Each opening in sampling tube is filled with cellulose acetate diffusion barrier (cotton wool). The smoke fume diffuses into the sampling tube in a controlled manner, keeping the cross section, tube length diffusion coefficient constant.

Extraction process

After sampling, adsorption tubes were labeled and closed with special caps to avoid contamination and desorption. The samples were placed in tightly closed special plastic bags and kept in a freezer until they were processed. Before analysis, contents of both sections of the adsorption tubes were placed into two different pre-weighed glass sample tubes, and 10ml dichloromethane added as the desorption solvent to each tube. Samples were extracted by shaking them in corked bottles using a magnetic stirrer (Jenweary) for 30min. Ammonia was intermittently used to elute the sample in the bottles. The extracted samples were then purified in a micro chromatographic column filled with silica gel (60-129 mesh) stored in a freezer until they were detected [6].

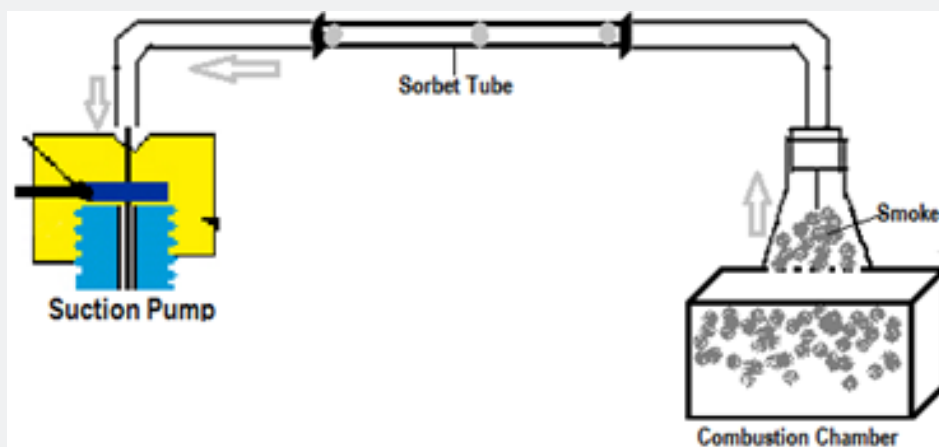


Figure 2: VOCs Adsorption process.

Characterization

The VOCs compounds in the extracted solutions were detected immediately after each desorption experiment using gas chromatography coupled with mass spectrometric detection (GC-MS). The model of the GC-MS used is Agilent GC 7890B, MSD 5977A, Agilent Technologies, USA. The GC column was eluted with an initial oven temperature of 30°C increased to 60°C after holding for 3min at a rate of 3°C min⁻¹ and finally to 240°C at the rate of 45°C min⁻¹. Helium was used as carrier gas at a constant flow rate of 40ml min⁻¹.

Results and Discussion

Table 1 provides the Local, English and Scientific names of the three toxic tree plants used for the charcoal products indicated with their corresponding samples codes (GWK, KWB and TPK). Similarly, the VOCs, HCHO and Particulate Matters (PM_{2.5} & PM₁₀) detected from the smoke of the GWK, KWB and TPK are shown in Table 2. The VOCs clearly indicated in Figure 2 is the total VOCs

and HCHO emitted which might be potential sources of the toxin from the point of combustion of the charcoal samples. The highest VOCs of 2.98mg/l was detected in the GWK Sample and TPK had the least with 1.98mg/l recorded. These values are much higher than value of 430µg/l reported for VOCs detected in the very busy Apapa Industrial layout acclaimed to be a highly polluted site in a the densely polluted city of Lagos [7]. This suggests the quality of smoke emitted from these charcoals is obviously not environmentally friendly. On the other hand, formaldehyde (HCHO) detected was in the range 0.33-1.24mg/l widely reported to cause burning sensation to sensitive body organs like; nose, throat and eyes. In severe case causes respiratory problem and allergies. It has also been reported to cause cancer of the nasal cavity [8]. Constant exposure to these chemical substances by using these charcoals for cooking and heating, leaves the users under health threats as some of the VOCs (formaldehyde, toluene etc) emitted are reported to be toxic, with other labelled as potential carcinogens [9] (Figure 3).

Table 1: List of Tree Species identified used for Charcoal Production.

| Local Name | English Name | Scientific Name | Charcoal Product |
|------------|---------------|--------------------------------|------------------|
| Gwaskaa | Sasswood | <i>Erythrophleum guineense</i> | GWK |
| Kwalbiya | Spike thorn | <i>Prosopis spp</i> | KWB |
| Tukpoku | African tulip | <i>Spathodea campanulata</i> | TPK |

Table 2: Multi- Gas (Air Master) Detector Analysis of the Charcoal Smoke Samples.

| Charcoal Samples | PM _{2.5} (µg/l) | PM ₁₀ (µg/l) | HCHO (mg/l) | VOCs(mg/l) | RH (%) |
|------------------|--------------------------|-------------------------|-------------|------------|--------|
| GWK | 29 | 40 | 1.24 | 2.98 | 19.2 |
| KWB | 38 | 51 | 0.46 | 1.98 | 19.93 |
| TPK | 89 | 103 | 0.33 | 2.1 | 15.54 |

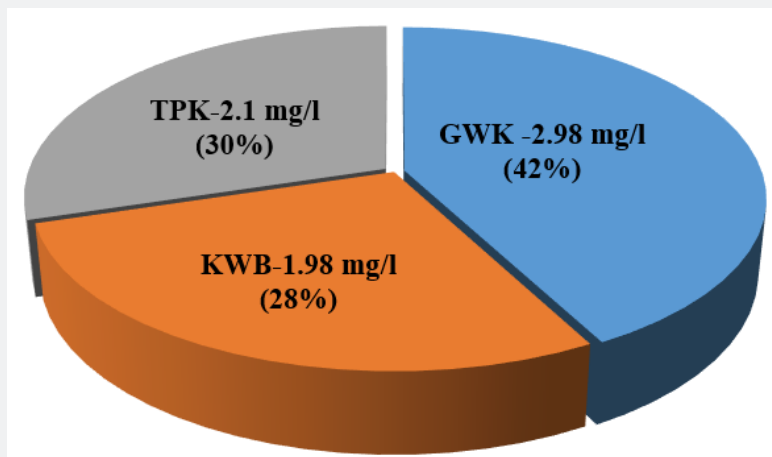


Figure 3: Total VOCs (TVOCs) Detected from GWK, KWB & TPK.

On characterising the VOCs emitted from the samples using GC-MS after sorption, desorption and purification, the following compounds were detected; toluene, carbonyl compounds (formaldehydes, 9-octadecenoic acid etc), silane, 3,4-methylenedioxyamphetamine (MDMA) methylene homolog, octadiene and phenol (Figures 3, 4 & 5). Most of these are VOCs of interest owing to toxicity linked to them [10,11]. Toluene for instance, was detected in GWK and KWB with composition of 2% and 1% respectively. In terms of dominants, 5-diazo-1,3-cyclopentadiene was detected in TPK with composition of 100% (Table 3). Although there is limited literature on the toxicity of this compound, more work still needs to be done on it to establish its toxicity. It is however reported to be in the family of compounds formed during pyrolysis [12]. This was followed by total carbonyl compounds detected from TPK smoke with composition of 93% and a little with composition of 2% detected from KWB. Some of the detected substances are; 9-octadecenoic acid, methyl ester dodecanoic acid, 9,11-methyl ester-(E,E)-octadecadienoic

acid, heptadecanoic acid, 9,12-octadecadienal, cyclopentane undecanoic acid, methyl stearate (Table 3). The compounds eluted within the retention times range of 30 to 50min, at this point the temperature is quite high in the oven (Figure 6). Since these compounds were stable at relatively high temperature, inhaling the hot smoke will expose end-users to toxic compounds. Most VOCs are widely known for toxicity of varying degrees [13], as they take part in photochemical reactions that yield harmful or even toxic products [14]. For instance, the strategic signs and symptoms associated with exposure to VOCs include: conjunctival irritation, nose and throat discomfort, headache, allergic skin reaction, dyspnea, decline in serum cholinesterase levels, nausea, emesis, epistaxis, fatigue and dizziness [15]. These form the bulk of complaints received on interacting with communities that are using charcoal samples from these tree plants. It may not be too far to affirm the report that VOCs cause serious health problems as a number of them exhibit toxic, carcinogenic, mutagenic or neurotoxic properties [16].

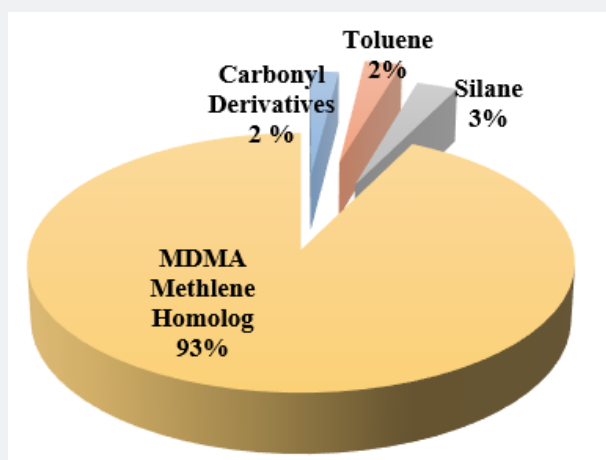


Figure 4: Composition of VOCs from GWK.

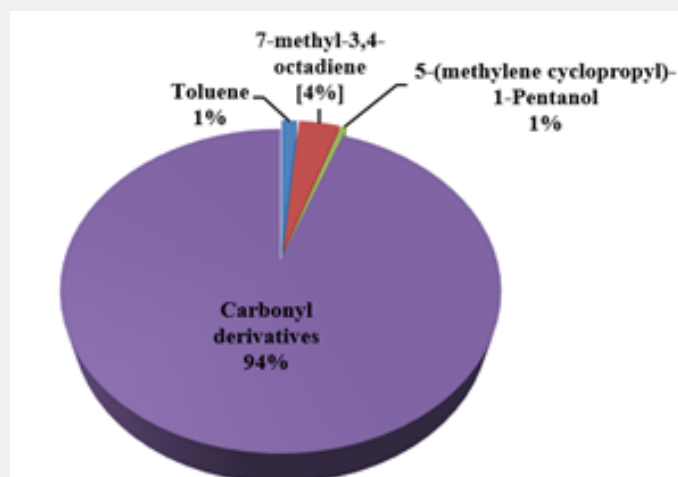


Figure 5: Composition of VOCs from KWB.

Table 3: The GC-MS Analysis of GWK, TPK and KWB.

| GWK | | | |
|-----|---|--------|---------------|
| S/N | Compound | RT | % composition |
| 1 | Toluene | 3.801 | 1.972 |
| 2 | Dodecanoic acid, methyl ester | 34.721 | 1.165 |
| 3 | 9-Octadecenoic acid (Z)-, methyl ester | 55.603 | 1.413 |
| 4 | Trimethylsilyl-di(trimethylsiloxy)-silane | 77.952 | 1.132 |
| 5 | Trimethylsilyl-di(trimethylsiloxy)-silane | 80.804 | 1.656 |
| 6 | MDMA methylene homolog | 91.483 | 92.663 |
| TPK | | | |
| 1 | 5-Diazo-1,3-cyclopentadiene | 3.8057 | 100 |
| KWB | | | |
| 1 | Toluene | 3.778 | 1.35 |
| 2 | 3,4-Octadiene, 7-methyl- | 39.993 | 3.52 |
| 3 | 9,15-Octadecadienoic acid, methyl ester, (Z,Z)- | 40.738 | 10.6 |
| 4 | 9,12-Octadecadienal | 41.849 | 7.11 |
| 5 | 1-Pentanol, 5-(methylenecyclopropyl)- | 43.42 | 0.48 |
| 6 | Methyl stearate | 45.172 | 0.83 |
| 7 | Hexadecanoic acid, methyl ester | 49.789 | 5.17 |
| 8 | 9,11-Octadecadienoic acid, methyl ester, (E,E)- | 55.499 | 45.3 |
| 9 | 11-Octadecenoic acid, methyl ester | 55.738 | 18.61 |
| 10 | cis,cis,cis-7,10,13-Hexadecatriena | 56.019 | 0.6 |
| 11 | Heptadecanoic acid, 16-methyl-, methyl ester | 56.372 | 1.2 |
| 12 | 9,17-Octadecadienal, (Z)- | 71.611 | 0.84 |
| 13 | Cyclopentaneundecanoic acid | 82.721 | 1.43 |
| 14 | Methyl d-glycero-.beta.-d-gulo-hep toside | 85.784 | 1.81 |
| 15 | Methyl d-glycero-.beta.-d-gulo-hep toside | 87.494 | 0.49 |
| 16 | Trehalose | 96.478 | 0.65 |

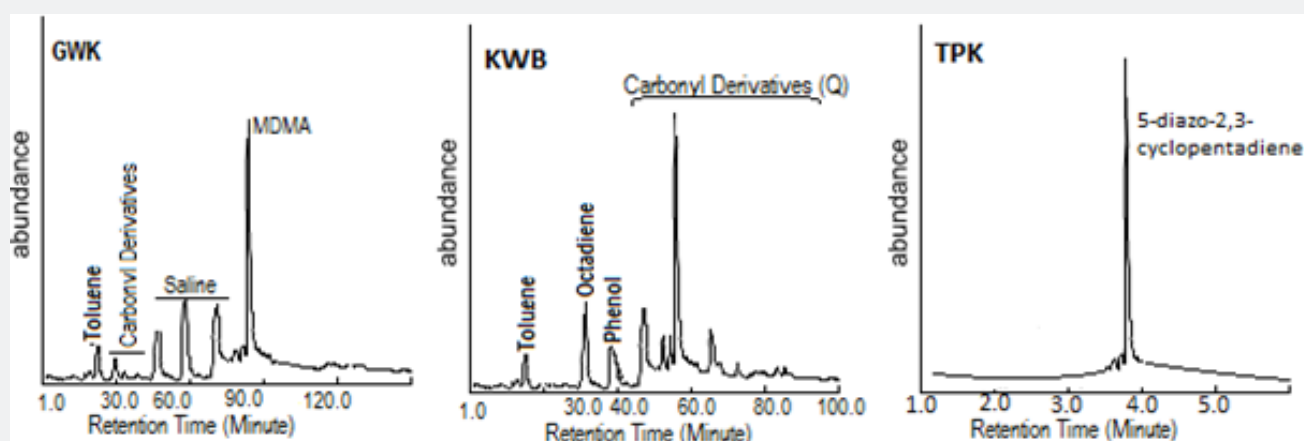


Figure 6: GC Chromatographic profile of major VOCs in smoke from GWK, KWB & TPK.

The occurrence of MDMA in GWK reported as a psychoactive drug widely banned in most countries [17,18] with composition of 92% is has answered the research question on the toxicity of this charcoal as many of the end users end up complaining of one health setback or other on long time exposure. With this revelation, it is best not to use the plant (Gwaskaa) for charcoal production. If there is no option, it must be remediated from this compound before it is used.

Conclusion

Various VOCs were detected in the charcoal samples and some of them are potentially toxic. Owing to the toxicity of the detected VOCs from these plants, this work recommends that there should be careful examination of any charcoal material used, because of the likelihood of exposure to compounds that are injurious to human health.

Acknowledgement

The Nigerian Government Tertiary Education Trust Fund (TETFund) is acknowledged for supporting this research financially. The authors would like to thank the Management and Staff of University of Jos, Nigeria for allowing free access to Laboratory facilities needed for this work.

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DOI: [10.19080/IJESNR.2021.27.556222](https://doi.org/10.19080/IJESNR.2021.27.556222)

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