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The Chemistry of Tobacco Charcoal: A Potentially Harmful Residue from Tobacco Burning

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Abstract

The events occurring during tobacco burning are complex. Consequently, more than 7000 compounds are generated during cigarette smoking. Particulate inhalants including tobacco thermal emissions carrying with them aggressive free radicals are a serious health concern to tobacco researchers and public health authorities. This paper investigates tobacco charcoal as a source of thermal particulates and environmentally persistent free radicals considered deleterious to cigarette smokers and the natural environment. From a clinical perspective, free radicals and particulate emissions are capable of initiating carcinogens, mutagens, and ageing ailments. Standard procedures representative of cigarette smoking (ISO 3402:1999) were observed in this study. The particulate nature and surface morphology of tobacco thermal char was examined using a Field electron gun scanning electron microscope (FEG SEM) while Electron paramagnetic resonance (EPR) was used to explore the presence of free radicals on tobacco charcoal. On the other hand, Fourier transform infrared (FTIR) spectroscopy was used to investigate the surface functionality of tobacco char. At a pyrolysis temperature of 600 ºC, the mean size of small particulates from tobacco burning measured using image J was found to be 16.66±1.88 nm and that of the large particulates was found to be 26.90±2.52 nm. Electron paramagnetic resonance (EPR) gave a g-value of 2.0029 typical of carbon-centred radicals such as the benzyl radical. A broad peak at 3460 cm^{-1} was due to –O-H absorption while the peak at 1630 cm^{-1} was attributed to –C=C stretching. This study has demonstrated that particulate size of tobacco emissions are ultrafine (PM0.1) and can possibly be deposited in the tracheobronchial and alveoli regions of the lungs thus precipitating serious harm to cigarette smokers as well as second hand smokers. Sensitization on the dangers of cigarette smoking will reduce the socio-economic burden associated with clinical problems arising from tobacco use.

Key Words: Free Radicals, Particulate Inhalants, Thermal Char, Tobacco

INTRODUCTION

Tobacco burning chemistry is strongly influenced by both cigarette design variables, tobacco flavorings, and tobacco growing conditions (Baker, 2006). The cigarette smoking conditions such as residence time and the puffing speed influence significantly the formation of tobacco char and resulting particulate matter (Liu *et al.*, 2011). Fresh smoke emerging from the mouth-end of the cigarette is termed "mainstream smoke" and consists of approximately 10^{10} particles per cm^3 and the majority of the aerosol particles have a particle size between 0.1 to 1.0 µm (Adam *et al.*, 2009). When a cigarette is lit, the temperature of the burned tobacco rises to over 900 °C resulting to the formation of a hot carbonaceous charcoal and heat mediated synthesis of over 7000 sub-molecular constituents (Wiebel, 2015; Rodgman and Perfetti, 2016). Studies conducted on the burning characteristics of tobacco has shown that the interior of the burning zone of tobacco is oxygen-deficient and hydrogen-

rich thus resulting to an endothermic pyrolysis/distillation zone which produces residual char - tobacco charcoal. Large amounts of volatile and semi-volatile smoke constituents are produced in this region (Muramatsu, 2005).

Pyrolysis is the thermochemical conversion of organic materials under a limited amount of oxygen and has a potential application for converting tobacco biomass into various reaction chemicals including tobacco charcoal (Shafizadeh, 1982; Kawamoto *et al.*, 2003). The basic phenomena that takes place during pyrolysis is the initiation of pyrolysis reactions as a result of increased temperature leading to release of organic volatiles and formation of char (Babu, 2008). Studies have shown that fractional pyrolysis of tobacco leads to the generation of free radicals in char and tar, at temperatures >380° C and the concentration of these radicals in the char residue increases as the pyrolysis temperature is increased to a maximum concentration of ~1.2×10^{19} spins/g of char at 480° C after which the concentration decreases with increased temperature (Chaouachi, 2009).

The presence of free radical species in cigarette smoke has been known since the 1950s (Rodgman and Perfetti, 2016) but little information is known on the persistence of these radicals on tobacco charcoal. Thus the study of environmentally persistent free radicals in tobacco char is critical in assessing the environmental and biological harm precipitated by tobacco charcoal. Partial decomposition of polyphenolic and catecholic containing structures in tobacco forms simple gas-phase radicals such as methoxy and TPM-associated radicals like semiquinone-type radicals and benzyl radicals among other stable and transient radicals (Dellinger *et al.*, 2011).

The biological and environmental consequences of free radicals induced by the generation of reactive oxygen species (ROS) on tobacco particulates is a serious concern to the cigarette smoking community because the labile species being produced during physico-chemical processes of tobacco burning as free radical intermediates may initiate grave health impacts in the biological system since their ability to generate ROS may cause oxidative stress, cardiac problems, and cancerous tumours in living organisms (Jebet *et al.*, 2017). The production of ROS can results in severe oxidative stress within cells via the formation of oxidized cellular biological molecules such as lipids, proteins, and DNA (Moridani *et al.*, 2004). These radicals are capable of causing cell injury in the biological environment (Dellinger *et al.*, 2001). As a result, free radicals from cigarette smoke can be taken as the major precursors for the formation of ROS usually considered harmful to human health (Jebet *et al.*, 2017).

This study investigates tobacco charcoal as a source of thermal particulates and environmentally persistent free radicals believed to cause deleterious impacts on primary cigarette smokers as well as second hand cigarette smokers in addition to the natural environment. Radicals interact with lipids and the body's defense mechanisms causing acute responses such as coughing, or in extreme cases, emphysema, cardiopulmonary disease and cancer (Dellinger *et al.*, 2011). This study therefore is significant for policy formulation by both public health and medical practioners towards tobacco control and tobacco cessation.

MATERIALS AND METHODS

Processed tobacco was purchased from a local vendor and conditioned for 1 week under controlled humidity according ISO conditions set by Bush *et al.* (2012) and Fresenius (1985). The image instrumentation was a German Field emission gun electron microscope (FEG SEM) while the electron paramagnetic spectrometer was an X-band Bruker EMX-20/2.7. The surface functional groups adsorbed on char was explored using Agilent FTS 7000e FTIR bench top spectrometer. The methanol used is this study had a purity of 99.99% and was purchase from Kobian Ltd, Kenya.

The Thermal Degradation of Tobacco

Processed tobacco (confidentially coded AE1) of 30 ± 2 mg was weighed and packed in a

quartz reactor of volume ≈1.6 cm^3 and thermally degraded in an inert environment of nitrogen at a flow rate of 17.5 mL/s (puff volume 35 mL at a puff residence time of 2 s) at 1 atm, consistent with the ISO smoking regimes as set by the International Organization for Standardization of cigarette smoking (Busch *et al.*, 2012). The smoking apparatus used in this work contains different units: the reactor compartment inside a muffle furnace, and the temperature control device which controls the degradation temperature within a gradient of ±5 ºC.

Reactor System

The internal heating compartment of the muffle consists of a temperature regulating knob with a scale between 20° C and 1000° C. The transfer line from the pyrolysis gas passes through the muffle furnace and connects the reactor as presented in Fig. 1. The sample holder in the heating compartment is a quartz reactor which can withstand high temperatures of up to 1200° C. The reactor has a volume of 1.6 cm^3 capacity.

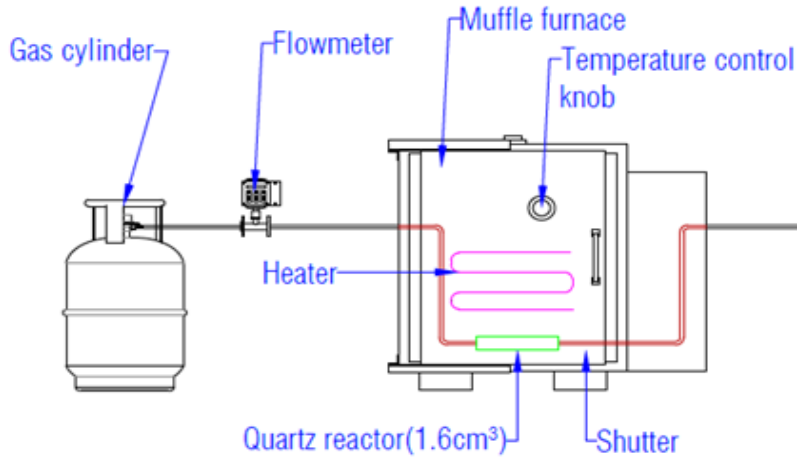

Fig. 1. The Thermal Degradation Apparatus

Scanning Electron Microscopy Analysis

Approximately 5 mg of thermal tobacco charcoal was introduced into 2 mL methanol and gold grids dipped into the prepared thermal charcoal sample (Keng *et al.*, 2011). Twisters were used to remove the gold grids from the charcoal sample. The sample was then adhered to aluminum SEM stubs with a carbon tape. These were then gold coated in a Quorum Q150 RES sputter coater. The grids air dried before inserting them into the analysis chamber of a Zeiss Ultra Plus (Germany) Field emission gun scanning electron microscope (FEG SEM). All images were taken at an angle of 45º in order to increase the clarity of the surface morphology of tobacco thermal char (Kibet *et al.*, 2017). The images (micrographs) were then saved for further analysis and comparison at various magnifications (Russ, 2012). Image J software was used to determine the size of the smoke particulates and a distribution curve of particulate size was estimated using Igor ver. 5.0 graphing software. The measurement of particulates adsorbed on tobacco char was done in replicates. A total of 80 particulates were conducted for four micrographs in order to enhance the validity of the data collection.

Fourier Transform Infra-Red Spectrometry (FTIR)

Absorption spectra was collected using an Agilent FTS 7000e FTIR bench top spectrometer connected to a liquid nitrogen cooled mercury cadmium telluride detector heated at 65.1° C and connected to a seven-reflection diamond ATR crystal (Concentrate IR, Harrick Scientific Products, Pleasantville, NY) . Attenuated total reflection Fourier-

transform infrared (ATR-FTIR) spectroscopy was used in this study. ATR-FTIR spectra (256 co-added scans) were collected at the 4 cm^{-1} resolution over the wave number range of 4,000–400 cm^{-1} at an average cycle of 4 scans (Hands *et al.*, 2014).

Electron Paramagnetic Resonance Spectroscopy

Tobacco charcoal of about 5 mg was analyzed using a Bruker EMX-20/2.7 EPR spectrometer (X-band) with dual cavities, modulation and microwave frequencies of 100 kHz and 9.516 GHz, respectively. The EPR characteristic parameters were a sweep width of 200 G, EPR microwave power of 1−20 mW, and modulation amplitude of ≤6 G. The time constant was varied appropriately. The sweep time was set at 16 s and the number of scans was fixed at 10. The g-value was computed using Bruker's WINEPR program on a windows PC. The exact g-value for the key spectrum was determined by comparing with a 2, 2-diphenyl-1-picrylhydrazyl (DPPH) standard (Jebet *et al.*, 2017).

RESULTS AND DISCUSSION

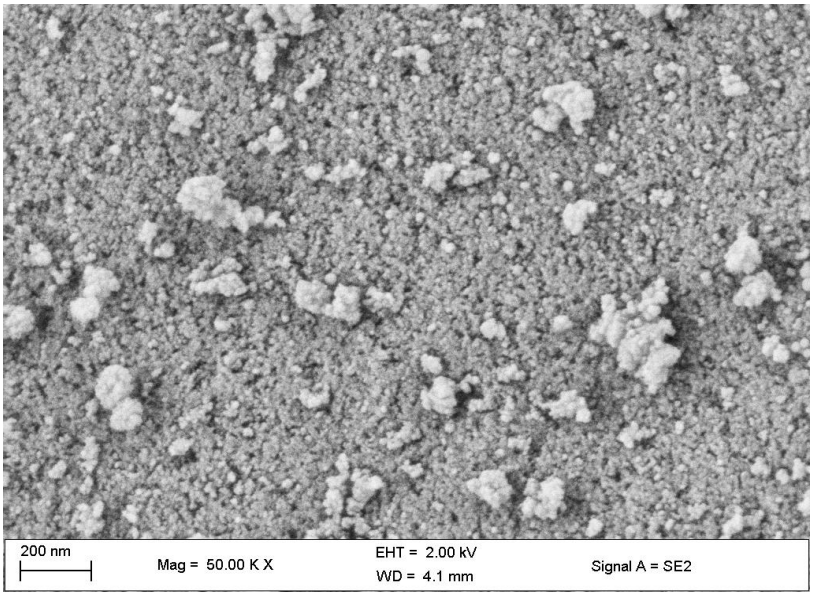

Fig. 2. Particulate Matter from AE1 Cigarette Tobacco Char

The particulate matter of tobacco charcoal was examined at a magnification of X50,000 as shown in Fig.2. Image J was used to determine the sizes of the tobacco charcoal and size distribution was obtained using Igor software. Fig. 3 gives the size distribution of the particulate matter. The mean diameter of the small particulates of the tobacco charcoal was found to be 16.66 ± 1.88 nm and that of the larger particulates was 26.90 ± 2.52 nm. From the data reported in this work tobacco charcoal gives rise to ultrafine particulates. It is however; important to note that these particulate emissions did not pass through the tobacco filter in order to accurately simulate the tobacco particulates that may enter the respiratory airway of the cigarette smoker. This experiment was conducted with the aim of determining the particulate size of tobacco in the absence of a filter and more importantly, the nature of tobacco residue that forms during cigarette smoking. Fig. 3 therefore shows two classifications of tobacco particulates during tobacco burning. It can be noted that the two classes of particulates are not significantly different in size because they all fall under ultrafine category of airborne particulates.

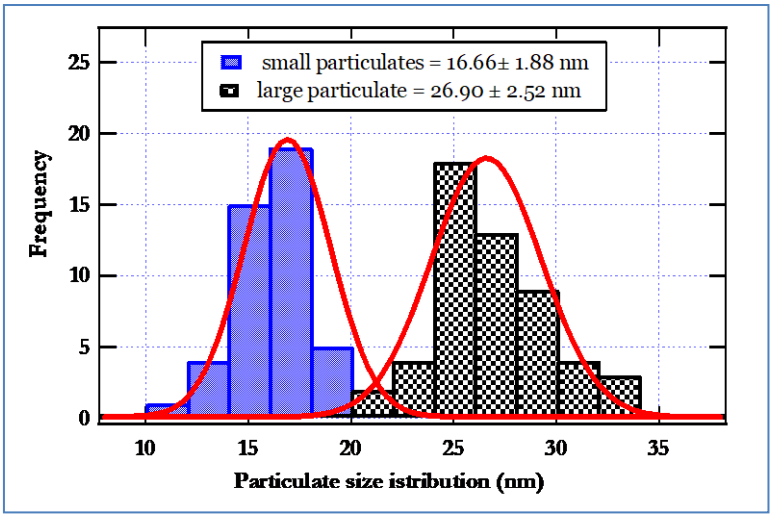

Fig. 3. Particulate Size Emissions from the Burning of AE1 Cigarette Tobacco

These ultrafine particulates when inhaled into the respiratory tract may precipitate serious harm to cigarette smokers and natural ecosystems due to compromise of air quality. According to Kleeman *et al*. (2008), cardiovascular disease is a consequence of exposure to ultrafine particles. This epidemiological proposition may be explained by translocation of these ultrafine particles from the respiratory epithelium and subsequent toxicity to vascular endothelium, biological change in blood coagulation which ultimately triggers the autonomic nervous system reflexes and eventually altering the cardiac frequency and function. Once deposited deeply into the lung, ultrafine particles appear to access the blood circulation by different transfer routes and mechanisms resulting in distribution throughout the body including the brain and may be associated with potential neurotoxic consequences (Kleeman *et al.*, 2008).

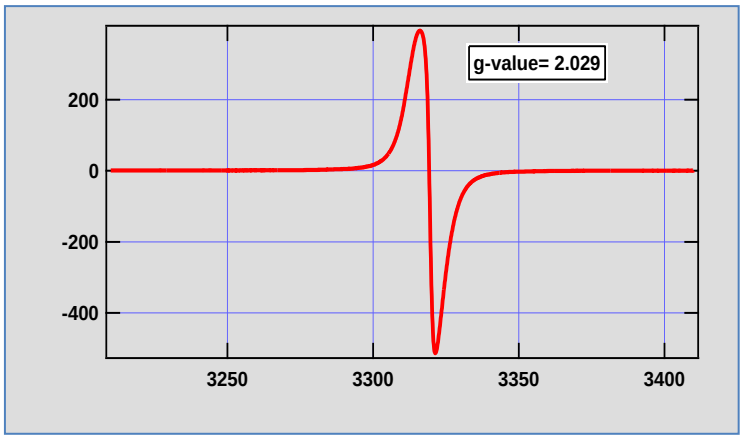

Fig. 4. Electron Paramagnetic Resonance Spectrum for AE1 Cigarette Tobacco Charcoal

The interaction between the electrons and the molecule structure leads to the g-value which is characteristic of a particular class of compounds and is important for identification of the compound. Fig. 4 shows the EPR spectrum for AE1 tobacco charcoal with a g-value of 2.0029 typical of carbon-centred radicals such as the benzyl radical and bi-

phenyl radicals. The spectrum is asotropic with magnetic field of 3320 G. This shows that the EPR spectrum of tobacco thermal char at elevated temperatures is symmetrical implying a single type of electronic species. The free radical species which may be carried along by particulate emissions from tobacco are capable of causing fatal respiratory diseases such as chronic obstructive pulmonary disease, cancer, and cardiac arrest. Remarkably, the free radicals detected in this study can interact with biological structures such as DNA, nuclei acids, and lipids to initiate the release of reactive oxygen species (ROS) which can cause cellular damage (Valko *et al.*, 2006). ROS are potential precursors for oxidative stress, ageing, and mass wasting among cigarette smokers.

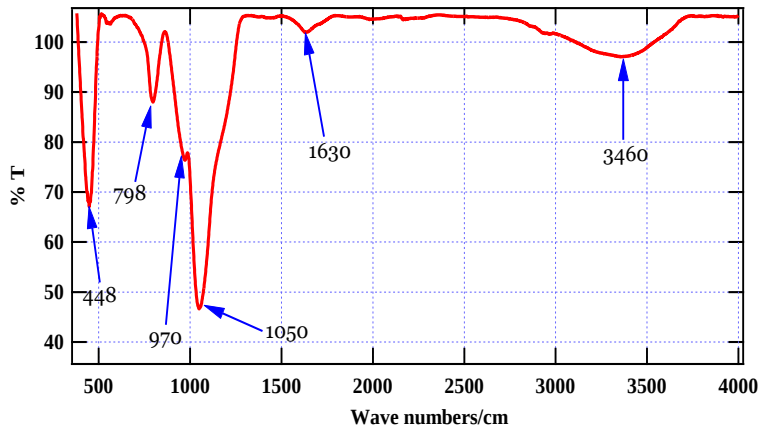

Fig. 5. Fourier Transform Infrared Spectrum of AE1 Cigarette Tobacco Charcoal

The FTIR spectrum presented in Fig. 5 shows a very weak characteristic broad absorption band at 3460 cm-^{1} which may be due to the O-H functional groups adsorbed on the surface of tobacco char while the frequency band at 1630 cm^{-1} represents the C=C stretching vibrations. The absorption bands at 1050 and 798 cm^{-1} are consistent with δ(–CH_2) signature vibrations for in-plane and out of plane bending modes in aromatic compounds respectively. Therefore the presence of the C=C shows and –CH_2 functional groups in tobacco char shows that the tobacco residue is aromatic. The sharp peak at 448 cm^{-1} may be attributed to the presence of heteroatoms correspond to in-plane bending of the O=C-N groups.

CONCLUSION

This study has therefore demonstrated that tobacco burning gives rise to ultrafine inhalants which have the potential to cause cellular harm in the human biological system. These nano level particulates may carry with them environmentally persistent free radicals into the respiratory airway thus triggering the production of reactive oxygen species and ultimately oxidative stress among other tobacco related ailments; ageing, cancer, and mass wasting. The clearance of ultrafine particulates by the respiratory system is very poor because these type of particulates can easily be incorporated into the blood circulation system leading to cardio pulmonary death and cardiac arrest. This study has also predicted the presence of benzyl radical using FTIR spectroscopy. Besides, electron paramagnetic resonance g-value has established that tobacco charcoal is largely aromatic. Remarkably, literature studies and the findings from this investigation have indicated that benzyl radical may be a good candidate for cell damage as well as a precursor for oxidative stress among the cigarette smoking communities.

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