ANALYSIS OF EMISSION PROFILES FROM CHARCOAL PRODUCED FROM DIFFERENT TREE SPECIES BY DIFFERENT PYROLYSIS METHODS

TOM JUSTUS SHIKORIRE

N50/CTY/PT/23014/2011

A thesis submitted in partial fulfillment for the Degree of Master of Environmental Science in the School of Environmental Studies of Kenyatta University

May 2015

DECLARATION

This thesis is my original work and has not been presented for any award or degree in any other University.

Tom Justus Shikorire (Bsc. Industrial Chemistry)
N50/CTY/PT/23014/2011
Department of Environmental Science

Signature……………………………….... Date…………………………………

This thesis has been submitted with our approved as University Supervisors.

Dr. Margaret Mwihaki Ng'ang'a
Chemistry Department
Kenyatta University

Signature…………………………….. Date.…………………………………

Dr. Gathu Kirubi
Department of Environmental Science
Kenyatta University

Signature…………………................. Date………………………………….

DEDICATION

This work is dedicated to my mom Mrs. Mary Chilande, dad Mr. Norman Akali and my brothers Maurice, Lawrence and William.

ACKNOWLEDGEMENT

I am deeply indebted to my supervisors; Dr. Margaret Ng'ang'a, Dr. Gathu Kirubi and Prof. Ahmed Hassanali of Kenyatta University for all the insightful ideas, guidance, encouragement and critical discussion that they provided throughout the study period. Most importantly, my overwhelming gratitude goes to Prof. Ahmed Hassanali for proposing this fascinating topic of study.

I also appreciate Mr. Murefu Baraza of energy environment and development advisory whose insightful lectures in the renewable energy technologies class gave me a strong foundation and passion to pursue this course. The laboratory work would not have been possible without the unrelenting and kind help of Mr. Elias Maina, chief technician in Chemistry Department who helped fabricate the glassware used in this study.

Although there aren't enough superlatives to express how grateful and lucky I am for having the best parents and brothers in the world I would like to thank my mother Chilande, father Akali and brothers Maurice, Laurence and William. This work could not have been possible were it not for their steadfast love, support and believing in me especially during tough times.

Last but not least, my profound appreciation extends to my colleagues in the Environmental Science Department, and the staff at the Chemistry Department for their prompt assistance during the study period.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Charcoal is a major form of biomass fuel for approximately 80% of the Kenyan population. However, the use of charcoal is associated with indoor air pollution where charcoal users are continually exposed to compounds of incomplete combustion which are known to have detrimental effects to human health. This study analyzed the emission profiles of different types of 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 methods were collected from charcoal producers in Thika, Machakos and Kitengela. The volatiles were collected using a fabricated chimney placed on clay cook-stove such that smoke was vented to a glass canula where it was condensed. Extracted volatiles were then analyzed by gas chromatography-linked mass spectrometry (GC-MS). A total of 22 PAHs were identified together with other groups of compounds that included ketones, aldehydes, phenols, alkanes, alkenes, carboxylic acids, phthalate, esters, and alcohols. The major compounds found in the smoke extracts with known health effects included naphthalene (3), 1-methylnaphthalene (14), 2-methylnaphthalene (5), fluorene (6), phenanthrene (9), anthracene (11), 1-methyl-phenanthrene (14), fluoroanthene (10), benzo(a)anthracene (12) and chrysene (13).There were significant differences ($P<0.05$) in the concentrations of fluorine, naphthalene and pyrene emitted from *A. polyacantha* and *A. xanthophlea* prepared by traditional pyrolysis. From *A. polyacantha* concentrations were naphthalene (110.00µg/g), fluorine (72.00µg/g) and pyrene (60.00µg/g) while from *A. xanthophlea*, concentrations were naphthalene (140.42µg/g), Fluorene (97.35µg/g) and pyrene (71.82µg/g). The volatile emissions from charcoal prepared by traditional pyrolysis had higher concentration of PAHs relative to the accepted levels of 0.1 - 0.2mg/m^3. Charcoal prepared by traditional pyrolysis emitted the highest number of PAHs at 6.25mg/m^3 while those prepared by efficient pyrolysis produced the lowest concentration at 0.73mg/m^3 both from *A. xanthophloea*. Therefore, there is need to use efficient pyrolysis methods of charcoal production. This will ensure the production of charcoal with low volatile content that are less harmful to the end users.

ACRONYMS AND ABBREVIATIONS

BaP	Benzo[a]pyrene
CCME	Canadian Council of Ministries of Environment
Cap^{-1}	Per Capita
CDM	Clean development mechanism
CO_2	Carbon dioxide
CO	Carbon monoxide
Day^{-1}	Per Day
DNA	Dinitronucleic acid
EJ	Exajoules (10^{18} joules)
EUC	European commission
GC	Gas Chromatography
GJ	Gigajoule (10^{9} Joules)
GJIC	Gap Junction Intercellular Communication
GOK	Government of Kenya
HP	Hewlett Packard
HPLC	High Performance Liquid Chromatography
IACR	International Agency for Cancer Research
IEA	International Energy Agency
IIED	International Institute for Environment and Development
KEFRI	Kenya Forestry Research Institute
LPG	Liquid Petroleum Gas
MOE	Ministry of Energy
MS	Mass Spectrometry
NMHC	Non Methane Hydrocarbons
PAC	Practical Action
PAH	Polycyclic Aromatic Hydrocarbons
PEM	Portable Emissions Monitor
PISCES	Policy Innovation Systems for Clean Energy security
PM	Particulate matter
WHO	World Health Organization

CHAPTER ONE: INTRODUCTION

1.1. Background

Charcoal is a wood based secondary form of energy produced by the pyrolysis of wood in the absence of air (Macqueen and Korhaliller, 2011). This is achieved by cutting wood to pieces and burning them in a kiln where the flow of air is controlled. Charcoal is widely used as a fuel in approximately 80% of Kenyan households and will continue being an important fuel for many years to come (Mugo and Gathui, 2010a). While much emphasis has been placed on promoting efficient energy mainly electricity, formal records estimate 84% of the Kenyan population rely on traditional use of biomass in form of firewood, charcoal and crop residue as the primary source of fuel (International Energy Agency, 2014). Data on the Kenyan government expenditure shows that a bigger portion of government financing, subsidies and international development aid is aimed at developing electricity that mainly caters for the needs of the urban based formal sector, commercial and industrial sectors, and medium and affluent urban and peri-urban households (Karekezi *et al*., 2008a). This has however not phased out the consumption and demand for charcoal.

Charcoal is mainly consumed in urban areas since it is affordable and convenient while its consumption rate is lower in rural areas due to the abundance of firewood and the high costs of charcoal. Studies by (Kituyi et al., 2001a) revealed that the per capita daily consumption rates of charcoal in urban areas were 0.37Kg $cap^{-1}day^{-1}$ in urban areas and 0.26Kg cap^{-1} day^{-1} in rural areas. National economies especially in the sub Saharan region have not performed well in the past ten years and employment opportunities and household-level income generating have diminished - thus the family savings to facilitate transition to and investment in efficient energy are minimal (Kituyi, 2002). It is therefore plausible to conclude that biomass (mainly firewood and charcoal) will continue being the main sources of energy for most of sub Saharan Africa for many years to come (Kituyi, 2002; Gustafson, 2001; UNDP, 2000).

Whereas the overreliance on biomass fuels is mainly linked to poor communities, charcoal is also consumed by affluent groups due to its unique properties. Urban households prefer charcoal because it is affordable, economical, convenient, it does not produce a lot of smoke relative to wood. Its calorific value is double that of wood and it consequently lasts longer more so when used with improved cook stoves (Karekezi *et al*., 2008a). The high demand for charcoal especially in the urban areas puts a lot of pressure on the surrounding forests and woodlands (Karekezi *et al.*, 2008a). Kenya has a wood supply potential of 31.4 million m^3 against a national demand of 41.7 million m3 hence a current deficit of 10.3 million m^3. Forecasts for a 20 year period indicate a 20.0% increase in supply and 21.6% increase in demand by the year 2032 which signifies a gradually increasing deficit (MEWNR, 2013).

Excessive reliance on charcoal can result in deterioration of land when charcoal is produced unsustainably especially in areas surrounding urban regions. Some analysts argue that the main problem facing poor people in developing nations is their overreliance on biomass sources of fuel such as charcoal (Macqueen and Korhaliller, 2011). This has led to the introduction of intervention programs initiated by governments and nongovernmental organizations aimed at reducing forest cover loss through sustainable charcoal production. Such programs include the provision of seedlings to farmers, promotion of other sources of energy such as biogas and even imposing total bans on charcoal trade (Githiomi *et al.*, 2012; Githiomi and Oduor, 2012; Mugo and Gathui, 2010a). Two of the most protracted endeavors have been the advancement of energy efficient pyrolysis methods and environmentally stable improved cook-stoves for urban and rural poor (Karekezi *et al.*, 2005).

Wood is commonly pyrolized into charcoal using earth, brick or steel drum kilns in small to large quantities depending on the producer that is either small scale or large scale producers (Kammen and Lew, 2005b). Wood is collected and cut into desired size then placed into an underground or above ground kiln. The kiln is lit and the wood fired up and begins to carbonize. The charcoal producer seals most of the air pockets and leaves just enough to allow some smoke and moisture to escape. The process may take a few hours to weeks to complete with half of the primary energy lost through the process (Seidel, 2008; Bailis, 2005; Karekezi *et al.*, 2005). The energy efficiency of the process is influenced by factors such as; the kiln, moisture content of the wood, wood species, wood arrangement and the experience of the charcoal producer (Kammen and Lew, 2005a).

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, (PAHs), formaldehyde and other compounds that may be detrimental to human health. Impurities contained in biomass fuels eventually lead to formation of inorganic compounds including sulfur dioxide, nitric oxide and ammonia. A myriad of compounds have been identified in wood smoke revealing the complexity of these emissions (IARC, 2010; Lim and Seow, 2012).

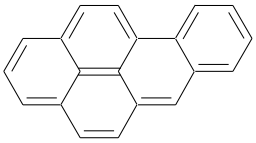
The emissions produced during the combustion of charcoal may depend on the method used to carbonize the wood and also the type of species from which the charcoal is being produced (Hindi, 2012). The chemical makeup of wood which is mainly lignin, hemicelluloses, cellulose and organics varies from one tree species to the other (Pettersen, 1984). It is reported that thermal decomposition of wood begins at 100^{o}C while hemicelluloses, cellulose and lignin are degraded at 200-260 °C, 240-350 °C and 280-500 °C respectively (Hindi, 2012). Thus the conditions under which the charcoal was produced affects the chemical composition of the charcoal produced and hence emitted compounds when the same charcoal is burnt on a cook-stove. The cook-stove type chosen for charcoal combustion determines the quality and quantity of emissions (Roden *et al*., 2009).

In the year 2000, indoor air pollution from solid fuel use was responsible for more than 1.6 million annual deaths (400,000 in sub Saharan Africa) and 2.7% of the global burden of disease, making indoor air pollution the second largest environmental contributor to ill health after unsafe water and sanitation (Takama *et al*., 2011; Haller *et al*, 2006;).The emissions produced when solid fuels such as charcoal are burnt contribute to indoor air pollution causing diseases that lead to approximately 2 million deaths annually (WHO, 2010). Examples of these diseases include pneumonia, chronic obstructive pulmonary disease, ischemic heart disease and lung cancer. People mostly affected are women and children from poor backgrounds (Patel *et al.*, 2013; IARC, 2010; WHO, 2010).

It is estimated (in a business as usual scenario) that the use of biomass by households will result in 8.1 million lower respiratory infection (LRI) deaths among young children and 1.7 million chronic obstructive pulmonary deaths (COPD) among adult women in Sub Saharan Africa between 2000 and 2030 (Bailis *et al*., 2007).

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 polycyclic aromatic hydrocarbons (PAH) 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 (IARC 1987, 1985, 1984,). PAHs are widespread environmental pollutants that are formed in the combustion process of carbonaceous materials at high temperature (Nikolaou *et al*, 1984). 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 (WHO, 2010b; Zhang and Tao, 2009; Baek *et al*., 1991).

A study by (Gachanja *et al*., 1992) showed the presence 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 reported to be contained in food cooked over open flames for example roasted meat with concentrations of BaP present at 30ppb (Badry, 2010).



1

Source: (Haynes, 2011)

The current study aimed at finding out the emission profiles of three tree species commonly used for charcoal production. The research also aimed to make comparisons of the emission profiles of charcoal produced by efficient pyrolysis methods and by traditional pyrolysis methods. The tree species of interest are; *E. grandis, A. polyacantha* and *A. xanthophloea*. These were collected directly from the charcoal producers in Thika (Kakuzi Limited), Kitengela (Kitengela arboretum) and from Machakos. Kitengela and Thika were selected since there are known sustainable charcoal producers (Kakuzi limited and Kitengela arboretum farm). They specialize in planting trees and producing charcoal using efficient pyrolysis methods (Mugo and Gathui, 2010b; PAC, 2010). The kilns used by these farmers are the brick kiln and the 'Kinyanjui' metal drum kilns (Oduor *et al*., 2009). On the other hand, Machakos was chosen due to the abundance of acacia trees in the region and the traditional pyrolysis methods of charcoal production employed by the charcoal producers.

1.2. Problem statement

Complete combustion of charcoal should theoretically result in the emission of carbon dioxide and water vapor. However, this is difficult to achieve due to factors such as low efficiency of cook-stoves and use of charcoal that is not completely carbonized. Thus compounds of incomplete combustion such as PAHs, formaldehyde and carbon monoxide among others are emitted. These environmental pollutants are linked to indoor air pollution resulting to pneumonia, chronic obstructive pulmonary disease, ischemic heart disease and lung cancer (Smith, 2006; WHO, 2010; Zhang and Smith, 2005). Indoor air pollution is rported to be the second largest contributor to ill health after unsafe water and sanitation.

The world health organization estimates that two million deaths occur annually due to exposure to emissions from biomass fuels and coal (WHO, 2010). There is therefore a compelling research need to investigate and determine the quality and quantity of pollutants in biomass fuels. This study fills this important research gap by analyzing the emissions from commonly used trees species subjected to different pyrolysis processes. The results will help charcoal producers in making choices regarding tree species and pyrolysis methods for production of charcoal with minimal health effects when used.

1.3. Justification

Charcoal is a vital fuel used by a majority of both the urban and rural populations in Sub-Saharan Africa. However charcoal users are exposed to contaminants in the charcoal smoke that might cause various health risks. Of most concern is the possible exposure to compounds of incomplete combustion specifically PAHs. These are ubiquitous pollutants and are found in biomass smoke, fossil fuel smoke and cigarette smoke. A number of studies on the carcinogenicity and mutagenicity of these compounds have shown positive results in laboratory animals through chronic exposure (WHO, 2010b;Straif *et al*., 2005; Mumtaz *et al*., 1996; Jerina *et al*., 1980). Thus there is a high possibility that the same health effects could be exhibited in humans. The International Agency for Cancer Research (IARC) has classified these compounds into five major groups (Table 1.1) based on available evidence regarding their carcinogenicity (IARC, 2010a).

Table 1.1: IARC classification of PAHs

Group 1	Sufficient evidence in humans and animals and strong theoretical data in humans
Group 2A	Limited evidence in humans and strong evidence in animals
Group 2B	Limited evidence in humans and less than sufficient evidence in animals
Group 3	Inadequate evidence in humans and inadequate or limited evidence in animals
Group 4	Lack of carcinogenicity in animals or humans

Source: (IARC, 2010a).

Charcoal is currently used by about 80% of the Kenyan population and will continue to be used as a fuel for long time to come (Karekezi *et al*., 2008b; Bailis, 2005a; Kituyi *et al*., 2001a). The study was conducted to characterize emissions from various types of charcoal so as to identify the specific compounds that end charcoal users may be exposed to.

1.4. Research questions

The study sought to answer the following research questions:

a) What quality and quantities of products of combustion are formed when charcoal made from a different tree species are subjected to different pyrolysis methods?

b) Is there a significant difference in the quality and quantities of products of combustion emitted by charcoal made from the *A. polyacantha, A. xanthoploea* and *E. grandis* species?

1.5. Hypotheses

a) There is no significant difference between the quality and quantities of emissions from *A. polyacantha, A. xanthophloea* and *E. grandis* charcoal
b) There is no significant difference between the quality and quantities of emissions from *A. polyacantha, A. xanthophloea* and *E. grandis* charcoal prepared by efficient and traditional pyrolysis methods.

1.6. Objective of the study

The overall objective of the study was to profile the potential contaminants produced when charcoal is used as a fuel for domestic purposes such as roasting, cooking and indoor space heating

Specific Objectives

i. To determine the quality and quantities of emissions from charcoal produced from *A. polyacantha*, *A. xanthoploea* and *E. grandis* tree species
ii. To determine the quality and quantities of emissions from charcoal produced by traditional and improved pyrolysis methods.
iii. To determine significant differences in the quantities of emissions from charcoal.

1.7. Scope and Limitations of the study

Emission profiles of charcoal prepared using a traditional earth mound kiln and a dome shaped brick kiln were studied. Charcoal was prepared from *A. polyacantha, A. xanthoploea* and *E. grandis* species. A clay cook-stove (Jiko) with an efficiency of 50% was used throughout the study.

1.8. Conceptual framework

The proposed framework in measuring emissions from charcoal produced using different tree species and by different pyrolysis methods is as shown in Figure 1.1 below.

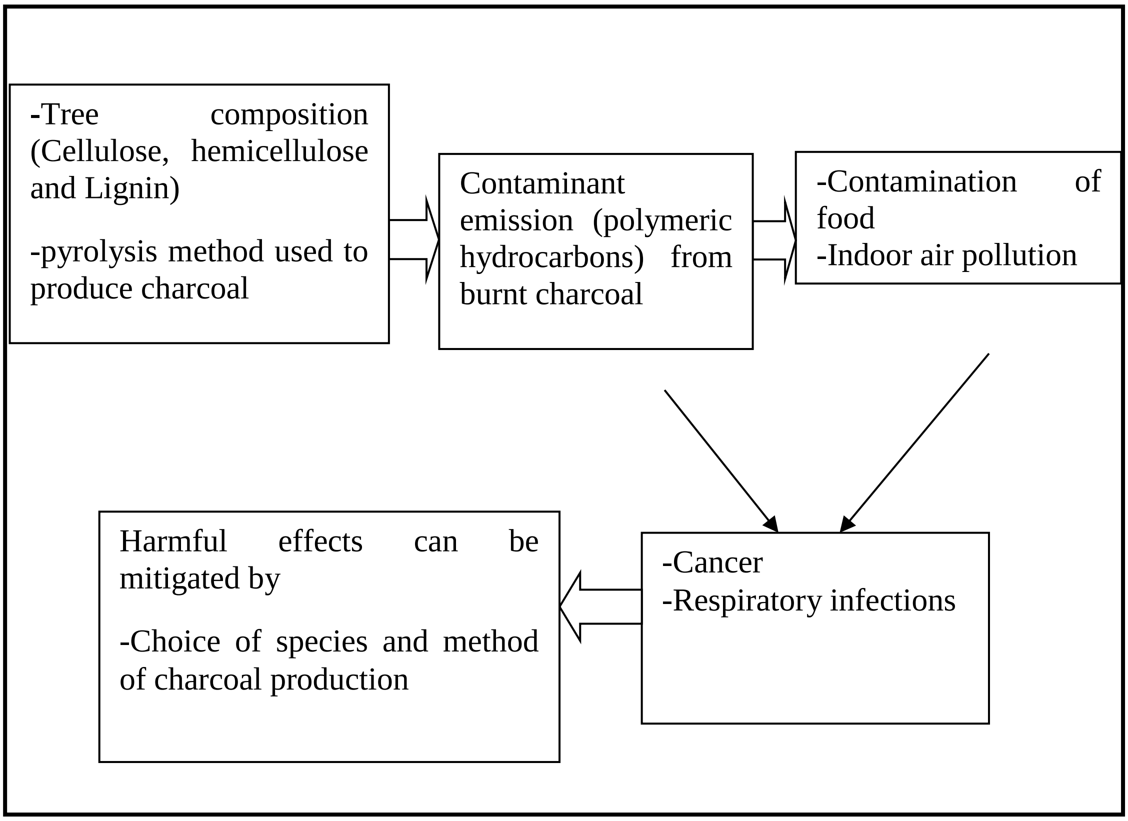


Figure 1.1: The conceptual framework of the study

Wood used for charcoal are composed mainly of cellulose, lignin and hemicelluloses. These compounds are converted into charcoal during pyrolysis. When charcoal is used as a fuel for domestic purposes, products resulting from the incomplete combustion of the charcoal are emitted. These compounds are inhaled by the immediate end users of charcoal and also contaminate food. Some of the products of incomplete combustion are carcinogenic and also cause respiratory infections especially to women and children. The research therefore aims to find out the types of contaminants that are produced when charcoal is used domestically as a fuel.

CHAPTER TWO: LITERATURE REVIEW

2.1. Charcoal consumption

Charcoal is a prevalent cooking fuel for a majority of households in Africa and its demand continues to increase due to the rapid increase in population (Kituyi et al., 2001b). Demand for charcoal is predominant in urban areas as opposed to rural areas where prevailing poverty impedes even the charcoal producers from using the fuel (Kammen and Lew, 2005b). It is projected that about two thirds of the world's population will live in urban areas by the year 2050 (Urdal and Hoelscher, 2009). This will further increase demand for charcoal and in retrospect leaving rural populations with less supply of biomass (Kammen and Lew, 2005b). Urbanization consistently reduces fuel-wood use and increases charcoal consumption while the per capita fuel-wood consumption increases with increased forest cover (Arnold and Persson, 2003). It has been further reported that as income increases, urban households tend to switch to more convenient fuels. Charcoal is generally the primary 'transition' fuel to which they switch to (Barnes *et al*., 2013).

Charcoal is mainly used for space heating and cooking and is preferred since it is easily accessible, easier to transport, cheap and can be used for other specific applications for example roasting (Karekezi *et al*., 2008b). In addition, purchased charcoal is low priced, readily available and largely has a steady supply and market in relation to efficient alternatives (Ellegard and Nordström, 2003). Charcoal has a higher calorific value and does not produce much smoke as compared to wood (IEA, 1996). For example the calorific value of wood from *A. polyacantha* is 4.0kj/g while that of charcoal from the same tree species is 6.5kj/g (Oduor *et al*., 2012). The unique cooking characteristics of charcoal make it difficult for consumers to make a total switch to other fuel types that might be available. This has been evident in Sudan where the price of charcoal was a third more than liquid petroleum gas (LPG) but many household still bought charcoal (Mugo and Gathui, 2010a).

Charcoal is also associated with poverty in numerous ways and at multiple scales. At the macro level, charcoal constitutes a significant productive sector of the economies of many sub-Saharan African (SSA) countries and contributes to poverty reduction through national development, employment, and household income generation (Angelsen and Wunder, 2003). Charcoal alone was approximated to add 650 million dollars to Tanzania’s economy, 5.8 times the combined value of coffee and tea production while at the same time providing income to several hundred thousands of households in urban and rural areas (World Bank, 2009).

Burgeoning urban charcoal demand and markets present opportunities for income generation from the production of charcoal in rural areas where it is generally the most commercialized resource (Arnold *et al*., 2006). The charcoal market also grants urban households with an affordable, convenient and reliable source of energy and related energy services at comparatively stable prices (Desanker *et al*., 2003). However, charcoal production can also have degenerative effects on poverty. These entail negative health impacts at the production and use sites normally affiliated with smoke inhalation and carbon monoxide inhalation (Ezzati and Kammen, 2001b). Unfavorable social effects include exploitation of producers and traders by middlemen, official corruption that inflates transaction costs and unequal gender relations that overburden women or expose them to health risks (Zulu and Richardson, 2013; Ribot, 2009). Charcoal is also linked to poor energy services and quality of life in relation to cleaner alternatives such as liquefied petroleum gas (LPG) and electricity (Arnold *et al*., 2003; Desanker and Zulu, 2001). Despite the negative aspects of charcoal, it still remains up the energy ladder as a transitional fuel and is used by majority of households in SSA.

2.2. Technologies for charcoal production

Charcoal is a wood based fuel produced by carbonization / pyrolysis of wood in the absence of oxygen (Macqueen and Korhaliller, 2011). Carbonization occurs in the absence of air at temperatures of between 450 - 600^{o}C (Macqueen and Korhaliller, 2011). Charcoal produced at low temperatures has high content of volatile material which produces poisonous fumes when burnt while charcoal produced at high temperatures contains low content of volatiles (Seidel, 2008). Charcoal production has improved over the years with the innovation of efficient kilns which have increased the efficiency and improved the quality of charcoal produced.

Soft burned charcoal is resistant to shattering, is rich in volatile matter and low fixed carbon content and it tends to smoke during burning (FAO, 1987). On the other hand, hard burned charcoal is high in fixed carbon content, low in volatiles and is much more friable (except charcoal carbonized at very high temperatures around 1000°C, which is essentially pure carbon and can be quite firm. This type of charcoal is hardly seen on the market and is hardly produced for commercial purposes (FAO, 1987). Hard burned charcoal burns cleanly but may be difficult to ignite (FAO, 1987). The optimal compromise product when dry has a fixed carbon content of about 75%; a volatile content of about 20%; an ash of about 5% and a bulk density of around 250-300 kg/m^3. It is moderately friable.

Technologies for charcoal production can be classified as traditional and efficient/improved pyrolysis methods. The key challenge in sustainable charcoal production is the provision of technology that is affordable and one that guarantees maximum yield from the wood used during pyrolysis. Most charcoal producers rely on the traditional earth mound kiln for charcoal production since they are unable to purchase better technologies.

2.2.1. Traditional earth mound kiln

The traditional earth mound kiln entails wood that is neatly and tightly stacked on the ground and a layer of green material (leaves and grass) placed over the pile as indicated in Figure 2.1. The stacked wood is then covered with soil thick enough to prevent air entry into the wood. The layer of green material acts as buffer holding the soil and preventing it from collapsing into the spaces in the wood. A small ignition area exposes part of the wood stack to air and is completely covered once the wood begins to burn. The charcoal producer remains on site for the entire pyrolysis process constantly sealing every outlet that may expose the wood to air usually signaled by smoke oozing out of the covering soil.

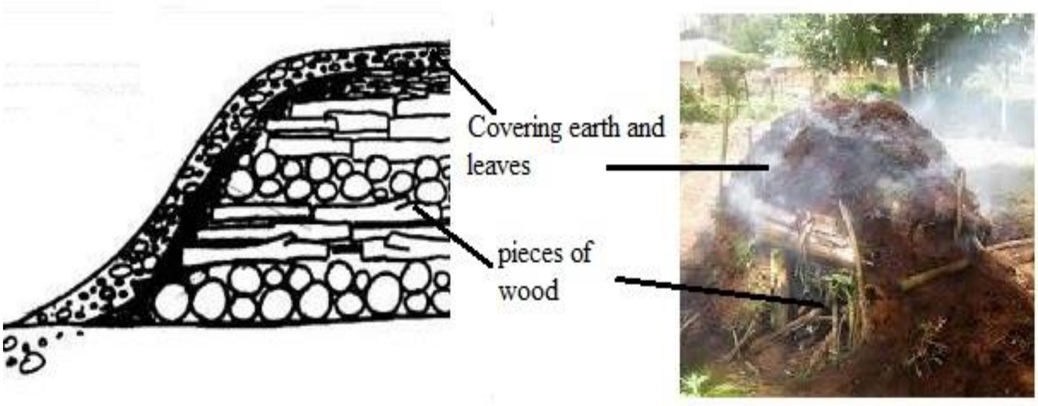


Figure 2.1: The traditional earth mound kiln

Traditional charcoal making methods lead to disintegration and depletion of national tree resources (Seboka, 2009). During the carbonization of wood into charcoal by traditional earth mound kilns, approximately 35% of wood is converted into charcoal while the rest is lost into the atmosphere in form of greenhouse gases such as CO_2 and CH_4 (Seboka, 2009). For example, the production of one tone of charcoal using a traditional kiln will require 0.1 hectares of woodland while it will only require 0.05 hectares to produce the same amount of charcoal using a efficient kiln (Oduor *et al*., 2012).

Approximately 60 - 85% of the wood is burnt to produce heat enough to carbonize the rest of the wood (Girard, 2002). This method is still in use today despite the availability of improved efficient kilns since it is cheap to most charcoal producers. This method of charcoal production yields charcoal of inconsistent quality and at very low yield to feedstock ratio (approximately 1:12 Kilograms. Earth mound kilns and pit kilns are the simplest technology for charcoal production with no costs but are labor intensive and can only achieve efficiencies of 8- 15 % (Seidel, 2008). The low yield in charcoal results in environmental pollution since most of the feedstock is lost and released to the environment in form of greenhouse gases (Girard, 2002).

2.2.2. Efficient pyrolysis methods

A dome shaped brick kiln (Figure 2.2) consists of bricks placed in two layers to ensure minimal loss of energy. Air inlets are constructed at the base while chimneys which control flow are placed mid-way to the top. Construction of this type of kiln is expensive thus it is mostly used by large scale charcoal producers like Kakuzi limited. It is stationary and requires the charcoal producer to transport wood over long distances thus attracting extra charcoal production costs. However, the charcoal produced by this kiln is uniformly carbonized with smaller amounts of volatiles compared to the traditional earth mound kiln. This is due to the uniformly constructed brick walls that reduce energy losses as well as enhance uniform carbonization of wood. The efficiency is also higher (30%) hence charcoal yields are higher compared to the earth mound kilns.

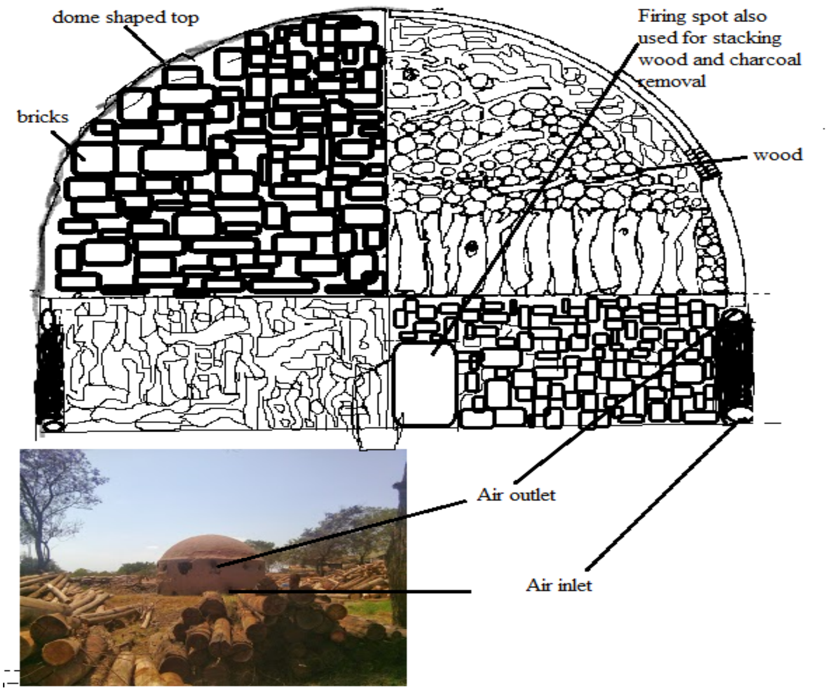


Figure 2.2: The dome shaped brick kiln

Improved kilns can play a big role in the sustainable production of charcoal. However their dissemination has been hampered by their high investment costs, their stationary nature and the need for special skills to construct and operate them (Seidel, 2008). A study by Mugo *et al*. (2003) identified three systems of charcoal production in Kenya. These include charcoal produced from ranches (45%), small scale farms (40%) and government land (15%). It is also reported that four types of kilns (Table 2.1) are mainly used in charcoal production, these include; traditional earth kilns with 10-15% efficiency, improved earth kilns 24-30%, masonry kilns 28-30% and metal kilns with

19-30% efficiency. The financial capabilities of the charcoal producer and portability of the kiln directly affect the choice of the kiln used (Mugo *et al.*, 2003). A dome shaped brick kiln (Figure 2.2) was used to produce charcoal for this study.

Table 2.1: Types of efficient kilns

Kiln Type	**Efficiency**	**Remarks**
Casamance Kiln (improved earth mound kiln)	30%	-Requires capital investment for the chimney -Difficult to construct
Brick kilns	30%	-Suitable for semi industrial production -Carbonization 13-14 days -Cost intensive and stationary
Steel kilns	27-35%	-Carbonization after 16- 24 -Cost intensive -Promoted as community kilns in Kenya
Adam Retort	40%	-Noxious emissions reduced by 70% -Carbonization within 24-30 hours -Cost intensive and suitable for semi industrial use
Traditional kiln	*8-15%	-Simplest method with no cost. -Labor intensive -Charcoal of inconsistent quality and at very low yield to feedstock ratio

*(Seidel, 2008) |**Source:** (Kammen and Lew, 2005a)

2.3. Sustainable versus non sustainable charcoal production

Sustainable charcoal production and consumption means that wood stocks are harvested in a way that ensures that they are not depleted in the long term (Bailis *et al.*, 2003a). The demand for charcoal especially in the urban areas has been rising at unimagined rates. This has put pressure on existing forests and woodlots resulting in deforestation where trees are harvested more than they are replanted. This has led to governments, concerned about the threat to forests by charcoal production, to put in place intervention programs such as fuel substitution to total banning of charcoal production (Girard, 2002). However, these intervention efforts have often led to unemployment, increased rural to urban migration- as charcoal producers seek alternative forms of employment. Banning of charcoal production as was done in Kenya and Mauritius has proved ineffective since bans drive producers underground making it difficult to control production procedures (Girard, 2002).

The environmental impacts of charcoal production and utilization are majorly linked to the inefficiency of carbonization, forestry and land degradation and the long transportation distances. Despite the improvements in kilns, the best kiln when properly used produces a maximum efficiency of 40% leading to energy losses of the fuel-wood in production process. Thus charcoal users end up consuming more fuel-wood than direct fuel-wood users (Kammen and Lew, 2005a). In most cases charcoal is produced from clear cutting of vegetation in preparation for planting thus it is rarely linked to sustainable forestry.

There is a link between the choice of kiln and the type of wood that should be harvested. Some kilns such as the portable “Kinyanjui” kiln when used for pyrolysis only requires the charcoal producer to harvest the tree branches and twigs for their charcoal (Kalenda *et al.*, 2011). Small quantities of charcoal can be made within six hours. This allows the trees to mature while providing energy needs for the household in the meantime. The same kiln can be used for carbonization of farm residues such as maize cobs and cocoa nut husks (Kalenda *et al.*, 2011). Specialized charcoal producers are reported to have achieved some element of sustainability in their charcoal production business. Mugo and Gathui, (2010a) documented one such example among others, of sustainable charcoal production by Kakuzi limited in

Thika. Kakuzi is a private company that is involved in planting of trees for charcoal production and treated poles. Brick kilns with an energy efficiency of between 28%-30% are used in the pyrolysis of wood found unsuitable for poles. The charcoal is then sold to vendors who in turn sell it to other consumers (Mugo and Gathui, 2010a).

However, complete sustainability goes beyond the charcoal production process. Kituyi, 2002 recommends a systems approach where the movement of material can be trailed from the time they are harvested to disposal so as to ensure sustainability throughout the wood fuel life cycle. That is, from wood harvesting, carbonization, charcoal utilization and ash disposal (Kituyi, 2002). What comes out clearly is that feedstock for charcoal production should match production, the kilns used for pyrolysis should be of high efficiency and cook-stoves used should have a high efficiency.

2.4. Tree species for charcoal production

Conventionally, all tree species can be carbonized to yield charcoal. This is achieved by cutting wood to pieces and burning them in a kiln where the flow of air is controlled (Mugo and Gathui, 2010b). The quality of charcoal produced depends on the individual tree species and the kiln chosen for the pyrolysis process. Thus some tree species are preferred over others because of the quality of the charcoal they produce. Good quality charcoal should have volatile matter content of less than 30% as the higher the volatile content, the lower the calorific value (Foley, 1986; Emrich, 1985). Charcoal quality also depends on chemical makeup of specific tree species used. Wood is basically made of cellulose, hemicellulose and lignin. Charcoal producers largely depend on traditional knowledge when choosing the best trees for their charcoal.

Traditional charcoal producers prefer dry well stacked savannah forests as opposed to dense humid rain forests (FAO, 1987). The savannah wood is usually dense, slow-growing and contains high quantities of lignin, which gives good charcoal yield when carbonized (FAO, 1987). Species that produce charcoal that burns for a long time consistent with high carbon content are mostly preferred since this is economical to the user. The species include *Casuarina equisetifolia, A. mearnsii, A. polyacantha, A. xanthophloea, A. spectabilis, E. camaldulensis, Leuceana leucocephala, Tectona grandis, Sesbania sesban* and other Acacia and Combretum species (Oduor *et al*., 2012). The characteristics that make these tree species suitable for charcoal production are mainly; production of little/ non- toxic smoke have dense wood with low moisture content, coppice and produce wood that does not spark when burning (Hines, 1993).

Species that produce dense charcoal such as the ones mentioned above are overly targeted by charcoal producers rendering them more vulnerable to overexploitation and in cases where coppicing and replanting are not supported, the woodlots / forests are eventually depleted (Girard, 2002).

A. polyacantha

A. polyacantha (Figure 2.3) is a large deciduous tree in the Fabaceae family that grows up to a height of 3.5 to 20 meters; the bark is yellow-brown and inclined to be thick or peeling in thick, corky flakes and loose strips. It grows in wooded grasslands, woodlands and bushlands, thriving in sites with high groundwater table and alluvial soils with a good mix of clay and sand. The species grows from sea level to an altitude of 1800 meters and does well with a mean annual rainfall of 300 - 1000 millimeters (Oduor *et al*., 2012b). It has a wood density of $0.467 g/cm^3$ and the calorific value of its wood and charcoal are 4.0kj/g and 6.5kj/g respectively.

Figure 2.3: A typical *A. polyacantha tree*

A. xanthoploea

A. xanthoploea (Figure 2.4) commonly known in English as the fever tree is a tree in the Fabaceae family. It is quick growing, 10-25m high. Leaves are bipinnate, with 4-7 pairs of pinnae and 10-17 pairs of leaflets per pinnae. Spines are white, straight and strong and arranged in pairs. Flowers are yellow, spherical and clustered on slender stalks in the axils of spines. Fruit are flat, papery, light brown pods, 5-19cm long, containing 5-10 seeds per pod. Seeds are elliptical, flattened. It has a wood density of 0.532g/m3 while the calorific value of wood and charcoal are 4.4kj/g and 7.9kj/g respectively (Oduor *et al*., 2012).

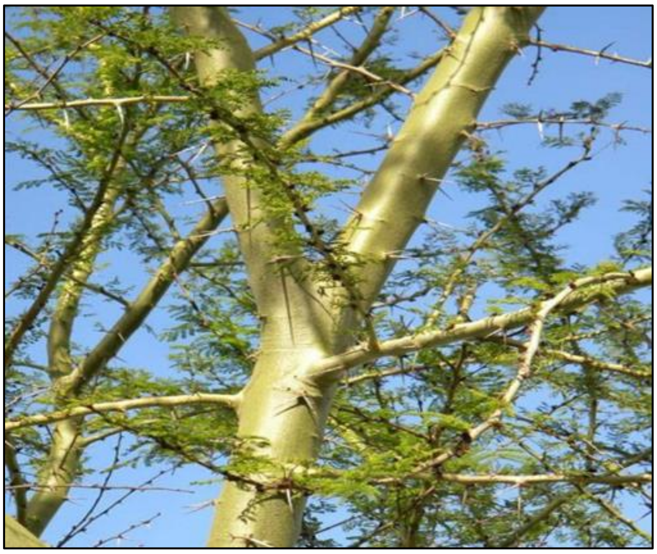


Figure 2.4: A typical *A. xanthoploea tree*

E. grandis

E. grandis (Figure 2.4) is an evergreen tree 40–60 m high with a tall straight trunk and 1–2 m in diameter. It grows spreading and thin in open; small and compressed in dense plantations. Its bark is white, gray or green, smooth, shedding in long narrow strips. Leaves are alternate, lanceolate, 10–20 cm long, 2–4 cm wide, acuminate, inaequilateral, wavy, glabrous. Umbels single at leaf base, 2.5–3 cm long with flattened stalk of 12 mm. Flowers are 5–12, short-stalked or stalkless while Buds are pyriform, 10 mm long, 5 mm wide (Githiomi and Kariuki, 2010). It has a wood density of 0.790g/m3 while the calorific value of wood and charcoal are 4.5kj/g and 7.5kj/g respectively (Oduor *et al*., 2012).

Figure 2.5: A typical *E. grandis tree*

2.5. Environmental impacts of charcoal production and consumption

The combustion of biomass including charcoal production and consumption as a domestic biomass fuel plays a significant role in the global carbon cycle *(Pennise et al*., 2001). It is estimated that biomass burning accounts for 25-45% annual global emissions of CO_2 , 15-50 % of CO, 3-10 % of CH_4 and 24 % of Total non-Methane Organic compounds (TNMOC) (Pennise *et al*., 2001; Levine, 1996). These are greenhouse gases that are directly linked to global warming and climate change (Levine, 1996).

Experiments have however shown that for situations of sustainable harvesting where CO_2 emissions are considered neutral, some improved stoves with better efficiency and ventilation assistance can lower the total warming impact of PICs by as much as 50-95% (Macqueen *et al*., 2011; MacCarty *et al*., 2008). Charcoal burning may produce less CO_2 than traditional wood burning but the PIC emissions are significantly much greater (MacCarty *et al*., 2008). Thus it is vital to characterize the emissions from biomass burning so as to obtain a broader scientific understanding of the chemical constituents of the emissions and their effects on humans and the environment (Pennise *et al*., 2001).

There is an increasing body of knowledge associating household use of traditional biomass to emissions of black carbon, which is a significant contributor to climate change (Takama *et al*., 2011). Residential biomass burning is bound to an estimated 18 percent of global black carbon emissions (Bond and Sun, 2005). Over forty thousand tons of wood is used daily in form of charcoal to serve the energy requirements of nearly three quarters of Kenyan households and small businesses (Bailis, 2005b). This kind of wood fuel consumption has overriding social and environmental consequences although not all impacts related to charcoal consumption are negative. The general extent to which charcoal consumption will impact the environment is dependent on the extent to which wood are sustainably harvested so that reserves do not decline (Bailis, 2005b).

Sustainable charcoal production and consumption means that wood stocks are harvested in a way that ensures that they are not depleted in the long term so that the greenhouse gases (GHG) produced in burning can be sequestered (Bailis *et al*., 2003). There should be care when balancing the equation of carbon sequestration during feedstock growth and carbon emissions during combustion. This is especially important if emission reductions are part of a short term plan, and standing forests (rather than new trees) are being cut for charcoal, there is an up-front carbon deficit – the immediate release of carbon- which will only be recompensed after a valuable time frame as the trees grow and take up carbon dioxide from the atmosphere (Macqueen *et al*., 2011). But even with thorough recycling of carbon, nonetheless, a charcoal fuel cycle can produce a net increase in global warming commitment (GWC-the total of global warming potentials of the gases emitted in a process) because of the emitted PIC (Pennise *et al*., 2001).

Whereas charcoal is a renewable resource, its soaring rate of extraction and inefficient use may render it a nonrenewable resource (Mugo and Gathui, 2010c). Even though some may try to delink charcoal production from deforestation due to other competing uses of forest land, many scientists agree that charcoal contributes to depletion of forests (Kristoferson, 1997). This is partly linked to the poor methods of charcoal production by use of inefficient traditional kilns which require large amounts of wood but yield low amounts of charcoal (Seidel, 2008). Greenhouse gas emissions, indoor air pollution and deforestation, reduction in ecological services of forests, biodiversity loss, soil erosion are among the major impacts associated with unsustainable utilization of forests (Mugo and Gathui, 2010c). Past arguments have suggested that charcoal production and consumption were causing destruction to vegetation cover (Eckholm, 1975). Be that as it may, a variety of tradeoffs and benefits associated with fuel wood production and consumption do exist and can be realized when charcoal is produced sustainably.

Charcoal production can also result in creation of jobs and hence poverty reduction. In 2005, Energy for Sustainable Development in Africa (ESDA) estimated that charcoal industry had an annual market value of over US$ 427 (32 billion Kenya shillings) and employing over 700, 000 people along the value chain (Mutimba and Barasa, 2005). It is projected that the production of wood for charcoal from commercially grown trees can produce two jobs per hectare of wood. This leads to about 496,000 jobs given that 298,000 hectares of wood are needed to produce the annual demand of 2.4 million tonnes of charcoal (Mugo and Gathui, 2010c). Other environmental services of forests such as carbon dioxide sequestration, watershed protection, aesthetic benefits, climate regulation and species conservation are also gained (Pattanayak *et al*., 2010). In addition, more jobs are created through the making of cook stoves and ovens and kilns (Mugo and Gathui, 2010c).

2.6. Emissions from Charcoal burning

The emissions of charcoal burning are classified into two groups: emissions produced during the carbonization of wood and the emissions produced during the end use of charcoal in a cook stove. The chemical composition of the wood and the method of charcoal production may affect the profile of the emissions when the charcoal is burnt (Hindi, 2012). It is reported that thermal decomposition of wood begins at 100^oC while hemicelluloses, cellulose and lignin are degraded at $200\text{-}260^oC$, $240\text{-}350^oC$ and $280\text{-}500^oC$ respectively (Hindi, 2012). In wood pyrolysis, the major contributor to volatile composition is hemicellulose and cellulose components (Park, 2010). A temperature range of between 450^oC and 500^oC is regarded as optimum and yields charcoal of a high carbon content with less volatiles (Park., *et al* 2010; FAO, 1987).

During the pyrolysis process, wood is reduced to a form of carbon by removing the volatile and other condensable constituents (Oyedun *et al*., 2012). Charcoal produced at low temperatures entails more volatiles and is easy to light but burns with a lot of smoke while charcoal produced at high temperatures is difficult to light but burns with less smoke (Oyedun *et al*., 2012). Thus, the condition under which the charcoal is produced affects the chemical composition of the charcoal and hence the compounds emitted when the same charcoal is burnt. There are varied opinions on the least amount of volatile matter or fixed carbon content charcoal must have before being regarded as good-quality. For example, Emrich (1985) as well as FAO (1987) reported that the volatile matter content of good quality charcoal must be less than 30%. Moreover, charcoal containing more volatile matter has lower calorific value (Foley, 1986).

In theory charcoal reacts with oxygen of the air at a glowing red heat to form colorless carbon monoxide gas, which then burns with a blue flame with more oxygen from the air to produce carbon dioxide gas and moisture (FAO, 1987). However, it is difficult to achieve such efficiency in the cook stoves commonly used in rural and urban areas (Smith, 2006). Cook-stoves with higher efficiency are costly and sophisticated. Those who could afford such sophistication would usually not be found burning charcoal but some other fuel of higher social prestige or convenience (FAO, 1987). Incomplete combustion of charcoal leads to the emission of organic compounds such as carbon monoxide, PAHs, formaldehyde and other compounds that may be detrimental to human health. Charcoal is mainly produced in rural areas using traditional earth mound kilns and is likely to contain a high percentage of volatile matter. Impurities contained in biomass fuels eventually lead to formation of inorganic compounds including sulfur dioxide, nitric oxide and ammonia. Many of these compounds have been identified in biomass smoke revealing the complexity of biomass emissions (Lim and Seow, 2012; IARC, 2010). Table 2.2 gives a summary of some of these compounds.

Table 2.2: Components of biomass smoke

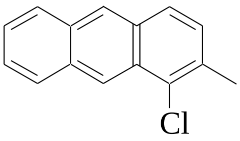
Class	**Constituents**
Inorganic compounds	Ammonia Carbon monoxide Nitric oxide Sulfur dioxide
Hydrocarbons	Alkanes and alkenes Aromatics including benzene and toluene PAHs
Other organic compounds	Aldehydes and ketones, alkanols Alkyl esters, carboxylic acids Coumarins and flavanoids Methylated phenolic compounds Phytosteroids Substituted aromatic compounds Sugar derivatives, terpenoids

Source: (IARC, 2010)

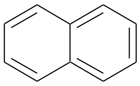
2.7. Polycyclic aromatic hydrocarbons (PAHs)

PAHs are a class of organic compounds produced by incomplete combustion of biomass, coal, oil, gas garbage or other organic substances such as tobacco and plastics (Silva *et al*., 2011). PAHs are ubiquitous in the environment and consist of two or more fused benzene rings containing mainly carbon and hydrogen. The difference in configuration of the benzene rings may lead to different properties. There are more than 100 different PAHs, the simplest of which is naphthalene **(3).**

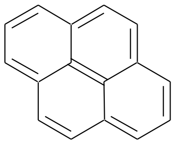
PAHs occur as part of a mixture of complex compounds, for example as part of combustion products such as soot, and not as single compounds. Some of the PAHs that have been identified from biomass sources include, benzo(a)pyrene **(1)**, 3-methylchloroanthrene **(2)** naphthalene **(3)** and pyrene **(4)** (Gachanja *et al*., 1992). PAHs of lower molecular weight (2-4 aromatic rings) are present mainly in the gaseous phase while those of higher molecular weight adhere to the particulates in the smoke. PAH’s also tend to adhere to the walls in the rooms where biomass stoves are used thus they may enter the human body through ingestion and dermal absorption (WHO, 2010a).



2



3



4

Source: (Haynes, 2011)

Emphasis has been placed on the mutagenic, genotoxic and carcinogenic effects of PAHs that may be contained in biomass smoke to which thousands of households are exposed (Silva *et al.,* 2011). The United States' occupational safety and health administration (OSHA, 2009) has mandated PAH workroom air standard (Table 2.3) to be an 8-hour time weighted average (TWA) permissible exposure limit (PEL) of 0.2mg/m^3 as indicated in Table 2.3. In addition, the WHO notes that no thresholds can be determined for PAHs and thus all indoor air exposures are considered relevant to health (WHO, 2010a)

.

Table 2.3: Standards and regulations for PAHs

Agency	**Medium**	**Level**	**Comments**
WHO/IARC	Air: Indoor	0.2mg/m^3	No threshold can be determined thus indoor exposures should be considered relevant to health Advisory: TLV[1] (8hour TWA[2])
WHO/IARC	Air: Indoor (naphthalene)	0.01mg/m^3	Annual average concentration
American conference of governmental industrial hygienists	Air: workplace	0.2mg/m^3	Advisory: TLV[1] (8hour TWA[2])
Occupational safety and health administration	Air: workplace	0.2mg/m^3	Advisory: REL[3] (8-hour TWA[2])
National institute for occupational safety and health	Air: workplace	0.2mg/m^3	Regulation: (benzene soluble fraction of coal tar volatiles) PEL[4] (8-hour workday)

[1] TLV threshold limit value

[2] TWA (time-weighted average): concentration for a normal 8-hour workday and a 40-hour workweek to which nearly all workers may be repeatedly exposed

[3] REL: recommended exposure limit

Source: (Kim *et al*., 2013)

2.8. Health effects of biomass burning

In developing countries, the use of solid fuel, often including biomass, in poorly ventilated buildings leads to exposure to a mixture of air pollutants (Kocbach., *et al*., 2009). Combinations of pollutants can lead to additive, and even synergistic effects. Combinations of exposure to wood, charcoal and tobacco smoke, radon and asbestos fibers provide examples of synergistic effects. The PAHs in tobacco, wood and charcoal smoke coupled with radon and asbestos fibers may act synergistically leading to lung cancer (Straif *et al*., 2005). There has been sustained emphasis on the health effects of polycyclic aromatic hydrocarbons in recent times due to their carcinogenic and mutagenic properties (Aas *et al*., 2000).

The international agency for research on cancer (IARC) has classified some PAHs as carcinogenic (group 1) or likely carcinogenic to humans (group 2) (IARC, 2010). Formal classification of individual PAHs as confirmed, probable or possible carcinogens is highly dependent on the degree to which they have been assessed using a variety of experimental and epidemiological approaches - especially for the large number of alkylated PAHs. Alkylated PAHs have been found to be more toxic as compared to their un-substituted congeners (Rhodes *et al*., 2005). Although not all PAHs have been classified as carcinogens, there is little doubt that at least some of the presently unclassifiable PAHs will be confirmed as potentially carcinogenic in future (CCME, 2008).

Individuals can be exposed briefly or throughout their lifetimes to chemicals in air, water and food; exposures may be environmental or occupational. The main routes of exposure are inhalation, ingestion and dermal contact (WHO, 2010). Food groups that tend to have the highest levels of PAHs include charcoal broiled or smoked meats, leafy vegetables, grains, and vegetable fats and oils (Yu *et al*., 2011). Individuals vary widely in their response to exposure to chemicals; each person has a pre-existing status (defined by, for example, age, sex, pregnancy, pulmonary disease, cardiovascular disease, genetic make-up) and a lifestyle, in which such factors as exercise and nutrition play key roles. All these different elements may influence a person’s susceptibility to chemicals (WHO, 2010c).

The most common mechanism of carcinogenesis induced by PAHs, as indicated in Figure 2.1, is DNA damage through the formation of adducts (Muñoz and Albores, 2012). Once in the body of an exposed individual, they are metabolized in a number of organs mainly the liver, kidney and lungs. They are excreted in the bile, urine or breast milk and stored to a limited degree in adipose tissue (Muñoz and Albores, 2012).The lipophilicity of PAHs enables them to readily penetrate cellular membranes (Yu *et al*., 2011). Subsequent metabolism renders them more water-soluble making them easier for the body to remove. However, PAHs can also be converted to more toxic or carcinogenic metabolites (Muñoz and Albores, 2010).

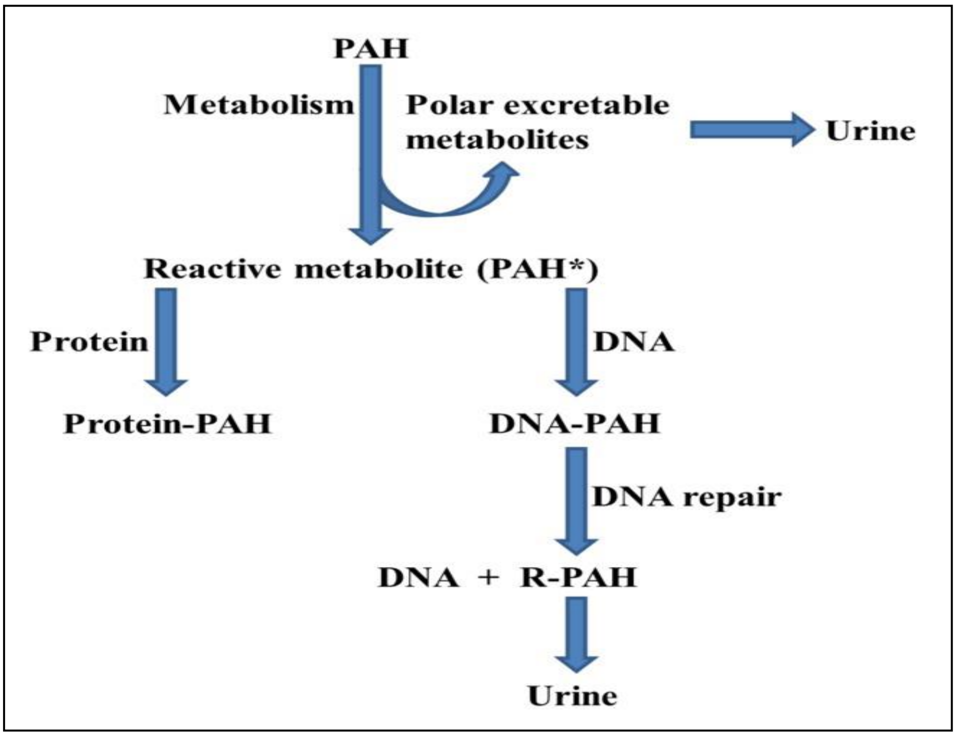


Figure 2.6: Metabolism of PAH leading to protein and DNA adducts
Source: (Pampanin, 2013)

PAHs undergo metabolic activation to reactive diol-epoxide enantiomers, which bind covalently to DNA (Straif *et al*., 2005). Afterwards, they form adducts or induce oxidative stress that provokes mutations. It has been reported that PAH metabolites have the capacity to enter redox cycles and induce the production of reactive oxygen species (ROS), thereby causing oxidative stress (An *et al*., 2011). If the rate of ROS generation is greater than their removal it is likely that more DNA damage will result.

PAHs may absorb light energy in ultra violet region (UVR) of (280-400 nm) region and may induce DNA damage by production of ROS (Muñoz and Albores, 2012). For example, chrysene induces apoptosis and DNA damage in human keratinocytes by generating ROS in response to UVB radiation (Ali *et al*., 2011).

DNA adducts caused by PAH metabolites are known to be essential components in the cause of cancer development (Pampanin, 2013). Thus, DNA adducts are used as biomarkers of exposure to PAHs and they represent a crucial end point, being a marker of genotoxicity (Pampanin, 2013). For example, some studies have revealed, by X-ray crystallography, structures of PAH-adducted oligonucleotides bound to bacterial DNA polymerases (Hsu *et al*., 2005; Ling *et al*., 2004).

PAH diol epoxides (PAHDEs) bind covalently to exocyclic amino groups of guanine and adenine, forming stable adducts within DNA (Lin *et al*., 2001). In addition, there are correlations between DNA adduct levels and mutagenesis. A number of studies have shown that the number of adducts formed is related to the degree of PAH exposure (Muñoz and Albores, 2012). However, other factors such as the age of the organism, concentration of PAHs and genetic profiles of individuals may affect the impact of exposure (Bolognesi *et al*., 1991). PAH exposure induces several molecular and cellular responses that modify the endogenous environment. Exposure to PAHs induces genes involved in apoptosis, cell cycle control and DNA repair (Torres *et al*., 2008). Molecular studies have demonstrated that adducts in DNA block polymerase replication activity, contributing to increased DNA damage by reducing repair activity (Hsu *et al*., 2005).

The failure of repair mechanisms and constant exposure to PAHs induces mutagenesis in cells. If DNA repair mechanisms are afflicted by the adduct formation rate the result is an accumulation of mutations in DNA that may induce carcinogenesis (Muñoz and Albores, 2012). These mutations are present in multiple genes including those that participate in cell survival. In particular, p53 mutations are associated with risk of carcinogenesis in PAH exposed individuals (Muñoz and Albores, 2012). Since the p53 protein is a transcription factor that regulates cell proliferation, differentiation, apoptosis, and DNA repair, mutations induced in this important protein could lead to severe damage in cells and genes. Some studies have linked p53 mutations to PAH exposure (Mordukhovich *et al.,* 2010; Yoon *et al.*, 2003).

Generation of adducts in DNA repair-related genes is not the only way mechanism by which PAHs induce carcinogenesis (Muñoz and Albores, 2012). A further problem amounts from their resemblance to steroid hormones allowing PAHs the ability to activate estrogen receptors (ER) and metabolism (Muñoz and Albores, 2012). The ability of several PAHs to displace natural estrogens and occupy ER binding sites, at least to some extent, implies a potential mechanism of action in endocrine tissues that is ER mediated (Santodonato, 1997). Nonetheless, the fundamental mechanism of carcinogenesis is a deficient DNA repair system in key genes involved in cell cycle control (Muñoz and Albores, 2012). Since chronic exposure to PAHs is related to a high rate of mutagenesis it is probable that damage to DNA is cumulative. A number of studies have associated chronic occupational PAH exposure to several types of cancer including cancer of the bladder, lung, kidney, liver, and breast (Karami *et al*., 2011; Shen *et al*., 2006; Boffetta *et al*., 1997; Dickey *et al*., 1997;).

The figure 2.1 adopted from Pampanin, (2013) is a schematic representation of DNA-PAH adducts formation process.

Cells are capable of repairing damage caused from PAH exposure, adduct formation, and ROS production through a number of molecular mechanisms. The most common mechanisms of repair used by cells exposed to PAHs are nucleotide excision repair (NER), base excision repair (BER), non-homologous end joining (NHEJ) of DNA double-strand breaks (DSBs), homologous recombination-al repair (HRR) and transcription coupled repair (TCR) (Muñoz and Albores, 2012). In addition, some studies indicate that DNA damage induced by PAHs is preferentially repaired by NER or BER and to a lesser extent by HRR (Meschini *et al*., 2010; Braithwaite *et al*, 1998). In the NER process, cells identify damaged DNA regions based on their unusual structure or chemistry. NER is considered the main pathway for removal of bulky DNA adducts (Braithwaite *et al*., 1998).

BER involves the combined activity of some specific proteins that recognize and excise DNA damage, replacing the damaged moiety with normal nucleotides (Braithwaite *et al*., 1998). The BER pathway deals with smaller damage to individual bases, such as oxidation, methylation, depurination, and deamination. If the adducts are left unrepaired, they may cause permanent mutations (Boysen and Hecht, 2003). Some studies have also proposed the use of molecules contained in natural compounds to decrease DNA damage caused by PAHs (Chan *et al*., 2003). In previous studies, the role of green tea polyphenols has been linked with protective effects against tumor induction in mice exposed to PAHs (Wang *et al*., 1989). Resveratrol - a natural phenol found on the skin of red grapes and other fruits and in the roots of Japanese knotweed (*Polygonum cuspidatum*) - reduced DNA oxidative damage and adduct formation induced by 7,12-dimethylbenz[*a*]anthracene in cells (Leung *et al*., 2009).

CHAPTER THREE: MATERIALS AND METHODS

3.1. Glassware and Solvents

3.1.1. Glassware

All the glassware that was used in this work was cleaned using chromic acid followed by washing detergent. They were then rinsed with distilled water followed by acetone and then kept in the oven at 80°C to dry. Before sample collection, the conical flasks and sample bottles were rinsed with distilled dichloromethane and dried in the oven. All this was done so as to avoid contamination.

3.1.2. Solvents

The solvent used was dichloromethane (DCM). This was of analar grade purchased from Sigma-Aldrich Company. DCM was used for the extraction of volatiles as well as washing of glassware. DCM is immiscible in water and can dissolve a wide range of organic compounds due to its medium polarity(Rossberg *et al.*, 2000). In addition, DCM has a low boiling point (39°C) thus it can be evaporated at low temperature without losing the extracted compounds

3.2. Apparatus

3.2.1. Chimney

A tailor made chimney used for this work (Figure 3:1) was fabricated by an artisan. Two conical shaped metal casings were joined together and clay placed between them so as to facilitate cooling of the emitted smoke from the clay jiko. The length between the smoke inlet and outlet were made as thin as possible to ease smoke movement.

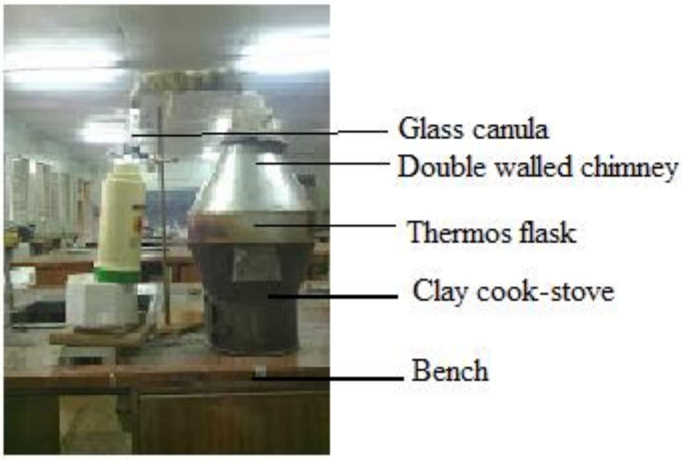


Figure 3.1: Experimental set up for collection of volatiles

3.2.2. Clay Jiko / Cook stove

A clay Jiko was also fabricated in a way that its edges were the same size as the chimney so as to minimize any smoke losses (Figure 3.1). The chimney was placed on top of the cook stove allowing the smoke to flow in one direction into the collecting cannula where the volatiles were condensed.

3.3. Sampling

Purposive sampling was employed in selecting charcoal producers from whom the charcoal samples were collected based on insights from published literature (Oduor *et al* 2012; Mugo *et al*., 2010; KEFRI, 2009). The species chosen were E. *grandis*, *A.polyacantha and A. Xanthophloea.* These species were chosen because they are mostly preferred and used by charcoal producers in Thika, Kitengela and Machakos (Oduor *et al*., 2012; Mugo and Gathui, 2010b).

3.3.1. Species identification

Tree species were identified by a taxonomist from Botany department, KU and voucher specimen deposited at the university herbarium and prepared for carbonization..

3.3.2. Charcoal production and sample collection

Two pyrolysis methods of charcoal production that is the traditional earth mound kiln and the dome shaped brick kiln (described in section 2.2) were used. Charcoal producers in Thika, Kitengela and Machakos were identified. In Thika, Kakuzi limited was identified as a semi industrial charcoal producer that uses *E. grandis* species and a dome shaped brick kiln for pyrolysis. Another charcoal producer specializing in charcoal production from *A. polyacantha* and *A. xanthoploea* among other tree species identified in Kitengela. This charcoal producer also used a dome shaped brick kiln similar to the one used by Kakuzi Limited.

Two other charcoal producers were identified in Machakos. These were specialized in production of charcoal using the traditional earth mound kiln (see section 2.2.1). Dry wood from *A. polyacantha* and *A. xanthoploea* was bought from a farmer in Machakos and given to the charcoal producers. They were paid to produce charcoal for the study. Kakuzi limited and the charcoal producer in Kitengela (Teddy Kinaynjui of ‘cookswell Jikos’) provided the charcoal samples at no cost since they were interested in the research findings.

1.5kg of each sample was randomly collected from the yield after pyrolysis and kept in labeled high density polythene bags and stored in a dry cabinet free from moisture.

3.4. Experimental setup

The set up shown in figure 3.1 and 3.2 was used to collect aliquot samples from the different types of charcoal under study.

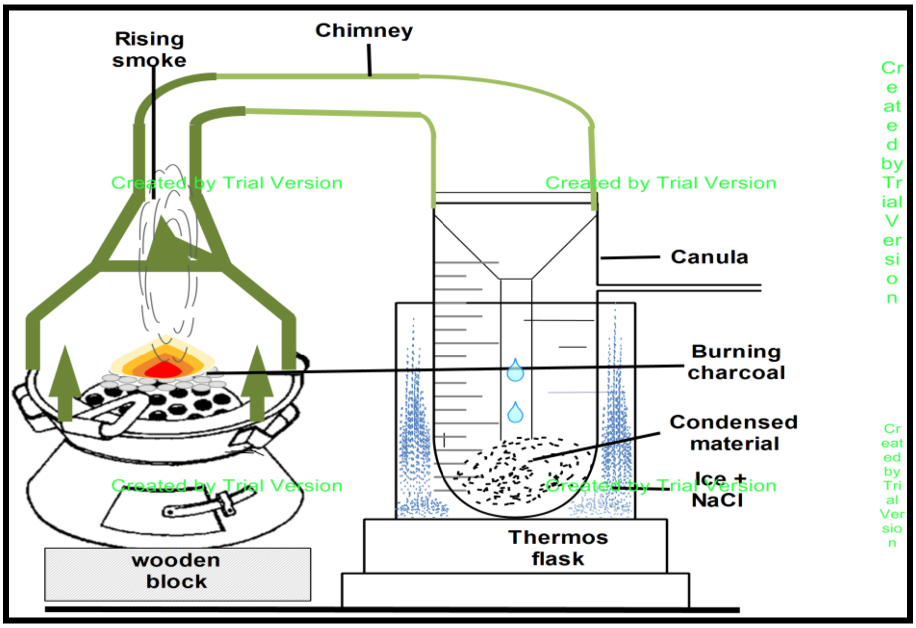


Figure 3.2: A schematic diagram of the experimental set up for collection of volatiles

Charcoal samples were burnt on a clay cook-stove / jiko and the smoke condensed in a canula tube held in a thermos flask containing ice and sodium chloride at negative 8 to 10 °C.

3.5. Extraction of Volatiles

The condensed volatiles were mixed with 30ml of dichloromethane (DCM) in a separating funnel and mixed vigorously for 5 minutes. 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. Sodium sulfate (Na_2SO_4) granules were dried in the oven at 105^0C for 2 hours. A scoopful of the dried anhydrous Na_2SO_4 was added to the extract in a conical flask and the flask swirled. More Na_2SO_4 was gradually added with swirling of the flask until all the water was removed completely. The dried extract was then filtered to remove the Na_2SO_4 using a filter paper. The process was repeated for all the other extracts. The dried extracts were transferred into a round bottomed flask and concentrated with a rotary evaporator at a temperature of 30°C.

3.6. Gas Chromatography- Mass Spectrometry analysis

The volatiles were analyzed using Gas Chromatography-linked Mass Spectrometry (GC-MS) and constituents characterized by their fragmentation patterns. This was compared with those from National Institute of Standards and Technology (NIST) library and their relative amounts determined. The conditions under which the analysis was done are as outlined in the Table 3.1.

Table 3.1: GC-MS Analysis Conditions

GC		**MS**	
Column	Rtx-35 (length 30 m, 0.32 mm I.D., df=0.25 µm	Interface temperature	300℃
Inlet Mode	Splitless	Ion source temperature	230℃
Vaporizing Chamber temp	300℃	Solvent elution time	3.5min
Column oven temp	90℃ (2min) →5℃→(10min) 320℃→ (12min)	Data sampling time	4.5 – 60min
Carrier gas	Helium	Measurement mode	Scan
Control mode	Constant linear velocity (43.7cm/sec)	Mass range	*m/z* 45-450
High pressure injection	150kPa (1.5min)	Event time	0.3sec
Purge flow rate	3 mL/min		
Injection rate	1.0 µL		

Source: (Mannino and Orecchio, 2008)

3.7. Experimental design

300g of each charcoal sample were separately combusted on a stove (see Figure 3.2 above). This was repeated three (3) times for each sample such that there were 18 extracted volatile samples as shown in the Table 3.1 below. Each of these sample extracts were injected into the GC-MS machine and the mean concentrations calculated and analyzed

Table 3.2: Experimental design

	Species		
	A. polyacantha	*A. xanthoploea*	*E. grandis*
Traditional	x	x	x
Efficient	x	x	x

X- Three extracts for each charcoal sample

3.8. Data analysis

Data obtained was subjected to statistical analysis using SPSS (Version 17). The SPSS version was used to analyze significant differences in the mean concentrations of emitted compounds. A one way analysis of variance test (ANOVA) was performed with the level of significance set at 0.05. Once a P value of less than 0.05 was obtained, the further analysis, separation of means, using SAS (version 9.1.3) software was undertaken so as to determine which specific concentrations were different. Duncan's Multiple Range test was used to separate the means. An independent T-tests was performed on the data to establish whether there were significant differences between concentration of emitted compounds emitted from two different samples. Results were presented in form of tables, figures and charts.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1. Emissions from charcoal prepared from *A. polyacantha* by traditional pyrolysis

GC-MS characterization of emissions obtained from *A. polyacantha* charcoal prepared by traditional pyrolysis revealed a total of 84 compounds. These included PAHs (6%), phenols (42%), benzene derivatives (15%), ketones (12%), alkanes (4%), alkenes (9%), phthalates (1%), aldehydes (1%), carboxylic acids (1%) and esters (2%).The total ion chromatogram of smoke emitted by charcoal prepared from *A. polyacantha* prepared by traditional pyrolysis is illustrated in Figure–4.1 below. Additionally, the retention times as well as relative abundances for all the identified compounds are given in Appendix 6.2.

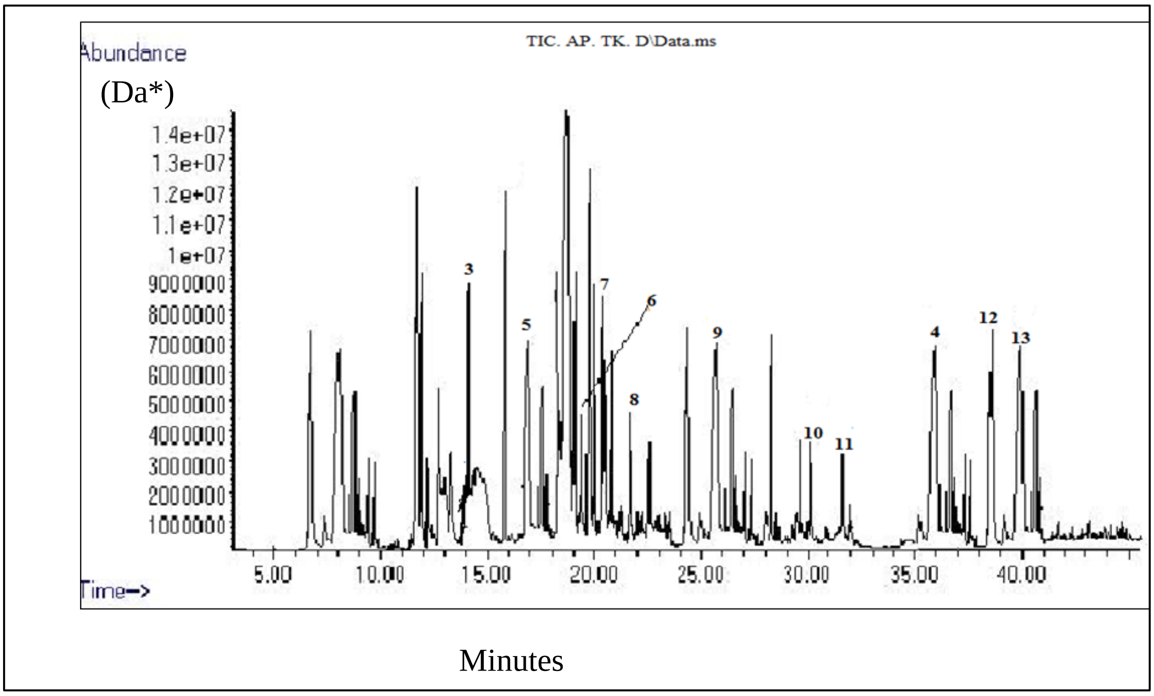
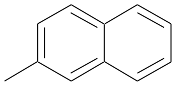
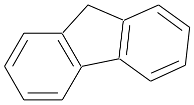


Figure 4.1: Total ion chromatogram of smoke emitted by charcoal prepared from *A. polyacantha* by traditional pyrolysis
* Daltons

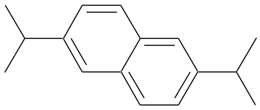
From the analysis, a total of eleven PAHs were identified and are indicated on the chromatogram. These were naphthalene (**3**), pyrene (**4**), 2-methylnaphthalene (**5**), fluorene (**6**), 2,6-diisopropylnaphthalene (**7**), 9H-fluoren-9-one (**8**), phenanthrene (**9**), fluoranthene (**10**), anthracene (**11**), benzo(a)anthracene (**12**) and chrysene (**13**).



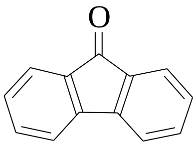
5



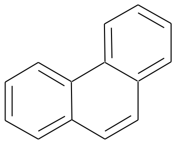
6



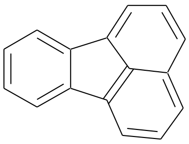
7



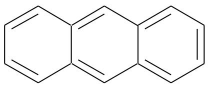
8



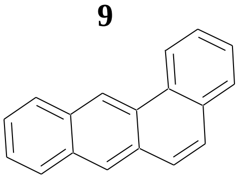
9



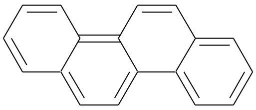
10



11



12



13

Source: (Haynes, 2011)

There was significant difference ($P<0.05$) in concentration of PAHs emitted from *A. polyacantha* charcoal prepared by traditional pyrolysis (Table 4.1). However, the concentrations of 2-methylnaphthalene, 9H-fluoren-9-one, fluoroanthene, and pyrene were not significantly different. Chrysene and fluorene as well as benzo(a)anthracene and phenanthrene concentrations were not significantly different (Table 4.1). Naphthalene, 2,6-diisopropylnaphlane and anthracene were significantly different.

Table 4.1: Concentrations of PAHs from *A. polycantha* charcoal prepared by traditional pyrolysis

PAHs	***Concentration x10^{-3}(µg/g)**	**WHO/NIOSH Exposure Limit x10^{-3}(µg/g)**
Naphthalene	110.00 ± 4.93^{a}	38.5
Benzo(a)anthracene	91.67 ± 10.82^{ba}	16.96
Phenanthrene	91.00 ± 2.08^{ba}	35.67
Anthracene	80.33 ±10.04^{bc}	35.67
Chrysene	74.67 ± 14.24^{bcd}	22.05
Fluorene	72.00 ± 4.58^{bcd}	31.43
Fluoranthene	66.67 ± 4.70^{cd}	38.24
2-Methylnaphthalene	64.00 ± 7.23^{cd}	33.06
Pyrene	60.00 ± 3.79^{cd}	31.43
9H-Fluoren-9-one	58.33± 6.36^{cd}	27.14
2,6-Diisopropylnaphthalene	53.67 ± 1.76^{d}	30.00

*Means separated using Duncan Multiple Range Test (DMRT) by the same letter are not significantly different ($P>0.05$) from each other

Naphthalene was the highest concentration (110.00 x 10^{-3}µg/g) while 2,6-diisopropylnaphthalene was the least in concentration (53.67 x 10^{-3}µg/g) as indicated in Figure 4.2. All the emitted (Figure 4.2)PAHs had concentrations that were higher as compared to the National Institute of Occupational Health permissible levels (NIOSH, 2010). 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 EPA priority pollutants list (EPA, 1996)

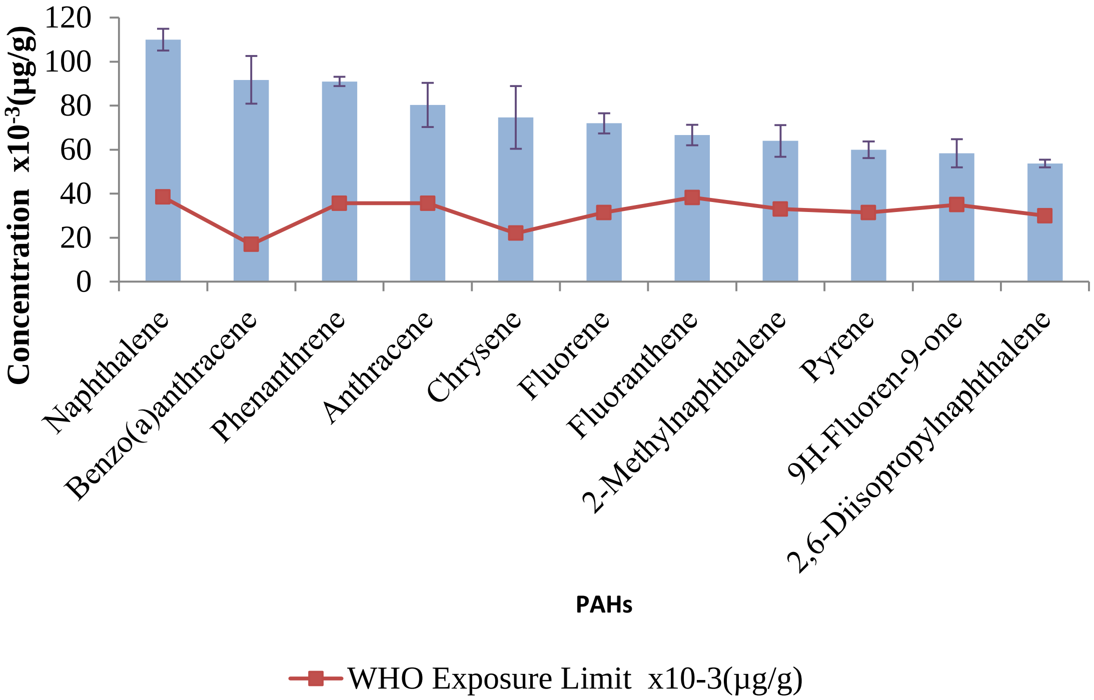


Figure 4.2: Concentrations of PAHs in volatile blend obtained from traditionally prepared *A. polyacantha* charcoal

The difference in the concentration of the emitted PAHs can be attributed to the different concentration of precursor compounds from which PAHs were formed. 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 has been linked with 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).

Phytochemical screening of *A. polyacantha* stem bark revealed the presence of flavonoids, steroids, carbohydrates, tannins, anthraquinones, cardiac glycosides, alkaloids, triterpenoids and saponins (Okpanachi *et al*., 2011). 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, phenantrene and fluoranthene were the most abundant in burning charcoal from water-pipe smoking (Nguyen *et al*., 2013).

4.2. Emissions from *A. polyacantha* charcoal prepared by efficient pyrolysis

GC-MS characterization of emissions obtained from *A. polyacantha* charcoal prepared by efficient pyrolysis revealed a total of 51 compounds. These included PAHs (8%), phenols (37%), benzene derivatives (11%), ketones (22%), alkanes (4%), alkenes (9%), phthalates (1%), alcohols (4%) and esters (4%), The total ion chromatogram of smoke emitted by charcoal prepared from *A. polyacantha* by efficient pyrolysis is given in Figure–4.3 and the retention times as well as relative abundances for all the identified compounds are given in Appendix 6.3. From the analysis, a total of four PAHs were identified and are indicated on the chromatogram. These were naphthalene (**3**), 2-methylnaphthalene (**5**), fluorene (**6**) and phenanthrene (**9**).

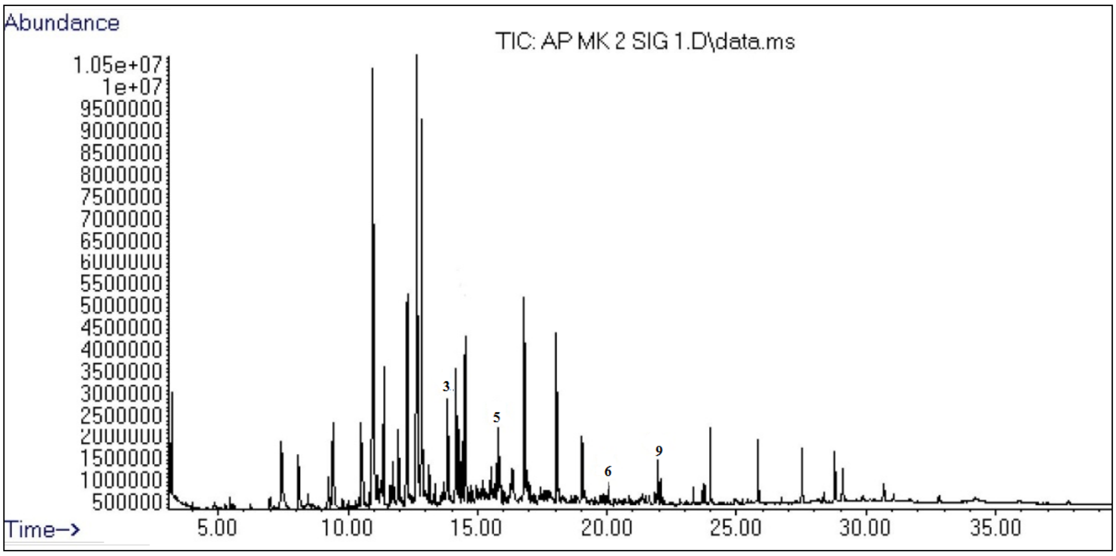


Figure 4.3: Total ion chromatogram of smoke emitted by charcoal prepared from *A. polyacantha* by efficient pyrolysis

There was significant difference ($P<0.05$) in concentrations of PAHs emitted from *A. polyacantha* charcoal that had been prepared by efficient pyrolysis There was also significant differences in the concentrations of emitted naphthalene (86.00 x 10^{-3}µg/g) and phenanthrene (71.33 x 10^{-3}µg/g) as indicated in Table 4.2. However, the concentration of 2-methylnaphthalene (54.67 x 10^{-3}µg/g) and fluorene (48.33 x 10^{-3}µg/g) were not significantly different.

Table 4.2: Concentrations of emitted PAHs from *A. polyacantha* charcoal prepared by efficient pyrolysis

PAH	***Concentration x 10^{-3}(µg/g)**	**NIOSH exposure limit x10^{-3}(µg/g)**
Naphthalene	86.00 ± 3.06^{a}	38.5
Phenanthrene	71.33 ± 0.88^{ab}	35.67
2-methylnaphthalene	54.67 ± 9.14^{b}	33.06
Fluorene	48.33 ± 1.67^{b}	31.43

*Means separated using Duncan Multiple Range Test (DMRT) by the same letter are not significantly different ($P>0.05$) from each other

Naphthalene was the highest in concentration (86 x 10^{-3}µg/g) followed by phenanthrene (71.33 x 10^{-3}µg/g) and 2-methylnaphthalene (54.67 x 10^{3}µg/g) respectively. Fluorene had the least concentration (48 x 10^{-3}µg/g) as indicated in the Figure 4.4. The mean concentrations of all the four emitted PAHs were higher than permissible exposure limits (NIOSH, 2010).

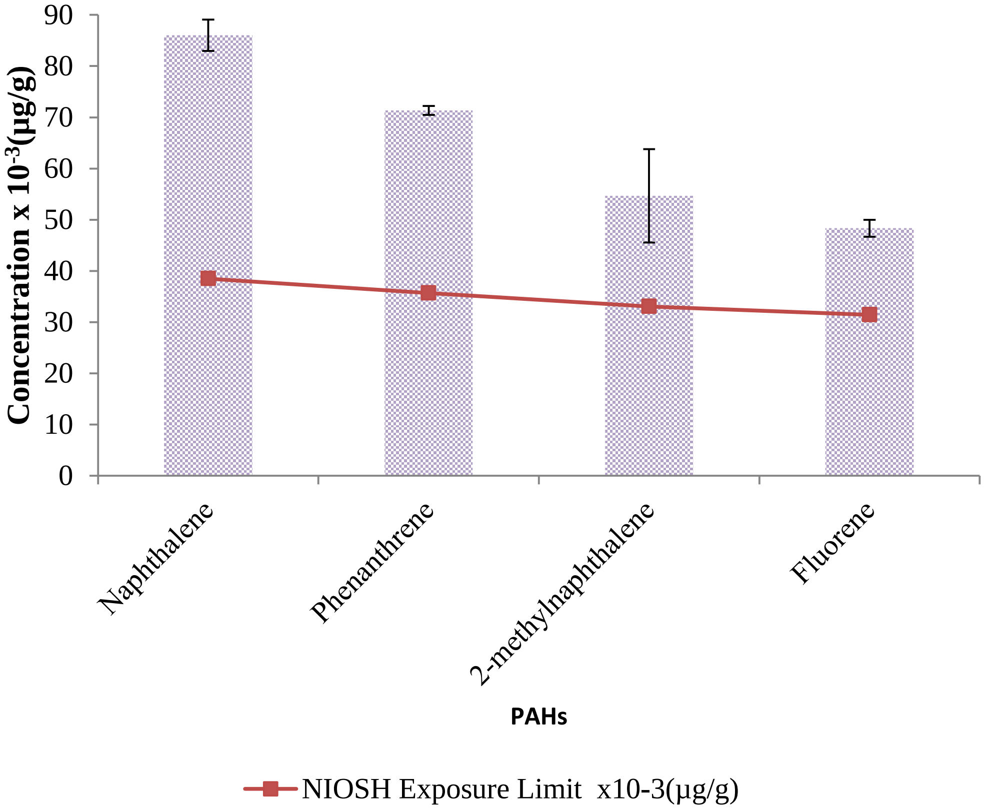


Figure 4.4: Concentration of PAHs in volatile blend obtained from *A. polyacantha* charcoal prepared by efficient pyrolysis

The significant differences in the concentration of emitted PAHs from *A. polyacantha* charcoal that was prepared by efficient pyrolysis can be attributed to the difference in concentrations of precursors from which the PAHs were formed. PAH synthesis during combustion has been linked with the precursors such as steroids, cellulose and alkenes in wood species (Britt *et el.*, 2004). Thus the high concentration of naphthalene may be attributed to the high concentration of the precursor compound from which it is being formed. However, because of the chemical complexity of biomass and its pyrolysis products, it is difficult to gain detailed information on the formation pathways of specific PAHs (Antal *et al*., 1985).

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

There was significant differences (t = -6.376, df = 2, P = 0.024) between fluorene emitted from *A. polyacantha* charcoal prepared by traditional and efficient pyrolysis (Table 4.3). In addition, there was significant differences (t = -11.529, df = 2, P = 0.007) between naphthalene emitted from *A. polyacantha* charcoal prepared by traditional and efficient pyrolysis (Table 4.3). There was significant differences (t = -14.750, df = 2, P = 0.005) between phenanthrene emitted from *A. polyacantha* charcoal prepared by traditional and efficient pyrolysis. However, there was no significant difference (t= -1.257, df = 2, P = 0.336) between 2-methylnaphthalene emitted from *A. polyacantha* charcoal prepared by both traditional and efficient pyrolysis (Table 4.3).

Table 4.3: Comparison of emissions from *A. polyacantha* prepared by efficient and traditional pyrolysis

PAH	**Traditional**	**Modern**	**P**
2-methylnaphthalene	64.00±7.23	86±3.06	0.336
Fluorene	72.00±4.58	71.33 ± 0.88	0.024
Naphthalene	110.00±4.93	54.67±9.14	0.007
Phenanthrene	91.00±2.08	48.33±1.67	0.005

The differences in the concentrations of the emitted fluorene, naphthalene and phenanthrene between charcoal prepared from *A. polyacantha* by traditional and efficient pyrolysis can be attributed to the difference in oxygen circulation during pyrolysis. Pyrolysis by traditional earth mound kilns lead to excess flow of oxygen into the carbonizing wood through openings in the covering soil and leaves. This results in the non-uniform carbonized charcoal which produces high concentrations of volatiles when burned on a cook-stove. On the other hand, charcoal production by efficient pyrolysis (brick kiln) results in uniformly carbonized charcoal. 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).

4.4. Emissions from *A. xanthophloea* charcoal prepared by traditional pyrolysis

GC-MS characterization of emissions obtained from *A. xanthophloea* charcoal prepared by traditional pyrolysis revealed a total of 62 compounds. These included PAHs (12%), phenols (33%), benzene derivatives (7%), ketones (2%), alkanes (12%), alkenes (10%),, phthalates (6%), carboxylic acids (8%), alcohols (4%)and esters (6%), The total ion chromatogram of smoke emitted by charcoal prepared from *A. xanthophloea* by traditional pyrolysis is given in Figure-4.5 and the retention times as well as relative abundances for all the identified compounds are given in Appendix 6.4.

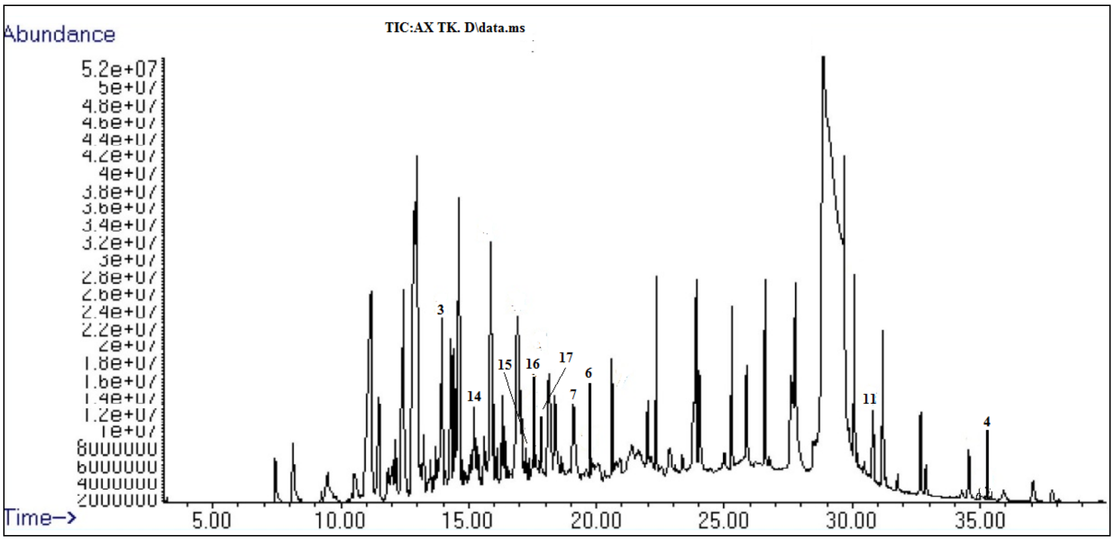
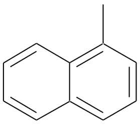
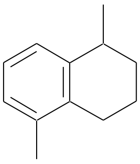


Figure 4.5: Total ion chromatogram of smoke emitted by charcoal prepared from *A. xanthophloea* by traditional pyrolysis

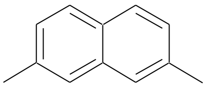
From the analysis, a total of eleven PAHs were identified and are indicated on the chromatogram. These were naphthalene (**3**), 1-methylnaphthalene (**14**), 1,5-dimethyl-1,2,3,4-tetrahydronaphthalene (**15**), 2,7-dimethylnaphthalene (**16**), 1,4-dimethylnaphthalene (**17**), fluorene (**6**), 2,6-diisopropylnaphthalene (**7**), anthracene (**11**) and pyrene (**4**).



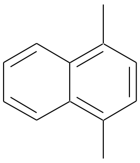
14



15



16



17

Source: (Haynes, 2011)

There was significant difference ($P<0.05$) in the concentration of PAHs emitted from *A. xanthophloea* charcoal prepared by traditional pyrolysis (Table 4.4). There was significant difference in the concentration of 2,6-diisopropylnaphthalene (201.54 x 10^{-3}µg/g), naphthalene (140.42 x 10^{-3}µg/g), 1,4-dimethylnaphthalene (65.64 x 10^{-3}µg/g) and 1,5-dimethyl-1,2,3,4-tetrahydronaphthalene (54.23 x 10^{-3}µg/g) as indicated in Table 4.4. There was however, no significant difference in the concentration of anthracene (84.80 x 10^{-3}µg/g), pyrene (71.82 x 10^{-3}µg/g) and 1-methylnaphthalene (70.11 x 10^{-3}µg/g), 2,7-dimethylnaphthalene 109.96 x 10^{-3}µg/g) and fluorene (97.35 x 10^{-3}µg/g) as indicated in Table 4.4.

Table 4.4: Concentrations of emitted PAHs emitted from *A. xanthophloea* charcoal prepared by traditional pyrolysis

PAH	***Concentration x 10^{-3} (µg/g)**	**NIOSH exposure limit x10^{-3}(µg/g)**
2,6-Diisopropylnaphthalene	201.54 ± 37.26^{a}	23.03
Naphthalene	140.42 ± 2.08^{b}	38.15
2,7-Dimethylnaphthalene	109.96 ± 3.07^{cb}	31.3
Fluorene	97.35 ± 5.90^{cd}	29.42
Anthracene	84.80 ± 2.12^{cde}	27.44
Pyrene	71.82 ± 1.78^{cde}	24.18
1-Methylnaphthalene	70.11 ±1.60^{cde}	34.39
1,4-Dimethylnaphthalene	65.64 ± 1.97^{de}	31.3
1,5-Dimethyl-1,2,3,4-tetrahydronaphthalene	54.23 ± 3.38^{e}	30.51

*****Means separated using Duncan Multiple Range Test (DMRT) by the same letter are not significantly different ($P>0.05$) from each other

2,6-diisopropylnaphthalene had the highest concentration (201.54 x 10^{-3}µg/g) while 1,5-dimethyl-1,2,3,4-tetrahydronaphthalene had the lowest concentration(54.23 x 10^{-3}µg/g). All the concentrations of emitted compounds were higher than the WHO permissible levels as indicated in Figure 4.6

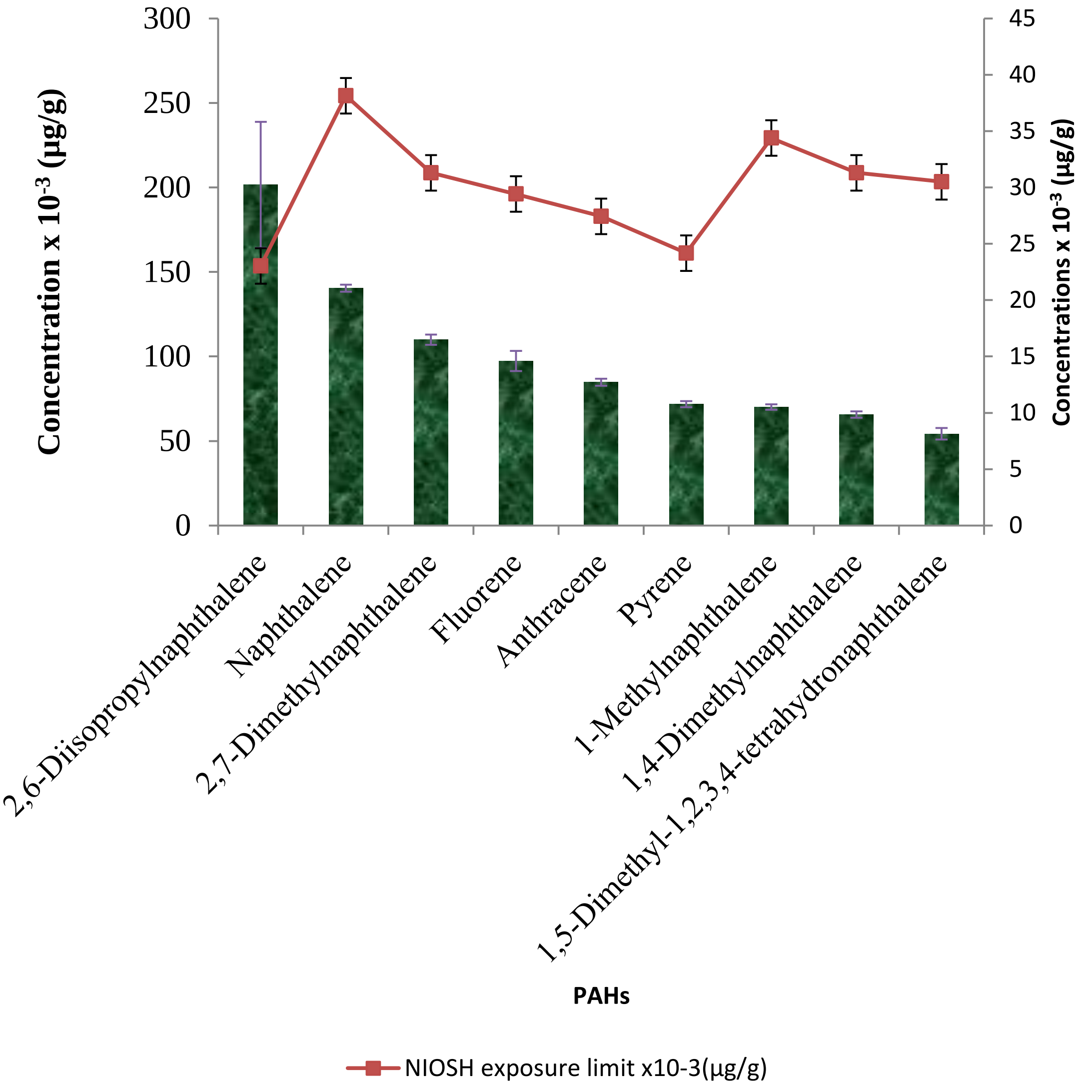


Figure 4.6: Concentrations of PAHs in volatile blend obtained from traditionally prepared *A. xanthophloea* charcoal

The difference in concentrations of 2,6-diisopropylnaphthalene, naphthalene, 2,7-dimethylnaphthalene, fluorene, 1,4-dimethylnaphthalene and 1,5-dimethyl-1,2,3,4-tetrahydronaphthalene can be attributed to the different concentrations of the precursor compounds from which they were formed. These precursors are mainly cellulose, hemicellulose, and extractives (Britt *et al*., 2004; Klass, 1998). The high concentration of 2,6-diisopropylnaphthalene can be attributed to the chemical composition of the *A. xanthophloea* which may contain a high concentration of precursors necessary for pyro-synthesis of this compound. It is reported that during the combustion and pyrolysis of biomass, PAHs are synthesized by reactions of radicals and precursors such as alkanes, phytochemicals and aromatics to form larger fused benzene structures (Britt *et al*., 2004).

4.5. Emissions from *A. xanthophloea* charcoal prepared by efficient pyrolysis

GC-MS characterization of emissions obtained from *A. xanthophloea* charcoal prepared by efficient pyrolysis revealed a total of 61 compounds. These included PAHs (4%), phenols (45%), benzene derivatives (16%), ketones (9%), alkanes (5%), alkenes (8%), phthalates (1%), aldehydes (5%) and esters (7%), The total ion chromatogram of smoke emitted by charcoal prepared from *A. xanthophloea* prepared by efficient pyrolysis is given in Figure-4.7 and the retention times as well as relative abundances for all the identified compounds are given in Appendix 6.5.

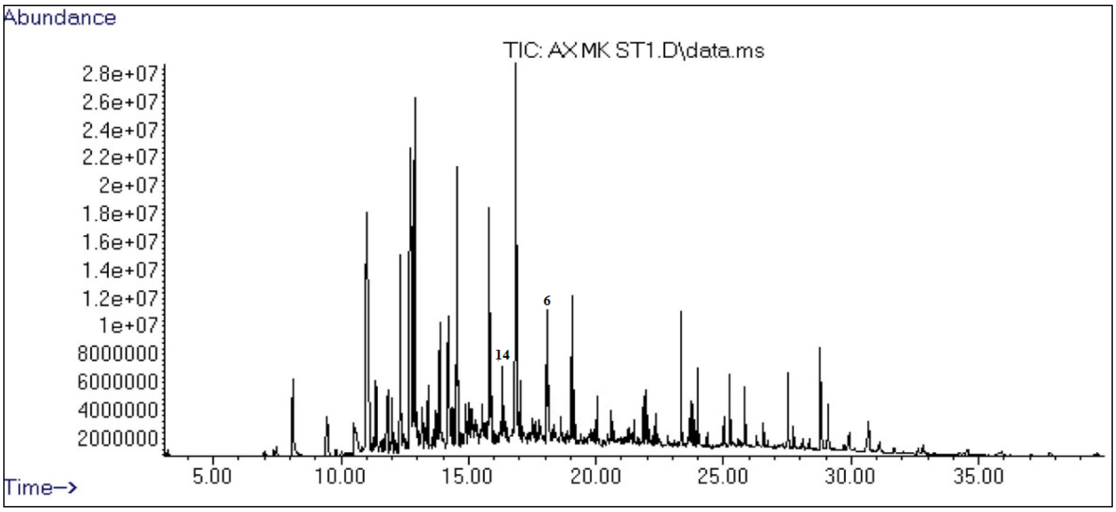


Figure 4.7: Total ion chromatogram of smoke emitted by charcoal prepared from *A. xanthophloea* by efficient pyrolysis

From the analysis, only two PAHs were identified and are indicated on the chromatogram. These were 1-methylnaphthalene (**14**) and fluorene (**6**)

There was no significant differences (P>0.05) in the concentrations of emitted 1-methylnaphthalene and (55.67 x 10^{-3}µg/g) fluorine (60.67 x 10^{-3}µg/g) from *A. xanthophloea* charcoal prepared by efficient pyrolysis as indicated in Figure 4.8. This may be attributed to the concentrations of precursor compounds from which they were synthesized during combustion that might have been present at similar concentrations.

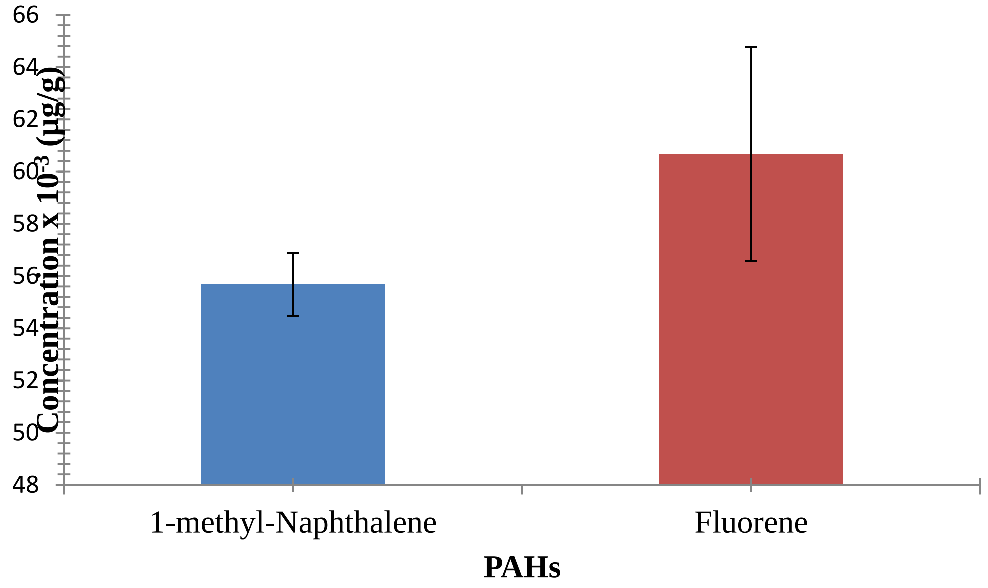


Figure 4.8: Concentrations of PAHs in volatile blend obtained from *A. polyacantha* charcoal prepared by efficient pyrolysis

4.6. Comparison of PAH emissions from *A. xanthophloea* charcoal prepared by traditional and efficient pyrolysis

There was a significant differences (t = -8.84, df = 2, P = 0.013) between 1-methylnaphthalene emitted from *A. xanthophloea* charcoal prepared by traditional and efficient pyrolysis (Table 4.5). There was a significant difference (t = -8.59, df = 2, P

= 0.013) between fluorene emitted from *A. xanthophloea* charcoal prepared by traditional and efficient pyrolysis (Table 4.5).

Table 4.5: Comparison of emitted PAHs from *A. xanthophloea* charcoal prepared by traditional and efficient pyrolysis

PAH	**t**	**df**	**P**
1-methylnaphthalene	-8.84	2	0.013
Fluorene	-8.59	2	0.013

The differences in concentrations of emitted 1-methylnaphthalene and fluorene from *A. xanthophloea* charcoal prepared by traditional and efficient pyrolysis can be attributed to the degree of carbonization of wood in the two pyrolysis methods owing to the amount of oxygen allowed to flow in during pyrolysis. Pyrolysis by traditional earth mound kilns is affected by entry of oxygen into the kiln through holes in the loose covering of soil and leaves. This results in production of unevenly carbonized charcoal which produces excessive volatiles when burned in a cook-stove (Seidel, 2008). On the contrary, the double brick walls of a brick kiln ensure that pyrolysis takes place at airtight conditions. The walls also provide proper insulation retaining most of the heat produced inside the kiln. In the traditional earth mound kiln, temperatures are relatively low when compared to the brick kiln since the covering of soil and leaves is not as compact as the double layers of bricks in a brick kiln. Thus there is poor retention of heat leading to production of charcoal at lower temperatures. It is reported that charcoal produced at high temperatures has low quantity of volatiles relative to charcoal produced at low temperatures (Seidel, 2008).

This results in charcoal that is uniformly carbonized and which produces less fumes when burned (Seidel, 2008; FAO, 1987).

4.7. Emissions from *E. grandis* charcoal prepared by traditional pyrolysis

GC-MS characterization of emissions obtained from *E. grandis* charcoal prepared by traditional pyrolysis revealed a total of 74 compounds. These included PAHs (7%), phenols (45%), benzene derivatives (19%), ketones (9%), alkanes (5%), alkenes (4%), phthalates (1%),aldehydes (3%) alcohols (6%) and esters (1%), The total ion chromatogram of smoke emitted by charcoal prepared from *E. grandis* by traditional pyrolysis is given in Figure-4.9 and the retention times as well as relative abundances for all the identified compounds are given in Appendix 6.6.

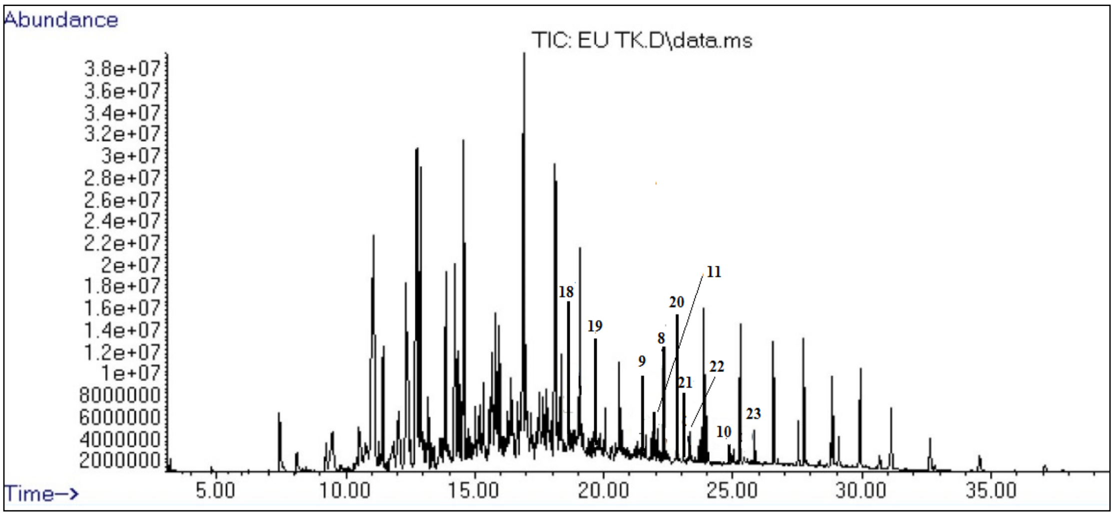
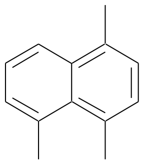
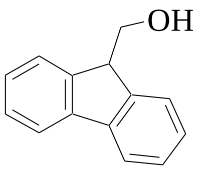


Figure 4.9: Total ion chromatogram of smoke emitted by charcoal prepared from *E. grandis* by traditional pyrolysis

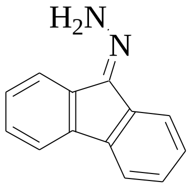
From the analysis a total of ten PAHs were identified and indicated on the chromatogram. These were 1,4,5-trimethylnaphthalene (**18**), fluorene-9-methanol (**19**), 9H-fluorene-9-one (**8**), anthracene (**11**), phenanthrene (**9**), 9H-fluoren-9-one, hydrazone (**20**), 1-methylphenanthrene (**21**), 4-methylphenanthrene (**22**), fluoroanthene (**10**) and 1,4-dimethyl-9,10-anthracenedione (**23**).



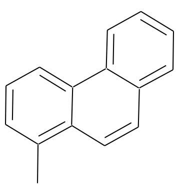
18



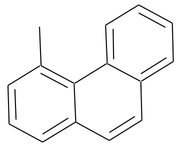
19



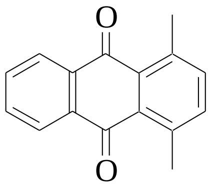
20



21



22



23

Source: (Haynes, 2011)

There was significant difference ($P<0.05$) in concentration of PAHs emitted from *E. grandis* charcoal prepared by traditional pyrolysis (Table 4.6). The concentration of 1,4-dimethyl-9,10-anthracenedione (31.00 x 10^{-3} µg/g), 4-methylphenanthrene (35.33 x 10^{-3} µg/g) , 9H-fluoren-9-one (32.47 x 10^{-3} µg/g) and fluoranthene (25.67 x 10^{-3} µg/g) were not significantly different (Table 4.6). However, the concentration of 1-metheylphenanthrene (48.00 x 10^{-3} µg/g), 1,4,5-trimethylnaphthalene (94.00 x 10^{-3} µg/g), 9H-fluoren-9-one, hydrazone (79.33 x 10^{-3} µg/g), fluorene-9-methanol (92.00 x 10^{-3} µg/g) and phenanthrene (59.00 x 10^{-3} µg/g) were significantly different as indicated in Table 4.6.

Table 4.6: Concentrations of PAHs emitted from *E. grandis* charcoal prepared by traditional pyrolysis

PAH	***Concentration x10^{-3} (µg/g)**	**NIOSH exposure limit x10-3(µg/g)**
Phenanthrene	59.00 ± 5.51^{a}	35.67
1,4,5-Trimethylnaphthalene	94.00 ± 2.65^{b}	29.00
Fluorene-9-methanol	92.00 ± 4.62^{b}	25.00
9H-Fluoren-9-one, hydrazone	79.33 ± 2.03^{c}	25.00
Anthracene	67.33 ± 2.60^{d}	35.67
1-Methylphenanthrene	48.00 ± 4.36^{e}	38.22
4-Methylphenanthrene	35.33 ± 4.67^{f}	38.22.00
9H-Fluoren-9-one	32.47 ± 6.26^{f}	27.00
1,4-dimethyl-9,10-Anthracenedione	31.00 ± 4.04^{f}	21.00
Fluoranthene	25.67 ± 2.85^{f}	38.24

*Means separated using Duncan Multiple Range Test (DMRT) by the same letter are not significantly different (P>0.05) from each other

Phenanthrene had the highest concentration (0.159µg/g) while fluoroanthene had the lowest concentration (0.02567µg/g) as indicated in Figure 4.10.

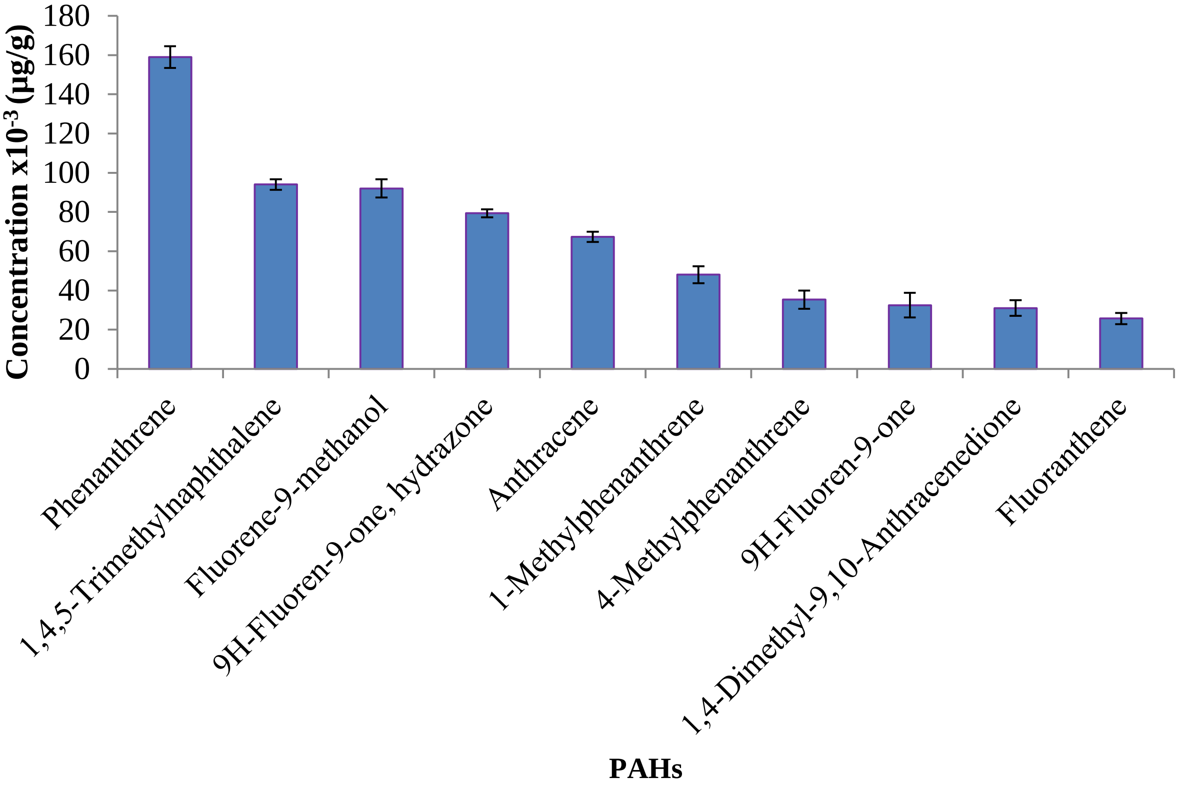


Figure 4.10: Concentrations of emitted PAHs from *E. grandis* charcoal prepared by traditional pyrolysis

The difference in the concentration of emitted PAHs from combusted *E. grandis* charcoal that had been prepared by traditional pyrolysis can be attributed to the different concentration of precursor compounds from which the PAHs were formed during combustion. For example, phenanthrene is reported to be a pyro-synthesis product of steroids in biomass (Britt *et al.*, 2004). Steroids, tannins, saponins, phenolic compounds and flavonoids are reported to be present in eucalyptus species (Vasantharaj *et al.*, 2013). Thus the concentration of steroid, as a precursor for pyro-synthesis of phenanthrene, could have been higher than other precursors leading to more emission of phenanthrene than fluoranthene.

4.8. Emissions from *E. grandis* charcoal prepared by efficient pyrolysis

GC-MS characterization of emissions obtained from *E. grandis* charcoal prepared by efficient pyrolysis revealed a total of 69 compounds. These included PAHs (6%), phenols (21%), benzene derivatives (23%), ketones (6%), alkanes (10%), alkenes (17%), phthalates (2%), Aldehydes (1%), alcohols (5%) and esters (9%), The total ion chromatogram of smoke emitted by charcoal prepared from *E. grandis* by efficient pyrolysis is given in Figure 4.10 and the retention times as well as relative abundances for all the identified compounds are given in Appendix 6.7.

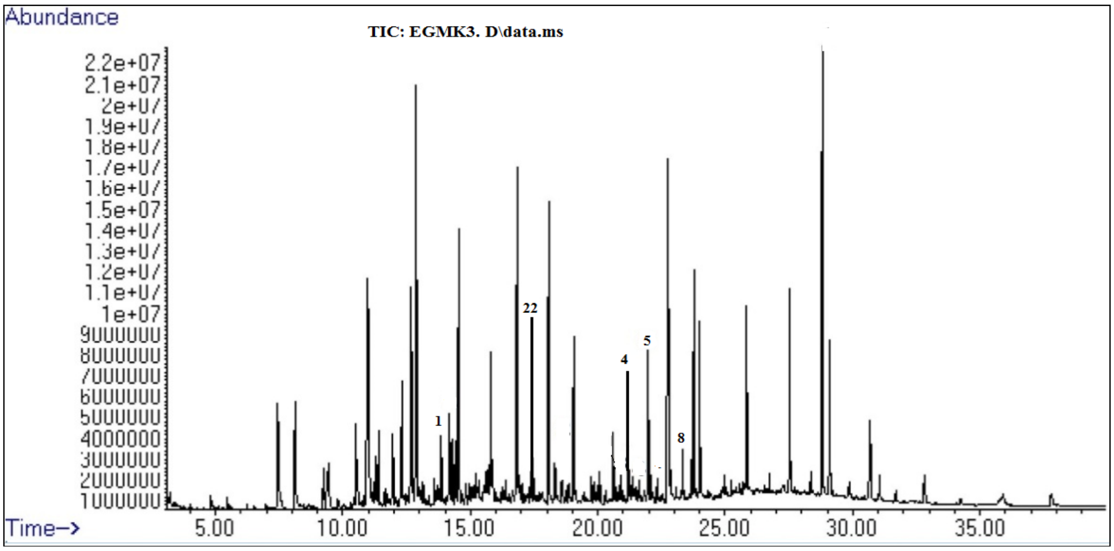
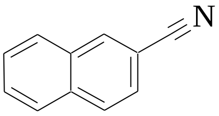


Figure 4.11: Total ion chromatogram of smoke emitted by charcoal prepared from *E.*grandis by efficient pyrolysis

From the analysis, five PAHs were identified and are indicated on the chromatogram. These were naphthalene (**3**), 2-naphthalenecarbonitrile (**24**), 2,6-diisopropylnaphthalene (**4**), 9H-fluoren-9-one (**8**), and anthracene (**11**).



24

Source: (Haynes, 2011)

There was significant difference ($P<0.05$) in the concentration of the emitted PAHs from *E. grandis* charcoal prepared by efficient pyrolysis (Table 4.7). There was also significant difference in the concentration of anthracene (35.67 x 10^{-3} µg/g). However, there was no significant difference in the concentration of emitted naphthalene (69.00 x 10^{-3} µg/g) and 2-naphthalenecarbonitrile (64.67 x 10^{-3} µg/g). Similarly there was also no notable significant difference in the concentration of 2,6-diisopropylnaphthalene (101.33 x 10^{-3} µg/g) and 9H-fluoren-9-one (96.67 x 10^{-3} µg/g) as indicated in Table 4.7.

Table 4.7: Concentrations of emitted PAHs from *E. grandis* charcoal prepared by efficient pyrolysis

PAH	*Concentration x 10^{-3}(µg/g)	NIOSH exposure limit x10-3(µg/g)
2,6-Diisopropylnaphthalene	101.33 ± 22.45^{a}	30.00
9H-Fluoren-9-one	96.67 ± 10.48^{a}	27.00
Naphthalene	69.00 ± 4.726^{ba}	38.5
2-Naphthalenecarbonitrile	64.67 ± 3.28^{ba}	31.00
Anthracene	35.67 ± 2.91^{b}	35.67

*Means separated using Duncan Multiple Range Test (DMRT) by the same letter are not significantly different (P>0.05) from each other

2,6-Diisoprpylnaphthalene (0.10133µg/g) and 9H-fluoren-9-one (0.09667µg/g) had the highest concentration while anthracene (0.035 µg/g)had the least concentration (Figure 4.12).

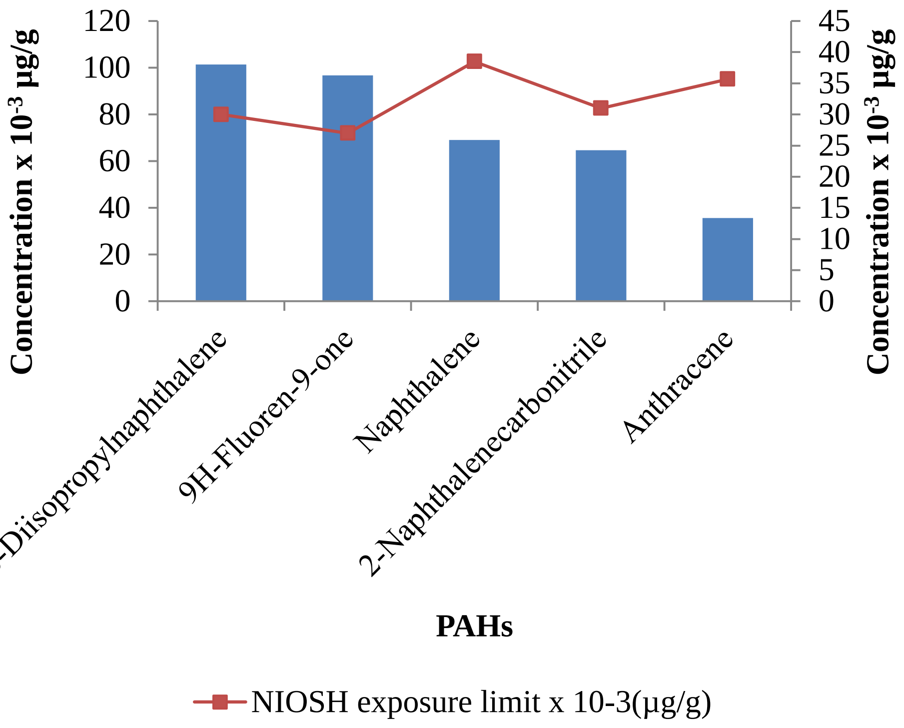


Figure 4.12: Concentration of emitted PAHs from *E. grandis* charcoal prepared by efficient pyrolysis

The high concentration of 2,6-diisopropylnaphthalene and 9H-fluoren-9-one may be as a result of more presence of precursors, vital for their pyro-synthesis, as compared to those needed for formation of anthracene. PAHs are reported to be formed from extractives/ phytochemicals in biomass present at different concentrations (Britt *et al*., 2004). Such phytochemicals that have been found in *E. grandis* include steroids, alkaloids and tannins (Vasantharaj *et al*., 2013).

4.9. Comparison of PAH profiles emitted from *A. polyacantha* and *A. xanthophloea* charcoal prepared by traditional pyrolysis

There was significant difference (t = -4.677, df = 2, p = 0.043) between fluorene emitted from *A. polyacantha* and *A. xanthophloea* charcoal prepared by traditional pyrolysis (Table 4.8). There was significant differences (t = -7.40, df = 2, P = 0.018) between naphthalene emitted from *A. polyacantha* and *A. xanthophloea* charcoal prepared by traditional pyrolysis. However, there was no significant difference (t = -4.168, df =2, P = 0.053) between 2,6-diisopropylnaphthalene emitted from *A. polyacantha* and *A. xanthophloea* charcoal prepared by traditional pyrolysis (Table 4.8). There was no significant differences (t = -0.528, df = 2, P = 0.65) between anthracene emitted from *A. polyacantha* and *A. xanthophloea* charcoal prepared by traditional pyrolysis (Table 4.8). There was also no significant difference (t = -2.539, df = 2, t = 0.126) between pyrene emitted from *A. polyacantha* and *A. xanthophloea* charcoal prepared by traditional pyrolysis.

.

Table 4.8: Comparison of emitted PAHs from *A. polyacantha* and *A. xanthophloea* charcoal prepared by traditional pyrolysis

PAH	***A. polyacantha***	***A. xanthophloea***	**P**
2,6-Diisopropylnaphthalene	53.67 ± 4.93	201.54 ± 37.26	0.053
Anthracene	80.33 ± 10.04	84.80 ± 2.12	0.650
Fluorene	72.00 ± 4.58	97.35 ± 5.90	0.043
Naphthalene	110.00 ± 4.93	140.42 ± 2.08	0.018
Pyrene	60.00 ± 3.79	71.82 ± 1.78	0.126

The difference in concentration of emitted naphthalene and fluorene can be attributed to the difference in the chemical composition of the two tree species from which the charcoal was obtained. The building blocks of wood are mainly cellulose, hemicellulose, lignin, extractives and mineral materials also called ash (Klaas, 1998). The difference in concentration of PAHs produced during combustion may be attributed 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, hemicellulos, 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 (Perez, 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). The ash content and minerals may vary from one tree species to another and consequently from one charcoal type to another. The minerals in the ash thus 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.

4.10. Comparison of PAH profiles emitted from *A. polyacantha* and *E. grandis* charcoal prepared by traditional pyrolysis

There was significant difference (t = -4.956, df = 0.038) between fluoroanthene emitted from *A. polyacantha* and *E. grandis* charcoal prepared by traditional pyrolysis (Table 4.9). There was significant difference (t = -9.714, df = 2, P = 0.01) between phenanthrene emitted from *A. polyacantha* and *E. grandis* charcoal prepared by traditional pyrolysis (Table 4.9).However, there was no significant difference (t = 1.18, df = 2, P = 0.359) between anthracene emitted from *A. polyacantha* and *E. grandis* charcoal prepared by traditional pyrolysis.

Table 4.9: Comparison of emitted PAHs from *A. polyacantha* and *E. grandis* charcoal prepared by traditional pyrolysis

PAH	***A. polyacantha***	***E. grandis***	**P**
Anthracene	80.33 ± 10.04	67.33 ± 2.60	0.359
Flouroanthene	66.67 ± 4.70	25.67 ± 2.85	0.038
Phenanthrene	91.00 ± 2.08	59.00 ± 5.51	0.01

The difference in concentration of emitted fluoroanthene and phenanthrene from *A. polyacantha* and *E. grandis* charcoal can be linked to the different chemical compositions of the tree species. The tree species were cultivated under different weather and soils. *E. grandis* and *A. polyacantha* wood for this research was obtained from Thika and Machakos respectively. Thika is characterized by black cotton soils with annual rainfall ranging from 500 – 1500mm. As such the area has been identified as a semi humid agro climatic zone with a relatively high agro-ecological potential (FAO, 1998). On the other hand, Machakos is a semi-arid climatic zone receiving annual rainfall ranging from 200 – 750mm (FAO, 1998). The different soil type and weather under which the tree species were grown might have influenced their chemical compositions thus leading to formation of different compounds at different concentrations when charcoal from these species was burned.

4.11. Comparison of PAH profiles emitted from *A. xanthophloea* and *A. polyacantha* charcoal prepared by efficient pyrolysis

There was significant difference (t = -4.737, df = 2, P = 0.042) between emitted fluorene from *A. xanthophloea* and *A. polyacantha* charcoal prepared by efficient pyrolysis. This can be attributed to the difference in the chemical composition of the two charcoal samples. The composition of ash in the charcoal samples of *A. xanthophloea* as well as *A. polyacantha* might have been different thus favoring the formation of fluorene at different concentrations. Ash is reported to be a minor component of biomass and contains carbonates, phosphates and sulfates of silica and metals from the first and second group of the periodic table which may catalyze PAHs and other hydrocarbons formation during combustion (Perez, 2008).

4.12. Comparison of PAH profiles emitted from *A. xanthophloea* and *E. grandis* charcoal prepared by efficient pyrolysis

There was significant difference (t = -6.425, df = 2, P = 0.023) between naphthalene emitted from *A. polyacantha* and *E. grandis* charcoal prepared by efficient pyrolysis. This might be attributed to the difference in concentration of the precursors, cellulose, hemicellulose and phytochemicals, from which naphthalene was formed during combustion.

4.13. Comparison of PAH profiles emitted from different types of charcoal

Table 4.10 shows the PAHs identified in the six charcoal smoke extracts. Smoke extracts from charcoal prepared by traditional pyrolysis had a greater number of PAHs as compared to those identified in charcoal prepared by efficient pyrolysis. 10 PAHs were detected in *A. polyacantha* extracts from traditional kiln compared to 4 PAHs from charcoal prepared by efficient pyrolysis. 9 PAHs were identified from the

A. xanthophloea charcoal smoke extracts prepared by traditional pyrolysis compared to 2 PAHs from the same species but prepared by efficient pyrolysis. 10 PAHs were identified from *E.grandis* charcoal smoke extracts prepared traditional pyrolysis compared to 4 PAHs from the same species but prepared by efficient pyrolysis (Table 4.10).

Table 4.10: A summary of identified PAHs from various tree species

No.	**Compound**	***A. polyacantha***		***A. xanthophloea.***		***E. grandis***	
		*** mg/m^3**		**mg/m^3**		**mg/m^3**	
		TP	**MP**	**TP**	**MP**	**TP**	**MP**
1	Naphthalene	0.58	0.45	0.74	-	-	0.36
2	1-Methyl-naphthalene	-	-	0.41	0.32	0.28	-
3	2-Methyl-naphthalene	0.37	0.32	-	-	-	-
4	1,2,3,4-Tetrahydro-1,5-dimethylnaphthalene	-	-	0.36	-	-	-
5	2,7-Dimethylnaphthalene	-	-	0.70	-	-	-
6	1,4-Dimethylnaphthalene	-	-	0.42	-	-	-
7	2-Naphthalenecarbonitrile	-	-	-	-	-	0.41
8	1,4,5-Trimethylnaphthalene	-	-	-	-	0.66	-
9	Fluorene-9-methanol	-	-	-	-	0.74	-
10	Fluorene	0.49	0.33	0.66	0.41	-	-
11	2,6-Diisopropylnaphthalene	0.47	-	1.75	-	-	0.88
12	9H-Fluoren-9-one	0.43	-	-	-		0.71
13	Phenanthrene	0.66	0.52	-	-	1.16	-
14	Anthracene	0.59	-	0.62	-	0.49	0.26
15	9H-Fluoren-9-one, hydrazone	-	-	-	-	0.63	-
16	1-Methyl-Phenanthrene	-	-	-	-	0.38	-
17	4-Methyl-phenanthrene	-	-	-	-	0.28	-
18	Fluoranthene	0.55	-	-	-	0.21	-
19	1,4-Dimethyl- 9,10-anthracenedione	-	-	-	-	0.3	-
20	Benzo[a]anthracene	0.86	-	-	-	-	-
21	Chrysene	0.69	-	-	-	-	-
22	Pyrene	0.49	-	0.59	-	-	-
	Total	**6.18**	**1.62**	**6.25**	**0.73**	**5.13**	**2.62**

*mg/m^3 = (µg/g value)(molecular weight)/24.45|24.45 is a conversion factor that represents the volume of one mole of gas at 273.15K and 1atm (STP)

Key:

TP	Traditional pyrolysis (traditional earth mound kiln)
MP	Efficient pyrolysis (dome shaped brick kiln)

All the emitted PAHs from the six different types of charcoal had concentrations higher than the permissible levels of 0.1mg/m^3 - 0.2mg/m^3. However, some concentrations were slightly close to the recommended levels while some were higher. For example, anthracene (0.26mg/m^3) emitted from *E. grandis* charcoal prepared by efficient pyrolysis (Table 4.10). 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 such as recommended exposure limit (REL) of 0.1 mg/m^3 for coal tar pitch volatile agents for a 10- hour workday (NIOSH, 2010).The American Conference of Governmental Industrial Hygienists (ACGIH) recommends a permissible exposure limit (PEL) of 0.2mg/m^3 for an 8-hour workday (ACGIH, 2005). Thus continuous chronic exposure to smoke from charcoal may have detrimental effects to charcoal users.

CHAPTER FIVE: CONCLUSION AND RECOMMENDATIONS

5.1. Conclusion

Charcoal is used by majority of households in sub-Saharan Africa and its use is projected to increase or remain the same for many years to come. The toxic effects of some of the group of compounds identified in this study, especially the PAHs, have been studied and their effects documented. The concentration of PAHs emitted from all the charcoal samples were above the permissible levels of 0.1 – 0.2mg/m^3.

The main objective of this study was to identify the specific contaminants in different types of charcoal derived from (i) different tree species and (ii) pyrolysis method. The following conclusions can be drawn from the study.

1) 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 6.18mg/m^3, 6.25 mg/m^3 and 5.18mg/m^3 respectively while the total concentration of PAHs from the same wood species charcoal prepared by efficient pyrolysis was 1.62mg/m^3, 0.73mg/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.
2) 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.

5.2. Recommendations

1) Charcoal production using tree species such as *A. xanthophloea*. Charcoals produced from this specie emit low quality and quantity of harmful pollutants such as polycyclic aromatic hydrocarbons.
2) Promote use of efficientenergy efficient pyrolysis methods of charcoal production especially by the rural poor. This will ensure the production and consumption of charcoal with lower volatile content hence reducing exposure to harmful compounds of incomplete combustion. The use of efficient pyrolysis methods will also enhance efficiency in charcoal production. This will increase output as less wood is consumed thus conserving forests.
3) Measures that reduce exposure to smoke in kitchens should be enhanced. Such measures include the dissemination of improved cook-stoves with high fuel burning rate, use of chimneys to vent out emitted gases and improved ventilation of cooking areas. These are important measures that when coupled with upgraded fuels, for example charcoal prepared by efficient pyrolysis methods will help improve the kitchen air quality thus reduce the impact of pollutants in smoke.

5.3. Areas of future Research

1. More studies for common species in key charcoal production hot spots such as Narok and Taita Taveta.
2. Further studies of PAHs from biomass fuels in a kitchen setting. In this regard, we further recommend for the development of tools and sampling methods

that can be deployed in a kitchen. This will enable scientists to ascertain the types and concentrations of PAHs in real life situations.

REFERENCES

Aas, E., Baussant, T., Balk, L., Liewenborg, B., & Andersen, O. K. (2000). PAH metabolites in bile, cytochrome P4501A and DNA adducts as environmental risk parameters for chronic oil exposure: a laboratory experiment with Atlantic cod. *Aquatic Toxicology*, *51*(2), 241–258.

Akpambang, V. O. E., Purcaro, G., Lajide, L., Amoo, I. A., Conte, L. S., & Moret, S. (2009). Determination of polycyclic aromatic hydrocarbons (PAHs) in commonly consumed Nigerian smoked/grilled fish and meat. *Food Additives and Contaminants*, *26*(7), 1096–1103.

Ali, D., Verma, A., Mujtaba, F., Dwivedi, A., Hans, R. K., & Ray, R. S. (2011). UVB-induced apoptosis and DNA damaging potential of chrysene via reactive oxygen species in human keratinocytes. *Toxicology Letters, 204*(2), 199–207.

Angelsen, A., & Wunder, S. (2003). Exploring the Forest—Poverty Link. *CIFOR Occasional Paper, 40*, 1–20.

An, J., Yin, L., Shang, Y., Zhong, Y., Zhang, X., Wu, M., … Huang, Y. (2011). The combined effects of BDE47 and BaP on oxidatively generated DNA damage in L02 cells and the possible molecular mechanism. *Mutation Research/Genetic Toxicology and Environmental Mutagenesis*, *721*(2), 192–198.

Antal Jr, M. J., Mok, W. S. L., Roy, J. C., Raissi, A. T., & Anderson, D. G. M. (1985). Pyrolytic sources of hydrocarbons from biomass. *Journal of Analytical and Applied Pyrolysis, 8,* 291–303.

Arnold, J. E., Köhlin, G., & Persson, R. (2006). Woodfuels, livelihoods, and policy interventions: changing perspectives. *World Development*, *34*(3), 596–611.

Arnold, M., Köhlin, G., Persson, R., & Shepherd, G. (2003). Fuelwood revisited. *What Has Changed*. Retrieved from http://www.ncsu.edu/project/amazonia/for414/Readings/OP-39%20fuelwood%20cifor.pdf

Arnold, M., & Persson, R. (2003). Reassessing the fuelwood situation in developing countries. *International Forestry Review*, *5*(4), 379–383.

Badry, N. (2010). Effect of household cooking methods and some food additives on polycyclic aromatic hydrocarbons (PAHs) formation in chicken meat. *World Appl. Sci. J*, *9*, 963–974.

Baek, S. O., Field, R. A., Goldstone, M. E., Kirk, P. W., Lester, J. N., & Perry, R. (1991). A review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. *Water, Air, and Soil Pollution*, *60*(3-4), 279–300.

Bailis, R. E. (2005a). *Fuel from the savanna: the social and environmental implications of the charcoal trade in Sub-Saharan Africa*. Citeseer. Retrieved from http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.136.6374&rep=rep1&type=pdf

Bailis, R. E. (2005b). *Fuel from the savanna: the social and environmental implications of the charcoal trade in Sub-Saharan Africa*. Citeseer. Retrieved from http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.136.6374&rep=rep1&type=pdf

Bailis, R., Ezzati, M., & Kammen, D. M. (2003a). Greenhouse gas implications of household energy technology in Kenya. *Environmental Science & Technology*, *37*(10), 2051–2059.

Bailis, R., Ezzati, M., & Kammen, D. M. (2003b). Greenhouse gas implications of household energy technology in Kenya. *Environmental Science & Technology, 37*(10), 2051–2059.

Bailis, R., Ezzati, M., & Kammen, D. M. (2007). Health and greenhouse gas impacts of biomass and fossil fuel energy futures in Africa. *Boiling Point*, *54*, 3–8.

Barnes, D. F., Krutilla, K., & Hyde, W. F. (2013). *The urban household energy transition: social and environmental impacts in the developing world*. Routledge. Retrieved from http://books.google.com/books?hl=en&lr=&id=6WZXuOaDXtkC&oi=fnd&pg=PR1&dq=BARNES,+D.F.,+KRUTILLA,+K.+and+HYDE,+W.+2002.+The+urban+energy+transition:+energy,+poverty+and+the+environment+in+the+developing+world&ots=dF9mETtq1M&sig=QwjSW0VMhY5INt1-cZdxVvzfXrc

Boffetta, P., Jourenkova, N., & Gustavsson, P. (1997). Cancer risk from occupational and environmental exposure to polycyclic aromatic hydrocarbons. *Cancer Causes & Control*, *8*(3), 444–472.

Bolognesi, C., Parrini, M., Aiello, C., & Rossi, L. (1991). DNA damage induced by 7, 12-dimethylbenz [a] anthracene in the liver and the mammary gland of rats exposed to polycyclic aromatic hydrocarbon enzyme inducers during perinatal life. *Mutagenesis*, *6*(2), 113–116.

Bond, T. C., & Sun, H. (2005). Can Reducing Black Carbon Emissions Counteract Global Warming? *Environmental Science & Technology, 39*(16), 5921–5926. http://doi.org/10.1021/es0480421

Boysen, G., & Hecht, S. S. (2003). Analysis of DNA and protein adducts of benzo [< i> a</i>] pyrene in human tissues using structure-specific methods. *Mutation Research/Reviews in Mutation Research*, *543*(1), 17–30.

Britt, P. F., Buchanan, A. C., & Owens Jr, C. V. (2004). Mechanistic investigation into the formation of polycyclic aromatic hydrocarbons from the pyrolysis of terpenes. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem*, *49*(2), 868.

Canadian Council of Ministers of the Environment. (2008). *Canadian soil quality guidelines carcinogenic and other polycyclic aromatic hydrocarbons (PAHS): (environmental and human health effects).* [Winnipeg, Man.]: Canadian Council of Ministers of the Environment.

Castorena-Torres, F., de León, M. B., Cisneros, B., Zapata-Pérez, O., Salinas, J. E., & Albores, A. (2008). Changes in gene expression induced by polycyclic aromatic hydrocarbons in the human cell lines HepG2 and A549. *Toxicology in Vitro*, *22*(2), 411–421.

Chan, H. Y., Wang, H., Tsang, D. S., Chen, Z.-Y., & Leung, L. K. (2003). Screening of Chemopreventive Tea Polyphenols Against PAH Genotoxicity in Breast Cancer Cells by a XRE-Luciferase ReporterConstruct. *Nutrition and Cancer*, *46*(1), 93–100.

Desanker, P., & Zulu, L. (2001). Gender, energy, development and environmental change in Southern Africa. *SAGEN—Southern Africa Gender and Energy Network & MEPC—Minerals and Energy Policy Centre*.

Dickey, C., Santella, R. M., Hattis, D., Tang, D., Hsu, Y., Cooper, T., … Perera, F. P. (1997). Variability in PAH-DNA Adduct Measurements in Peripheral Mononuclear Cells: Implications for Quantitative Cancer Risk Assessment. *Risk Analysis*, *17*(5), 649–656.

Eckholm, E. P. (1975). Desertification: a world problem. *Ambio*, *4*. Retrieved from http://agris.fao.org/agris-search/search/display.do?f=2012/OV/OV201204468004468.xml;SE19760083157

Elleg\a ard, A., & Nordström, M. (2003). Deforestation for the poor? *Renewable Energy for Development*, *16*(2), 4–6.

Emrich, W. (1985). *Handbook of charcoal making: the traditional and industrial methods.* D. Reidel Publishing Co. Retrieved from http://www.cabdirect.org/abstracts/19850603710.html

EPA, E. P. A. (1996). *Code of Federal Regulations: Priority Pollutants*. Title.

Ezzati, M., & Kammen, D. M. (2001). Quantifying the effects of exposure to indoor air pollution from biomass combustion on acute respiratory infections in developing countries. *Environmental Health Perspectives*, *109*(5), 481.

FAO. (1987). Simple Technologies for Charcoal Making. Food and Agriculture Organization of the United Nations, Rome (1987).

Foley, G. (1986). *Charcoal making in developing countries*. Earthscan, International Institute for Environment and Development London. Retrieved from http://library.wur.nl/WebQuery/clc/250191

Gachanja, A. N., Worsfold, P. J., Jardine, A., Dowle, C., Malyan, A., Davidson, C., … Norman, P. (1992). Determination of polycyclic aromatic hydrocarbons in biomass emissions by liquid chromatography with fluorescence and chemiluminescence detection. In *Analytical proceedings* (Vol. 29, pp. 61–68). Retrieved from http://pubs.rsc.org/en/content/articlepdf/1992/ap/ap9922900061

Girard, P. (2002). Charcoal production and use in Africa: what future? *Unasylva*, *53*(4), 30–35.

Githiomi, J. K., & Kariuki, J. G. (2010). Wood basic density of Eucalyptus grandis from plantations in Central Rift Valley, Kenya: Variation with age, height level and between sapwood and heartwood. *Journal of Tropical Forest Science*, 281–286.

Githiomi, J. K., Mugendi, D. N., & Kung'u, J. B. (2012). Analysis of household energy sources and woodfuel utilisation technologies in Kiambu, Thika and Maragwa districts of Central Kenya. *J. Hortic. For*, *4*(2), 43–48.

Githiomi, J. K., & Oduor, N. (2012). Strategies for Sustainable Wood fuel Production in Kenya. *International Journal of Applied*, *2*(10). Retrieved from https://www.fornis.net/system/files/Strategies%20for%20sustaibale%20wood%20fuel%20production%20in%20Kenya.pdf

Gustafson, D. (2001). The role of woodfuels in Africa. Retrieved from https://www.etde.org/etdeweb/details_open.jsp?osti_id=20211261

Haller, M., und Umweltschutz, F. E., & Tsatsaronis, I. G. (2006). Comparing CO2 Mitigation Options in the Electricity Sector: Nuclear Power, Renewable Energy and Carbon Sequestration. Retrieved from http://www.pik-potsdam.de/members/edenh/theses/diplomarbeit_markus_haller.pdf

Haynes, W. M. (2011). *CRC handbook of chemistry and physics*. CRC Press. Retrieved from http://books.google.com/books?hl=en&lr=&id=pYPRBQAAQBAJ&oi=fnd&pg=PP1&dq=National+instute+of+standards+and+technology+chemical+structures&ots=LSclh2CZ3r&sig=aaHODnI78UBEV087lk8Qso5iZJM

Hindi, S. S. (2012). Effect of Maximum Final Temperature on Properties of Wood Based Biocarbon of Tamarix Aphylla. Retrieved from http://arastirmax.com/en/system/files/dergiler/65306/makaleler/1/8/arastirmax_21752_pp_1-4.pdf

Hsu, G. W., Huang, X., Luneva, N. P., Geacintov, N. E., & Beese, L. S. (2005). Structure of a high fidelity DNA polymerase bound to a benzo [a] pyrene adduct that blocks replication. *Journal of Biological Chemistry*, *280*(5), 3764–3770.

International Agency for Research on Cancer, W. G. on the E. of the C. R. to H. (2010). *IARC monographs on the evaluation of carcinogenic risks to humans, volume 95, household use of solid fuels and high-temperature frying: this publication represents the views and expert opinions of an IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, which met in Lyon, 10 - 17 October 2006*. Lyon: IARC.

International Energy Agency. (2014). *World Energy Outlook*. Retrieved from www.iea.org

Jerina, D. M., Sayer, J. M., Thakker, D. R., Yagi, H., Levin, W., Wood, A. W., & Conney, A. H. (1980). Carcinogenicity of polycyclic aromatic hydrocarbons: the bay-region theory. In *Carcinogenesis: Fundamental Mechanisms and Environmental Effects* (pp. 1–12). Springer. Retrieved from http://link.springer.com/chapter/10.1007/978-94-009-9104-0_1

Kammen, D. M., & Lew, D. J. (2005a). Review of Technologies for the Production and Use of Charcoal. *Renewable and Appropriate Energy Laboratory Report*, *1*. Retrieved from http://rael.berkeley.edu/sites/default/files/old-site-files/2005/Kammen-Lew-Charcoal-2005.pdf

Kammen, D. M., & Lew, D. J. (2005b). Review of Technologies for the Production and Use of Charcoal. *Renewable and Appropriate Energy Laboratory Report, 1*. Retrieved from http://rael.berkeley.edu/sites/default/files/old-site-files/2005/Kammen-Lew-Charcoal-2005.pdf

Karami, S., Boffetta, P., Brennan, P., Stewart, P. A., Zaridze, D., Matveev, V., … Navratilova, M. (2011). Renal cancer risk and occupational exposure to polycyclic aromatic hydrocarbons and plastics. *Journal of Occupational and Environmental medicine/American College of Occupational and Environmental Medicine*, *53*(2), 218.

Karekezi, S., Kimani, J., & Onguru, O. (2008a). Energy access among the urban poor in Kenya. *Energy for Sustainable Development*, *12*(4), 38–48.

Karekezi, S., Kimani, J., & Onguru, O. (2008b). Energy access among the urban poor in Kenya. *Energy for Sustainable Development*, *12*(4), 38–48.

Karekezi, S., Kimani, J., Wambille, A., Balla, P., Magessa, F., Kithyoma, W., & Ochieng, X. (2005). The potential contribution of non-electrical renewable energy technologies (RETs) to poverty reduction in East Africa. *Africa Renewable Energy Policy Research Network (AFREPREN), Nairobi, Kenya*. Retrieved from http://www.afrepren.org/adb_finesse/Task%203/Background%20Material/AFREPREN%20Water%20Pumping%20Report.pdf

Kim, K.-H., Jahan, S. A., Kabir, E., & Brown, R. J. (2013). A review of airborne polycyclic aromatic hydrocarbons (PAHs) and their human health effects. *Environment International*, *60*, 71–80.

Kituyi, E. (2002). Towards Sustainable Charcoal Production and Use: a Systems Approach. In *Proceedings of a Regional Workshop on Wood fuel Policy and*

Legislation in Eastern and Southern Africa. Ed, Mugo, F., RELMA Nairobi (pp. 46–62). Retrieved from http://populationenvironmentresearch.org/papers/Kituyi_Paper.pdf

Kituyi, E., Marufu, L., Huber, B., O Wandiga, S., O Jumba, I., O Andreae, M., & Helas, G. (2001a). Biofuel consumption rates and patterns in Kenya. *Biomass and Bioenergy*, *20*(2), 83–99.

Kituyi, E., Marufu, L., Huber, B., O Wandiga, S., O Jumba, I., O Andreae, M., & Helas, G. (2001b). Biofuel consumption rates and patterns in Kenya. *Biomass and Bioenergy*, *20*(2), 83–99.

Klass, D. L. (1998). *Biomass for renewable energy, fuels, and chemicals*. Academic press. Retrieved from http://books.google.com/books?hl=en&lr=&id=udDHC3Ss7DAC&oi=fnd&pg=PP2&dq=Klass+D.L.+1998.+Biomass+for+Renewable+Energy,+Fuels+and+Chemicals,+Academic+Press,+San+Diego,+1998.&ots=Q16e6laztq&sig=athSN5PSvEpHQKtSGcVWL_1NR6w

Kocbach Bølling, A., Pagels, J., Yttri, K., Barregard, L., Sallsten, G., Schwarze, P. E., & Boman, C. (2009). Health effects of residential wood smoke particles: the importance of combustion conditions and physicochemical particle properties. *Particle and Fibre Toxicology*, *6*(1), 29. http://doi.org/10.1186/1743-8977-6-29

Kristoferson, L. (1997). Seven energy and development myths-are they still alive. *Renewable Energy for Development*, *10*(2). Retrieved from http://sei-international.org/mediamanager/documents/Publications/Climate/Red/red_1997_02.pdf

Leung, H. Y., Yung, L. H., Shi, G., Lu, A., & Leung, L. K. (2009). The red wine polyphenol resveratrol reduces polycyclic aromatic hydrocarbon-induced DNA damage in MCF-10A cells. *British Journal of Nutrition*, *102*(10), 1462–1468.

Levine, J. S. (1996). *Biomass Burning and Global Change: Remote Sensing, Modeling and Inventory Development, and Biomass Burning in Africa* (Vol. 1). The MIT Press. Retrieved from http://books.google.com/books?hl=en&lr=&id=kYr5FYNFtq0C&oi=fnd&pg=PR27&dq=Lavine+J.S.+1990+global+biomass+burning:+atmospheric,+climatic+and+biospheric+implications&ots=5xUfhoyXnx&sig=74tmrPtQY1Pzq1J68rzu_sqg9-E

Lim, W.-Y., & Seow, A. (2012). Biomass fuels and lung cancer. *Respirology*, *17*(1), 20–31. http://doi.org/10.1111/j.1440-1843.2011.02088.x

Lin, C. H., Huang, X., Kolbanovskii, A., Hingerty, B. E., Amin, S., Broyde, S., … Patel, D. J. (2001). Molecular topology of polycyclic aromatic carcinogens determines DNA adduct conformation: a link to tumorigenic activity. *Journal of Molecular Biology*, *306*(5), 1059–1080.

Ling, H., Sayer, J. M., Plosky, B. S., Yagi, H., Boudsocq, F., Woodgate, R., … Yang, W. (2004). Crystal structure of a benzo [a] pyrene diol epoxide adduct in a ternary complex with a DNA polymerase. *Proceedings of the National Academy of Sciences of the United States of America*, *101*(8), 2265–2269.

MacCarty, N., Ogle, D., Still, D., Bond, T., & Roden, C. (2008). A laboratory comparison of the global warming impact of five major types of biomass cooking stoves. *Energy for Sustainable Development*, *12*(2), 56–65.

MacCarty, N., Still, D., Ogle, D., & Drouin, T. (2008). Assessing Cook Stove Performance: Field and Lab Studies of Three Rocket Stoves Comparing the Open Fire and Traditional Stoves in Tamil Nadu, India on Measures of Time to Cook, Fuel Use, Total Emissions, and Indoor Air Pollution. *Aprovecho Research Center*. Retrieved from http://aprovecho.org/web-content/publications/assets/India%20CCT%20Paper_1.7.08.pdf

Macqueen, D., & Korhaliller, S. (2011). *Bundles of energy: the case for renewable biomass energy*. IIED. Retrieved from http://books.google.com/books?hl=en&lr=&id=BmTjC341TmkC&oi=fnd&pg=PT4&dq=the+case+for+renewable+biomass+energy+duncun+macqueen&ots=gTfWu6g57k&sig=R5vx0HxI4AMPJo67dLdyMR3CGJk

Macqueen, D., Korhaliller, S., & International Institute for Environment and Development. (2011). *Bundles of energy: the case for renewable biomass energy*. London, U.K.: International Institute for Environment and Development.

Mannino, M. R., & Orecchio, S. (2008). Polycyclic aromatic hydrocarbons (PAHs) in indoor dust matter of Palermo (Italy) area: extraction, GC–MS analysis, distribution and sources. *Atmospheric Environment*, *42*(8), 1801–1817.

Meschini, R., Berni, A., Marotta, E., Filippi, S., Fiore, M., Mancinelli, P., … Palitti, F. (2010). DNA repair mechanisms involved in the removal of DBPDE-induced lesions leading to chromosomal alterations in CHO cells. *Cytogenetic and Genome Research, 128*(1-3), 124–130.

MEWNR, M. of E., Water and Natural Resources. (2013). Analysis of Demand and Supply of Wood Products in Kenya. Retrieved from www.kenyaforestservice.org

Mordukhovich, I., Rossner Jr, P., Terry, M. B., Santella, R., Zhang, Y.-J., Hibshoosh, H., … Garbowski, G. (2010). Associations between Polycyclic Aromatic Hydrocarbon–Related Exposures and p53 Mutations in Breast Tumors. *Environmental Health Perspectives*, *118*(4), 511.

Mugo, F., & Gathui, T. (2010a). Biomass energy use in Kenya. In *A background paper prepared for the International Institute for Environment and Development (IIED) for an international ESPA workshop on biomass energy* (pp. 19–21). Retrieved from http://pubs.iied.org/pdfs/G02985.pdf

Mugo, F., & Gathui, T. (2010b). Biomass energy use in Kenya. Retrieved from http://erepository.uonbi.ac.ke/handle/11295/54948

Mugo, F., & Gathui, T. (2010c). Biomass energy use in Kenya. In *A background paper prepared for the International Institute for Environment and Development (IIED) for an international ESPA workshop on biomass energy* (pp. 19–21). Retrieved from http://pubs.iied.org/pdfs/G02985.pdf

Mumtaz, M. M., George, J. D., Gold, K. W., Cibulas, W., & Derosa, C. T. (1996). ATSDR evaluation of health effects of chemicals. IV. Polycyclic aromatic hydrocarbons (PAHs): understanding a complex problem. *Toxicology and Industrial Health*, *12*(6), 742–971.

Muñoz, B., & Albores, A. (2012). DNA Damage Caused by Polycyclic Aromatic Hydrocarbons: Mechanisms and Markers. Retrieved from http://www.researchgate.net/publication/216549753_DNA_Damage_Caused_by_Polycyclic_Aromatic_Hydrocarbons_Mechanisms_and_Markers/file/d912f510059375360f.pdf

Mutimba, S., & Barasa, M. (2005). *National Charcoal Survey: Exploring the Potential for a Sustainable Charcoal Industry in Kenya, 2005*. Energy for Sustainable Development Africa.

Nguyen, T., Hlangothi, D., Martinez III, R. A., Jacob, D., Anthony, K., Nance, H., & Saleh, M. A. (2013). Charcoal burning as a source of polyaromatic hydrocarbons in waterpipe smoking. *Journal of Environmental Science and Health, Part B, 48*(12), 1097–1102.

Nikolaou, K., Masclet, P., & Mouvier, G. (1984). Sources and chemical reactivity of polynuclear aromatic hydrocarbons in the atmosphere—A critical review. *Science of the Total Environment*, *32*(2), 103–132.

NIOSH, N. I. of O. H. and S. (2010). NIOSH Pokcet Guide to chemical Hazards. Retrieved from http://www.cdc.gov/niosh/about.html

Oduor, N., Kalenda, M., & Ngatia, J. (2009). Available Charcoal Technologies in Kenya: For sustainable Charcoal Production in the Drylands of Kenya. Retrieved from http://www.ke.undp.org/content/dam/kenya/docs/energy_and_environment/Charcoal_Production_kilns_study-1-.pdf

Oduor, N. M., Tameezan wa Gathui, & Wairimu. (2012). Sustainable Tree Management for Charcoal Production. Retrieved from r4d.dfid.gov.uk/Output/192622

Oduor, N., Wairimu, N., & wa-Gathui, T. (2012). Sustainable Tree Management for Charcoal Production. Retrieved from http://www.pisces.or.ke/sites/default/files/Acacia%20Pocketbook%20low%20res.pdf

Oyedun, A. O., Lam, K. L., & Hui, C. W. (2012). Charcoal Production< i> via</i> Multistage Pyrolysis. *Chinese Journal of Chemical Engineering*, *20*(3), 455–460.

PAC. (2010). Promoting Sustainable Charcoal Production and Marketing in Kenya: A Comparative Analysis through Participatory Market Mapping. PISCES.

Pampanin, M. (2013). Polycyclic Aromatic Hydrocarbons a Constituent of Petroleum: Presence and Influence in the Aquatic Environment. In V. Kutcherov (Ed.), *Hydrocarbon*. InTech. Retrieved from http://www.intechopen.com/books/hydrocarbon/polycyclic-aromatic-hydrocarbons-a-constituent-of-petroleum-presence-and-influence-in-the-aquatic-en

Park, W. C., Atreya, A., & Baum, H. R. (2010). Experimental and theoretical investigation of heat and mass transfer processes during wood pyrolysis. *Combustion and Flame*, *157*(3), 481–494.

Patel, N., Okocha, B., Narayan, S., & Sheth, M. (2013). Indoor Air Pollution from Burning Biomass & Child Health. Retrieved from http://ijsr.net/archive/v2i1/IJSRON2013300.pdf

Patel, N., Okocha, B., Narayan, S., & Sheth, M. (n.d.). Indoor Air Pollution from Burning Biomass & Child Health. Retrieved from http://ijsr.net/archive/v2i1/IJSRON2013300.pdf

Pattanayak, S. K., Wunder, S., & Ferraro, P. J. (2010). Show Me the Money: Do Payments Supply Environmental Services in Developing Countries? *Review of Environmental Economics and Policy*, *4*(2), 254–274. http://doi.org/10.1093/reep/req006

Pennise, D. M., Smith, K. R., Kithinji, J. P., Rezende, M. E., Raad, T. J., Zhang, J., & Fan, C. (2001). Emissions of greenhouse gases and other airborne pollutants from charcoal making in Kenya and Brazil. *Journal of Geophysical Research: Atmospheres (1984–2012)*, *106*(D20), 24143–24155.

Pettersen, R. C. (1984). The chemical composition of wood. *The Chemistry of Solid Wood*, *207*, 57.

Pocketbook, A. (2012). Sustainable Tree Management for Charcoal Production. Retrieved from http://www.pisces.or.ke/sites/default/files/Acacia%20Pocketbook%20low%20res.pdf

Rhodes, S., Farwell, A., Mark Hewitt, L., MacKinnon, M., & George Dixon, D. (2005). The effects of dimethylated and alkylated polycyclic aromatic hydrocarbons on the embryonic development of the Japanese medaka. *Ecotoxicology and Environmental Safety*, *60*(3), 247–258.

Ribot, J. C. (2009). Authority over forests: empowerment and subordination in Senegal's democratic decentralization. *Development and Change*, *40*(1), 105–129.

Roden, C. A., Bond, T. C., Conway, S., Osorto Pinel, A. B., MacCarty, N., & Still, D. (2009). Laboratory and field investigations of particulate and carbon monoxide emissions from traditional and improved cookstoves. *Atmospheric Environment*, *43*(6), 1170–1181. http://doi.org/10.1016/j.atmosenv.2008.05.041

Rossberg, M., Lendle, W., Pfleiderer, G., Tögel, A., Dreher, E.-L., Langer, E., … Mann, T. (2000). Chlorinated Hydrocarbons. In *Ullmann's Encyclopedia of*

Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA. Retrieved from http://dx.doi.org/10.1002/14356007.a06_233.pub2

Santodonato, J. (1997). Review of the estrogenic and antiestrogenic activity of polycyclic aromatic hydrocarbons: relationship to carcinogenicity. *Chemosphere*, *34*(4), 835–848.

Seboka, Y. (2009). 6. charcoal production: opportunities and barriers for improving efficiency and sustainability. *Bio-Carbon Opportunities in Eastern & Southern Africa*, 102.

Seidel, A. (2008). Charcoal in Africa importance, problems and possible solution strategies. *GTZ, Eschborn*. Retrieved from https://energypedia.info/images/2/22/Charcoal-in-africa-gtz_2008-eng.pdf

Shen, J., Desai, M., Agrawal, M., Kennedy, D. O., Senie, R. T., Santella, R. M., & Terry, M. B. (2006). Polymorphisms in nucleotide excision repair genes and DNA repair capacity phenotype in sisters discordant for breast cancer. *Cancer Epidemiology Biomarkers & Prevention*, *15*(9), 1614–1619.

Smith, K. R. (2006). Health impacts of household fuelwood use in developing countries. *Unasylva-Fao-*, *57*(2), 41.

Straif, K., Baan, R., Grosse, Y., Secretan, B., El Ghissassi, F., & Cogliano, V. (2005). Carcinogenicity of polycyclic aromatic hydrocarbons. *The Lancet Oncology*, *6*(12), 931–932.

Takama, T., Lambe, F., Johnson, F. X., Arvidson, A., Atanassov, B., Debebe, M., … Tsephel, S. (2011). Will African consumers buy cleaner fuels and stoves. *A Household Energy Economic Analysis Model for the Market Introduction of Bio-Ethanol Cooking Stoves in Ethiopia, Tanzania, and Mozambique*. Retrieved from http://sei-international.org/mediamanager/documents/Publications/SEI-ResearchReport-Takama-WillAfricanConsumersBuyCleanerFuelsAndStoves-2011.pdf

UNDP, U. (2000). WEC (2000) World Energy Assessment, Energy and the challenge of sustainability. *United Nations Development Programme, New York*.

Urdal, H., & Hoelscher, K. (2009). Urban youth bulges and social disorder: an empirical study of Asian and Sub-Saharan African cities. Retrieved from https://openknowledge.worldbank.org/handle/10986/4299

Vasantharaj, S., Sathiyavimal, S., & Hemashenpagam, N. (2013). Phytochemical and Antibacterial activity of Eucalyptus. *International Journal of Pharmaceutical Sciences Review & Research*, *21*(2).

Wang, Z. Y., Khan, W. A., Bickers, D. R., & Mukhtar, H. (1989). Protection against polycyclic aromatic hydrocarbon-induced skin tumor initiation in mice by green tea polyphenols. *Carcinogenesis*, *10*(2), 411–415.

Worl Bank. (2009). Environmental crisis or sustainable development opportunity? Transforming the charcoal sector in Tanzania. TheWorld Bank.

World Health Organization. (2010a). *WHO guidelines for indoor air quality: selected pollutants.* Copenhagen: WHO.

World Health Organization. (2010b). *WHO guidelines for indoor air quality: selected pollutants.* Copenhagen: WHO.

World Health Organization. (2010c). *WHO guidelines for indoor air quality: selected pollutants.* Copenhagen: WHO.

Yoon, J.-H., Lee, C.-S., & Pfeifer, G. P. (2003). Simulated sunlight and benzo [a] pyrene diol epoxide induced mutagenesis in the human p53 gene evaluated by the yeast functional assay: lack of correspondence to tumor mutation spectra. *Carcinogenesis*, *24*(1), 113–119.

Yu, M.-H., Tsunoda, H., & Tsunoda, M. (2011). *Environmental toxicology: biological and health effects of pollutants*. CRC Press. Retrieved from http://books.google.com/books?hl=en&lr=&id=zMCiWZiuTJsC&oi=fnd&pg=PP1&dq=Yu,+M.-H.+(2005).Environmental+toxicology:+biological+and+health+effects+of+pollutants+&ots=o-pMLfSiUq&sig=xD8f3gpe54VTWYAPzJfYIREDfNI

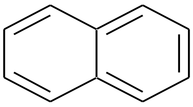
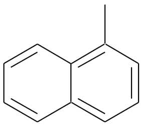
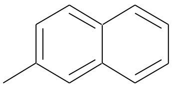
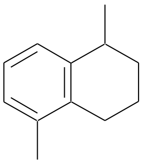
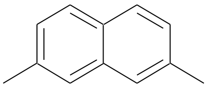
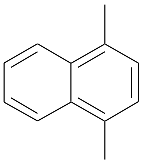
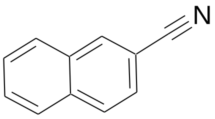
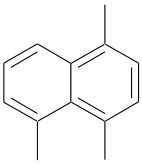
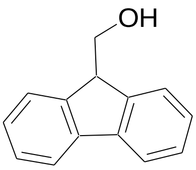
Zhang, J., & Smith, K. R. (2005). Indoor air pollution from household fuel combustion in China: a review. In *The 10th International Conference on Indoor Air Quality and Climate* (Vol. 9). Retrieved from http://www.cleancookstoves.org/resources_files/indoor-air-pollution-from.pdf

Zhang, Y., & Tao, S. (2009). Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004. *Atmospheric Environment*, *43*(4), 812–819. http://doi.org/10.1016/j.atmosenv.2008.10.050

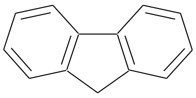
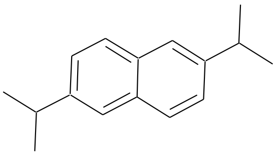
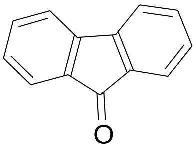
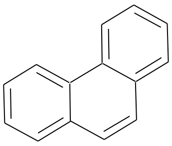
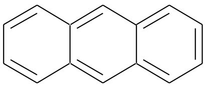
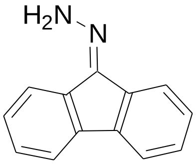
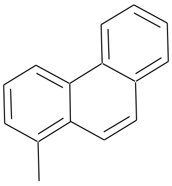
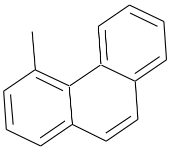
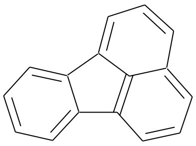
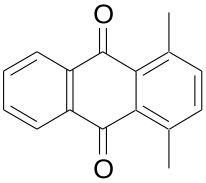
Zulu, L. C., & Richardson, R. B. (2013). Charcoal, livelihoods, and poverty reduction: Evidence from sub-Saharan Africa. *Energy for Sustainable Development*, *17*(2), 127–137. http://doi.org/10.1016/j.esd.2012.07.007

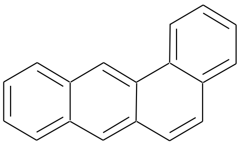
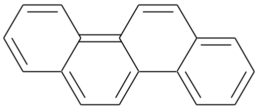
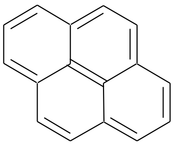
APPENDICES

Appendix 6.1: Properties and structure of identified PAHs

No.	Compound name	Formula	Molecular weight (g/mol)	Structure	WHO/IARC Exposure limit (μgg/g)*
1	Naphthalene	$C_{10}H_8$	128.17		0.03815
2	1-Methylnaphthalene	$C_{11}H_{10}$	142.20		0.03439
3	2-Methylnaphthalene	$C_{11}H_{10}$	142.20		0.03439
4	1,2,3,4-Tetrahydro-1,5-dimethylnaphthalene	$C_{12}H_{16}$	160.26		0.03051
5	2,7-Dimethylnaphthalene	$C_{12}H_{12}$	156.22		0.0313
6	1,4-Dimethylnaphthalene	$C_{12}H_{12}$	156.22		0.0313
7	2-Naphthalenecarbonitrile	$C_{11}H_7N$	153.18		0.03192
8	1,4,5-Trimethylnaphthalene	$C_{13}H_{14}$	170.25		0.02872
9	Fluorene-9-methanol	$C_{14}H_{12}O$	196.24		0.02492

*mg/m^3 = (μg/g value)(molecular weight)/24.45|24.45 is a conversion factor that represents the volume of one mole of gas at 25°C and 1atm (STP)| WHO Limit for PAHS = 0.2mg/m^3

No.	Compound name	Formula	Molecular weight (g/mol)	Structure	WHO/ IARC Exposure limit (μgg/g)
10	Fluorene	C13H10	166.22		0.02942
11	2,6-Diisopropylnaphthalene	$C_{16}H_{20}$	212.33		0.02303
12	9H-Fluoren-9-one	$C_{13}H_8O$	180.20		0.02714
13	Phenanthrene	$C_{14}H_{10}$	178.23		0.02744
14	Anthracene	$C_{14}H_{10}$	178.23		0.02744
15	9H-Fluoren-9-one, hydrazone	$C_{13}H_{10}N_2$	194.23		0.02518
16	1-methyl-Phenanthrene	$C_{15}H_{12}$	192.26		0.02543
17	4-methyl-phenanthrene	$C_{15}H_{12}$	192.26		0.02543
18	Fluoranthene	$C_{16}H_{10}$	202.25		0.02418
19	1,4-Dimethyl- 9,10-anthracenedione	$C_{16}H_{12}O_2$	236.27		0.0207

No.	**Compound name**	**Formula**	**Molecular weight (g/mol)**	**Structure**	**WHO/ IARC Exposure limit (µgg/g)**
20	Benzo[a] anthracene	$C_{18}H_{12}$	288.29		0.01696
21	Chrysene	$C_{18}H_{12}$	288.29		0.01696
22	Pyrene	$C_{16}H_{10}$	202.25		0.02418

Appendix 6.2: Emission profiles of smoke emitted by charcoal prepared from *A. polyacantha* by traditional pyrolysis

No.	Name of Compound	Retention Time	Relative abundance
1	Pyridine	7.01	0.16
2	Furfural	7.43	1.57
3	2-Furanmenthanol	8.10	0.89
4	Butyrolactone	9.45	1.57
5	2(3H)-Furanone	10.03	0.13
6	Benzaldehyde	10.43	0.15
7	2-Cyclopenten-1-one	10.52	1.39
8	2(5H)-Furanone	10.52	0.29
9	Phenol	10.99	3.83
10	1,2-Cyclopentanedione	11.75	0.62
11	2-Cyclopenten-1-one	11.97	1.11
12	ortho-Cresol	12.67	2.31
13	meta- Cresol	12.67	3.78
14	ortho-Guaiacol	12.87	3.21
15	2,6-Dimethylphenol	13.17	0.64
16	2-Ethyl-Phenol	13.68	0.27
17	2,6-Dimethylphenol	13.86	1.36
18	2,6- Dimethylphenol	14.17	1.41
19	2,3-Dimethylphenol	14.31	0.57
20	Naphthalene	14.42	0.93
21	2-Methoxy-para-Cresol	14.53	1.97
22	1,4:3,6- Dianhydro-.alpha.-d-glucopyranose	14.80	0.48
23	E-Cinnamaldehyde	14.98	0.35
24	2,4,6-Trimethylphenol	15.65	0.51
25	2,5-Dimethoxy toluene	15.81	1.28
26	2-Methyl-3-phenyl -2-Propenal-	15.97	0.38
27	2-Methyl-Naphthalene	16.08	0.43
28	N,N,3-Trimethyl Benenamine	16.17	0.14
29	2,3-Dihydro-2-methyl-1H-Inden-1-one	16.23	0.20
30	para-Vinyl-Guaiacol	16.32	0.40
31	2,3-Dihydro-2-methyl-1H-Inden-1-one	16.39	0.20
32	2,6-dimethoxy-Phenol	16.82	2.11
33	Tetradecane (C14)	17.35	0.54
34	Cyclopropyl-Benzene	17.67	0.19
35	2-Methyl-1H-Isoindole-1,3(2H)-dione	17.80	0.81

No	Name of Compound	Retention Time	Relative abundance
36	n-Dodecanol	18.34	1.93
37	4-Ethylbiphenyl	19.06	0.88
38	2,3-Dihydro-2,2-dimethyl-3,7-Benzofurandiol	19.15	0.37
39	Fluorene	19.84	0.36
40	2,6-Dimethoxy-4-(2-propenyl)-Phenol	19.95	0.75
41	(1-butylheptyl)-Benzene	20.29	0.54
42	i-Propyl tricosanoate	20.60	0.69
43	1-Dodecene	20.74	0.39
44	2,6-Diisopropylnaphthalene	20.85	0.32
45	3-(4-hydroxy-3-methoxyphenyl)-2-Propenoic acid	21.09	0.47
46	Dodecane	21.21	0.49
47	(1-pentylheptyl)-Benzene	21.34	0.88
48	(1-propylnonyl)-Benzene	21.54	0.28
49	9H-Fluoren-9-one	21.63	0.34
50	(1-ethyldecyl)-Benzene	21.77	0.33
51	1-(2,4,6-trihydroxy-3-methylphenyl)-1-Butanone	21.88	0.31
52	1-Hexadecene	21.97	0.49
53	Phenanthrene	22.10	0.39
54	Octadecamethyl-cyclononasiloxane,	22.33	0.82
55	(1-butylnonyl)-Benzene	22.46	0.30
56	Methyl hexadecanoate	23.33	0.59
57	gamma-Cuprenene	23.49	0.54
58	Estra-1,3,5(10)-trien-17.beta.-ol	23.67	0.39
59	Dibutyl phthalate	23.78	0.57
60	1- Eicosene	24.01	0.81
61	Octadecane, 1-chloro-	24.23	0.17
62	Hexadecane	25.37	0.19
63	4,4'-Bis(tetrahydrothiopyran)	25.44	0.41
64	1-Hexadecene	25.82	1.04
65	Tricosane	26.74	0.58
66	Methyldehydroabietate	27.29	0.52
67	1-Eicosene	27.52	0.69
70	1-Eicosene	24.01	0.81
71	1-Chloro-Octadecane	24.23	0.17
72	Hexadecane	25.37	0.19
73	4,4'-Bis(tetrahydrothiopyran)	25.44	0.42

No.	**Name of Compound**	**Retention Time**	**Relative abundance**
74	1- Hexadecene	25.82	1.04
75	Tricosane	26.74	0.58
76	o-Veratramide	27.10	0.26
78	1- Eicosene	27.52	0.69
79	Desmethyldoxepin	28.15	0.21
80	Octadecane (C18)	28.35	0.45
81	Di-n-octyl phthalate	28.82	1.04
82	Flouroantherene	33.29	0.97
83	1- Eicosene	29.09	0.74
84	Anthracene	30.87	0.65
85	Octacosyl trifluoroacetate	30.68	0.82
86	Pyrene	35.63	1.76
87	Benzo(a)anthracene	38.96	0.87
88	N-methyl-1-Octadecanamine	39.62	0.86
89	Chrysene	40.23	0.94
90	N-Dodecylmethylamine	37.35	0.16
91	N-Dodecylmethylamine	37.48	0.48
92	Cyanoacetylurea	37.80	0.58
93	Methylpent-4-enylamine	38.07	0.47
94	Benzenemethanol, .alpha.-[(methylamino)methyl]-	38.34	0.29
95	N-Dodecylmethylamine	38.47	0.54
96	Benzeneethanamine, 2-fluoro-.beta.,5-dihydroxy-N-methyl-	38.83	0.41
97	Benzenemethanol, .alpha.-[(methylamino)methyl]-	38.9446	0.33
98	N-Dodecylmethylamine	39.1238	0.49
99	1-Octadecanamine, N-methyl-	39.6389	0.93

Appendix 6.3: Emission profiles of smoke emitted by charcoal prepared from *A. polyacantha* by efficient pyrolysis

No.	Name of Compound	Retention Time	Relative abundance
1	Pyridine	4.83	0.35
2	Toluene	5.46	0.08
3	Cyclopentanone	6.22	0.18
4	2-methyl-Pyridine	6.98	0.29
5	2-Cyclopenten-1-one	7.43	2.24
6	2-Furanmethanol	8.13	1.96
7	2-methyl-2-Cyclopenten-1-one	9.25	0.69
8	2-methyl-2-Cyclopenten-1-one	9.49	2.32
9	3-methyl-2-Cyclopenten-1-one	10.52	1.68
10	Phenol	10.99	5.60
11	3,4-dimethyl-2-Cyclopenten-1-one	11.23	0.44
12	3-methyl-1,2-Cyclopentanedione	11.78	1.02
13	2,3-dimethyl-2-Cyclopenten-1-one	11.97	0.84
14	ortho-Cresol	12.31	2.27
15	m- Cresol	12.87	4.11
16	o-Guaiacol	13.16	0.71
17	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	13.36	0.49
18	2,6-Dimethylphenol	13.85	1.28
19	Phenol, 3,4-dimethyl-	14.17	1.45
20	2,3-dimethyl-Phenol	14.31	0.48
21	Naphthalene	14.53	1.69
22	4,5,6,7-tetrahydro-7-methyl-1H-Indazole	14.71	0.65
23	2,5-Dimethoxy toluene	15.81	1.33
24	2-methyl-naphthalene	16.32	0.62
25	2,6-dimethoxy-Phenol	16.82	1.60
26	Dihydro-Eugenol	17.02	0.26
27	4-hydroxy-3-methoxy-benzoic acid	18.07	1.04
28	5-tert-Butylpyrogallol	19.06	0.72
29	Fluorene	19.84	0.36
30	2,4-dimethyl-1-(phenylmethyl)-Benzene,	20.29	0.33
31	1-(2,4,6-trihydroxyphenyl)2-Pentanone	21.88	0.33
32	1-Hexadecene	21.97	0.36
33	Phenanthrene	22.10	0.49
34	1,2-Benzenedicarboxylic acid, butyl 2-ethylhexyl ester	22.84	0.52

35	Nonadecane (C19)	23.07	0.34
36	Methyl hexadecanoate	23.33	0.63
37	Dibutyl phthalate	23.78	0.35
38	Methyl octadecanoate	25.24	0.22
39	4,4'-Bis(tetrahydrothiopyran)	25.44	0.26
40	1- Hexadecene	25.82	1.03
41	Tricosane	26.74	0.63
42	Methyl dehydroabietate	27.29	0.41
43	1-Eicosene	27.52	0.76
44	Desmethyldoxepin	28.15	0.47
45	Octadecane (C18)	28.35	0.51
46	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	28.79	0.44
47	20-amino-, (3.beta.,20S)-pregn-5-en-3-ol	28.89	0.18
48	N-methyl-3-(4-nitrophenyl)-5-Isoxazolepropanamine	29.00	0.11
49	1- Docosene (C22)	29.09	0.67
50	Eicosane (C20)	29.87	0.42
51	1-Tricosene	30.68	1.20

Appendix 6.4: Emission profiles of smoke emitted by charcoal prepared from *A. xanthophloea* by traditional pyrolysis

No.	Name of Compound	RT	Peak Area
1	Toluene	5.43	0.01
2	2-Furanmethanol	8.14	0.53
3	2-methyl-2-Cyclopenten-1-one	9.26	0.08
4	Butyrolactone	9.51	0.50
5	Benzaldehyde	10.43	0.05
6	Phenol	11.19	2.84
7	ortho-Cresol	12.44	1.76
8	meta-Cresol	12.89	2.78
9	ortho-Guaiacol	13.01	2.36
10	Phenol, 2,6-dimethyl-	13.26	0.45
11	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	13.52	0.38
12	Phenol, 2-ethyl-	13.79	0.23
13	2,6-Dimethyl phenol	13.97	1.17
14	3-ethyl-phenol	14.31	1.20
15	Naphthalene	14.44	0.72
16	2-methoxy-para-Cresol	14.64	1.96
17	3,4-Dimethylanisole	14.78	0.46
18	3,4-Dimethoxy toluene	15.23	0.64
19	1-methyl -Naphthalene-	16.10	0.36
20	para-vinyl-Guaiacol	16.35	0.60
21	2,3-dimethyl-Benzofuran	16.44	0.33
22	2,6-dimethoxy-Phenol	16.91	2.24
23	dihydro- Eugenol acetate	17.06	0.46
24	1,5-dimethyl-1,2,3,4-tetrahydro-Naphthalene	17.17	0.20
25	Biphenyl	17.26	0.29
26	Tetradecane (C14)	17.47	0.23
27	2,7-dimethyl-Naphthalene	17.65	0.52
28	1,4-dimethyl-Naphthalene	17.80	0.36
29	1,2,4-Trimethoxybenzene	18.15	1.59
30	n-Dodecanol	18.39	1.11
31	1-Hexadecene	19.77	0.29
32	Fluorene	19.86	0.38
33	4-Propyl-1,1'-diphenyl	20.08	0.72
34	2,6-Diisopropylnaphthalene	20.91	0.61

No.	Name of compound	RT	Peak area
35	2,6-Diisopropylnaphthalene	21.39	1.45
36	1-Hexadecene	21.99	1.21
37	6,8-Dichloro-2-[4-chlorophenyl]-4-bromoacetylquinoline	22.35	0.91
38	1,2-Benzenedicarboxylic acid, bis(1-methylethyl) ester	22.89	0.99
39	Nonadecane (C19)	23.09	0.44
40	Methyl hexadecanoate	23.36	0.82
41	Eicosamethyl-cyclodecasiloxane	23.89	2.05
42	1-Eicosene	24.02	1.28
43	2,5-Furandione, 3-dodecyl-	24.81	0.66
44	1-Docosene (C22)	25.86	1.80
45	Hexadecane	26.24	0.92
46	Tricosane	26.76	0.88
47	1-Docosene (C22)	27.34	0.52
48	Diisooctyl adipate	27.61	1.62
49	6-ethyloct-3-yl 2-ethylhexyl ester -phthalic acid,	28.48	0.62
50	Di-n-octyl phthalate	28.88	20.48
51	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	29.69	2.77
52	Di-n-octyl phthalate	30.47	0.51
53	Anthracene	30.88	0.46
54	Octadecamethyl-cyclononasiloxane	31.19	1.09
55	2,4,7,14-Tetramethyl-4-vinyl-tricyclo[5.4.3.0(1,8)]tetradecan-6-ol	31.66	0.09
56	Heneicosane	31.78	0.43
57	n-Octadecanol	32.87	0.46
58	Heneicosane	34.28	0.16
59	Octadecamethyl-cyclononasiloxane	34.57	0.51
60	Pyrene	35.62	0.38
61	Octacosyl trifluoroacetate	35.94	0.28
62	Cyclononasiloxane, octadecamethyl-	37.08	0.33

Appendix 6.5: Emission profiles of smoke emitted by charcoal prepared from *A. xanthophloea* by efficient pyrolysis

No.	Compound	RT	Peak Area
1	N,N-dimethyl-acetamide	7.01	0.25
2	Furfural	7.48	0.33
3	Butyrolactone	9.47	0.72
4	3-Methyl-2-Cyclopenten-1-one	10.55	0.86
5	3-Methyl-2(5H)-Furanone	10.86	0.21
6	Phenol	11.04	3.7
7	3,4-Dimethyl-2-Cyclopenten-1-one	11.71	0.18
8	2-Hydroxy-3-methyl-2-Cyclopenten-1-one	11.84	0.68
9	2,3-Dimethyl-2-Cyclopenten-1-one	12.02	0.67
10	ortho-Cresol	12.34	1.52
11	meta- Cresol	12.74	3.72
12	2,5-Dimethyl-phenol	13.18	0.48
13	3-Ethyl-2-hydroxy-2-Cyclopenten-1-one	13.41	0.49
14	2-Ethylphenol	13.73	0.61
15	2,6-Dimethylphenol	13.88	1.61
16	3,5-Eimethylphenol	14.22	1.55
17	2-Methoxy-para- Cresol	14.55	1.88
18	1,4:3,6-Dihydro-glucopyranose	14.89	0.51
19	2,6-Dimethoxy-phenol	15.32	0.57
20	2,4,6-Trimethyl-phenol	15.67	0.3
21	2,3-Diethyl-pyrazine	15.74	0.28
22	2,5-Dimethoxytoluene	15.83	1.38
23	1-Methyl-naphthalene	16.08	0.27
24	2,3-Dimethyl-benzofuran	16.23	0.27
25	para-Vinyl-guaiacol	16.32	0.59
26	5-Indanol	16.73	0.67
27	2,6-Dimethoxy-Phenol	16.86	2.97
28	Dihydro-Eugenol	17.04	0.53
29	Skatole	17.35	0.28
30	Vanillin	17.53	0.64
31	7-methyl-Bicyclo[4.2.0]octa-1,3,5-triene	17.6	0.63
32	4-Hydroxy-3-methoxy-Benzoic acid	18.09	1.68
33	5-Tertbutylpyrogallol	19.08	1.15
34	Fluorene	19.84	0.91

No.	Name of Compound	RT	Peak area
35	2,6-Dimethoxy-4-(2-propenyl)-Phenol	19.97	1.06
36	1,1'-methylenebis[4-methyl-Benzene	20.29	0.49
37	4-methyl-Dibenzofuran	20.44	0.37
38	(Z)-5-Tetradecene	21.74	0.21
39	Cyclononasiloxane, octadecamethyl-	22.33	0.43
40	Phthalic acid, isobutyl octadecyl ester	22.84	0.36
41	Nonadecane (C19)	23.07	0.59
42	Methylhexadecanoate	23.33	1.16
43	Dibutyl phthalate	23.78	0.39
44	pi.-Cyclopentadienyl-dicarbonyl-ethylisonitril-trichlorgermyl-tungsten	23.87	0.39
45	1- Eicosene<	24.01	0.88
46	4-Oxo-dihydro-b-ionone	24.45	0.36
47	4-n-Hexylthiane, S,S-dioxide	24.61	0.43
48	(E)-9-Octadecenoic acid, methyl ester	25.01	1.02
49	Methyl octadecanoate	25.24	0.95
50	4-n-Hexylthiane, S,S-dioxide	25.57	0.25
51	1-Eicosene	25.84	0.81
52	Tricosane	26.74	0.36
53	4-n-Hexylthiane, S,S-dioxide	26.83	0.36
54	Eicosanoic acid, methyl ester	26.98	0.38
55	1-Eicosene	27.52	0.82
56	Eicosane (C20)	28.35	0.71
57	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	28.82	1.03
58	1-Docosene (C22)	29.09	0.55
59	Cyclononasiloxane, octadecamethyl-	31.13	0.35
60	Heneicosane	31.69	0.69
61	17-Pentatriacontene	32.81	0.4

Appendix 6.6: Emission profiles of smoke emitted by charcoal prepared from *E. grandis* by traditional pyrolysis

No.	Compound	RT	Peak Area
1	Pyridine	4.83	0.08
2	2-Methyl-Pyridine	7.01	0.08
3	2-Furanmethanol	8.10	0.29
4	2-Ethyl furan	8.37	0.06
5	2-Ethyl furan	8.57	0.05
6	2-Methyl-2-Cyclopenten-1-one	9.25	0.31
7	Butyrolactone	9.49	0.96
8	1-Methylcycloheptene	9.96	0.05
9	2-Methyl-2(5H)-furanone,	10.05	0.04
10	Benzaldehyde	10.43	0.15
11	5-Methyl-Furfural	10.55	0.65
12	2,4-Dimethyl-Furan	10.77	0.65
13	Phenol	11.11	4.28
14	2-Oxabicyclo[3.2.0]hepta-3,6-diene	11.58	0.15
15	3-Methyl-1,2-cyclopentanedione	11.87	0.71
16	2,3-Dimethyl-2-cyclopenten-1-one	12.07	1.05
17	o-Cresol	12.34	2.78
18	m-Cresol	12.76	4.26
19	o-Guaiacol	12.92	2.69
20	2,6-Dimethyl phenol	13.19	0.54
21	Maltol	13.34	0.29
22	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	13.4	0.20
23	2-Ethyl-Phenol	13.73	0.27
24	2,6-Dimethyl phenol	13.90	1.91
25	3-Hydroxy-4-methylbenzaldehyde	13.99	0.42
26	2,6-Dimethyl phenol	14.35	0.98
27	2-Methoxy-para-Cresol	14.44	0.65
28	2-Methoxy-para-Cresol	14.58	2.45
29	E-Cinnamaldehyde	15.00	0.64
30	4-Ethyl-3-methyl-Phenol	15.23	0.55
31	2,6-Dimethoxyphenol	15.34	0.75
32	3-Ethyl-5-methylphenol	15.56	0.58
33	3-Methoxy-1,2-Benzenediol	15.67	1.54
34	Tridecane	16.01	0.64
35	1,2,4-Trimethoxybenzene	16.66	0.65
36	2,6-Dimethoxy- Phenol	16.91	6.11
37	Methyl m-tolyl carbinol	17.51	1.11
38	7-Methylindan-1-one	17.71	0.38
39	2-Methyl-5-hydroxybenzofuran	17.78	0.97
40	4-Hydroxy-3-methoxy-Benzoic acid	18.14	3.38

41	1,2,3-Trimethoxy-5-methyl-Benzene	19.08	1.73
42	1,4,5-Trimethylnaphthalene	19.57	0.53
43	Fluorene-9-methanol	19.84	0.57
44	Syringaldehyde	20.69	0.70
45	9H-Fluoren-9-one	21.63	0.37
46	1-Eicosene	22.10	0.48
47	Anthracene	22.21	0.18
48	Phenanthrene	22.33	0.97
49	Cyclononasiloxane, octadecamethyl-	22.46	0.24
50	2-Chloro-1,3-bis(1-methylethyl)-Benzene	22.55	0.28
51	9H-Fluoren-9-one, hydrazone	22.84	0.48
52	Xanthone	22.93	0.25
53	Tetradecane (C14)	23.07	0.17
54	4-Methoxy-Stilbene	23.15	0.14
55	1-Methyl-Phenanthrene	23.27	0.22
56	Methyl hexadecanoate	23.33	0.46
57	4-Methyl-Phenanthrene	23.54	0.19
58	Hexadecanoic acid	23.69	0.27
59	Dibutyl phthalate	23.78	0.29
60	1-Eicosene	24.01	0.60
61	Fluoranthene	24.92	0.16
62	4,4'-Bis(tetrahydrothiopyran)	25.44	0.24
63	1,4-Dimethyl-9,10-Anthracenedione	25.66	0.14
64	Tricosane	26.74	0.29
65	N-[4-bromo-n-butyl]-2-Piperidinone	26.89	0.43
66	N-[4-bromo-n-butyl]-2-Piperidinone	27.41	0.09
67	1-Eicosene	27.52	0.51
68	Octadecane (C18)	28.35	0.32
69	n-Octadecanol	29.09	0.46
70	Octatriacontyl pentafluoropropionate	29.38	0.26
71	n-Octadecanol	30.68	0.34
72	Octadecamethyl-Cyclononasiloxane	34.55	0.50
73	Octadecamethyl-Cyclononasiloxane	37.09	0.57
74	N-Dodecylmethylamine	39.62	0.25

Appendix 6.7: Emission profiles of smoke emitted by charcoal prepared from *E. grandis* by efficient pyrolysis

No.	Compound	RT	Peak Area
1	Furfural	7.43	1.29
2	2-Furanmethanol	8.14	1.08
3	Styrene	8.84	0.11
4	2-Methyl-2-Cyclopenten-1-one	9.25	0.37
5	5-Methyl-2(5H)-Furanone	10.03	0.07
6	Benzaldehyde	10.43	0.12
7	3-Methyl-2(5H)-Furanone	10.84	0.14
8	Phenol	10.97	3.28
9	3,4-Dimethyl-2-Cyclopenten-1-one	11.19	0.19
10	o-Cresol	12.31	1.16
11	o-Guaiacol	12.87	2.71
12	2,6- Dimethyl phenol	13.86	0.68
13	Naphthalene	14.42	0.41
14	1,4:3,6-Dianhydro-.alpha.-d-glucopyranose	14.85	0.54
15	E-Cinnamaldehyde	14.98	0.26
16	Quinoline	15.27	0.64
17	1,3-Benzenedicarbonitrile	15.65	0.69
18	1,2,3-Trimethoxybenzene	16.26	0.33
19	1,2-Benzenedicarbonitrile	16.53	0.26
20	2,6-Dimethoxy-Phenol	16.84	2.98
21	1-Tetradecene	17.26	0.21
22	Tetradecane (C14)	17.35	0.33
23	1,2,3-trimethoxy-5-methyl-Benzene	17.47	0.33
24	7-Methylindan-1-one	17.6	0.17
25	2-Methyl-1H-isoindole-1,3(2H)-dione	17.8	0.58
26	4-Hydroxy-3-methoxy-Benzoic acid	18.07	1.76
27	Tetradecamethyl-cycloheptasiloxane	18.61	0.66
28	2-Naphthalenecarbonitrile	18.77	0.32
29	1,2,3-Trimethoxy-5-methyl-benzene	19.06	1.47
30	1-(4-hydroxy-3,5-Dimethoxyphenyl)-ethanone	19.55	0.25
31	1-Hexadecene	19.75	0.77
32	4-Propyl-1,1'-diphenyl	20.04	0.23
33	Benzene, 1-methyl-2-[(3-methylphenyl)methyl]-	20.29	0.33

No.	Name of compound	RT	Peak area
34	2,6-Diisopropylnaphthalene	20.92	0.44
35	Heptadecane (C17)	20.96	0.38
36	2,6-Diisopropylnaphthalene	21.34	0.78
37	9H-Fluoren-9-one	21.63	0.58
38	Benzoic acid, 4-hydroxy-3,5-dimethoxy-, hydrazide	21.86	0.32
39	1-Octadecene	21.99	0.89
40	Anthracene	22.1	0.56
41	Octadecamethyl-Cyclononasiloxane	22.33	0.38
42	Caffeine	22.77	3.99
43	Nonadecane (C19)	23.07	0.4
44	Methyl hexadecanoate	23.33	0.64
45	Dibutyl phthalate	23.78	1.27
46	1- Eicosene	24.65	1.71
47	1,7,11-trimethyl-4-(1-methylethyl)-Cyclotetradecane	24.45	0.38
48	2-Dodecen-1-yl(-)succinic anhydride	24.79	0.67
49	Nopinone	24.88	0.34
50	(Z)-9-Tricosene	25.1	0.34
51	Methyl octadecanoate	25.24	0.36
52	Eicosane	25.35	0.27
53	4,4'-Bis(tetrahydrothiopyran)	25.44	0.36
54	1-Eicosene	25.64	0.26
55	1-Eicosene	26.32	0.68
56	Eicosane (C20)	26.72	0.68
57	Eicosane (C20)	26.38	0.36
58	Eicosane	26.74	0.78
59	Dotriacontyl pentafluoropropionate	26.89	0.24
60	57.65 Methyl dehydroabietate	27.29	0.78
61	Dotriacontyl pentafluoropropionate	27.41	0.19
62	1-Eicosene	27.52	1.85
63	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	28.82	3.35
64	1-Docosene (C22)	29.09	1.25
65	1-Hexacosene	29.22	0.41
66	Pentacosane	29.38	0.45
67	Octadecane (C18)	29.87	0.75
68	n- Octadecanol<	30.68	1.36
69	Dotriacontane	31.69	0.58