Journal of Aerosol Science 95 (2016) 1–14

Contents lists available at ScienceDirect

Journal of Aerosol Science

journal homepage: www.elsevier.com/locate/jaerosci

Morphological and chemical characterization of soot emitted during flaming combustion stage of native-wood species used for cooking process in western Mexico

G. Carabali [a,*], T. Castro [b], W. De La Cruz [c], O. Peralta [b], A. Varela [a,e], O. Amelines [d], M. Rivera [d], G. Ruiz-Suarez [b], R. Torres-Jardón [b], E. Martines-Quiroz [e], R. Policroniades [e], G. Murillo [e], E. Moreno [e], F. Muñoz-Muñoz [c], L. Molina [f,g]

[a] *Instituto de Geofísica, Universidad Nacional Autónoma de México (UNAM), México*
[b] *Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México (UNAM), México*
[c] *Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México (UNAM), México*
[d] *Instituto de Física, Universidad Nacional Autónoma de México (UNAM), México*
[e] *Departamento de Aceleradores, Instituto Nacional de Investigaciones Nucleares (ININ), Carr. México-Toluca S/N, Ocoyoacac, Estado de México 52750, México*
[f] *Molina Center for Energy and the Environment, La Jolla, CA, USA*
[g] *Massachusetts Institute of Technology, Cambridge, MA, USA*

ARTICLE INFO

Article history:
Received 10 March 2015
Received in revised form
22 November 2015
Accepted 13 January 2016
Available online 22 January 2016

Keywords:
Wood burning cook stoves
Soot aggregates
Fractal dimension
HRTEM
XPS
PIGE

ABSTRACT

The morphology, microstructure and chemical composition of soot particles emitted directly from biofuel cook stoves have been studied by using high-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS) and ion beam analysis (IBA) techniques. Freshly emitted soot particles were collected using an eight stage cascade impactor that separates particles according to their size. The particulate matter is impacted on thin aluminum foil and copper grids for Transmission Electron Microscope. The analysis of HRTEM micrographs revealed the nanostructure and the particle size of soot chain. Results from the border-based fractal dimension indicated that main morphological differences observed in soot particles perhaps are associated to cook-stove chamber design. XPS analysis shows that particles are mainly composed by carbon and oxygen. The XPS C-1s spectra show carbon with three peaks corresponding to sp^2, sp^3 hybridization and carbon oxygen bond. Additionally, we determined the areal density (atoms/cm^2) of the soot films and the purity of the substrates by means of IBA techniques.

1. Introduction

It is estimated that two billion people use biomass fuel (wood, dung and fiber residues) as their primary energy source for domestic needs such as heating and cooking (Bond & Bergstrom, 2005). Biomass fuels account approximately 14% of the worldwide energy consumption, in which only ~3% is used in industrialized countries, but 43% is consumed by developing

* Corresponding author.
E-mail address: carabali@geofisica.unam.mx (G. Carabali).

http://dx.doi.org/10.1016/j.jaerosci.2016.01.008
0021-8502/

countries (Koziński & Saade, 1998). Approximately 27 million people in rural areas of Mexico, still use biomass for cooking (Berrueta, Edwards, & Masera, 2008), where fuelwood represents approximately 80% of energy used by rural households and 50% of total energy use in rural communities (Berrueta et al., 2008).

The biomass burning devices used for cooking are known in the literature by various names such as cook stoves, wood-burning cook stoves or biomass cook stoves. People who use these tools on a daily basis for food preparation are exposed to emissions originated by the inefficient combustion, causing serious adverse health effects that mainly affect women and children. In fact, the damage associated with inhaling smoke from open combustion origins acute respiratory infections, which cause nearly 1.2 million premature deaths annually among children less than 5 years of age (Berrueta et al., 2008) and chronic obstructive lung disease among adults (Norboo, Yahya, Bruce, Heady, & Ball, 1990; Boy, Bruce, Smith, & Hernandez, 2000; WHO, 1997; Pope & Dockery, 2006; Popovitcheva et al., 2000; Oberdörster, 2000).

Although work on improving biofuel stoves has been going on for many years, much of the effort has been directed at optimized biomass combustion and reducing fuel consumption mainly for economic and environmental reasons, rather than at reducing exposure levels within the home for health reasons (Boy et al., 2000; Lighty, Veranth, & Sarofim, 2000). However, efforts by the scientific community in Mexico have been made to promote new cook stoves that improve quality of life on rural communities (Berrueta et al., 2008).

It is clear that products of biomass combustion play significant roles in global atmospheric chemistry and the potential for global warming from an enhanced greenhouse gas effect (Seiler & Crutzen, 1980). Soot is an important product of incomplete combustion and comprised of black carbon (BC) and organic carbon (OC). BC absorbs incoming solar radiation (across the visible spectrum) and the OC primarily in the UV portion of the spectrum (Kuhlbusch et al., 1996; Bond & Bergstrom, 2005).

The vast literature on soot formation has been summarized in various reviews and specialized conferences on the subject (Boy et al., 2000). For example, studies on the main parameters that controls primary combustion particle size, morphology, and composition have been reported by Boy et al. (2000), Lighty et al. (2000), Fang, Leavey, and Biswas (2014), Ishiguro, Takatori, and Akihama (1997), Tumolva et al. (2010), Carabali et al., (2012) and Vander Wal, Bryg, and Hays (2011). Despite the above discussion, only few studies characterizing the direct emissions from wood burning cook stoves have been conducted.

The majority of the studies related to wood burning in cook-stoves, have been focused on measuring emission factors (Bhattacharya, Albina, & Salam 2002; Roden et al., 2006) and climate-relevant properties such as absorption and scattering (Martins et al., 1998). None of the studies have reported a physical characterization of soot emitted by cook stoves.

Carbon is a light element with relatively simple electronic structure. The hybridization bonded in soot can be identified by using the X-ray Photoelectron Spectroscopy (XPS) (Kaciulis, 2012; Vander Wal et al., 2011). The carbon electronic spectra contain only two main excitations: photoemission line of C 1s and Auger line, which are often called C KVV (so-called X-ray-induced Auger electron spectroscopy, AES). C KVV peaks can also be used to distinguish between different hybridization states of carbon. Several studies use XPS to analyze environmental particulate matter (PM) collected on filters (Song & Peng, 2009; Hutton & Williams, 2000; Zhu, Olson, & Beebe, 2001). It is important to mention that collected particles can be directly analyzed by XPS without further sample preparation, because it is capable to analyze insulating samples (Hutton & Williams, 2000; Gilham, Spencer, Butterfield, Seah, & Quincey, 2008).

Other important physical and chemical information about of soot particles may be collected by ion beam analysis (IBA). This technique uses high-energy proton beams (energies of few MeV) to excite the sample collected on the filters producing γ-rays or scattered characteristic on analyzed particles. These protons have sufficient energy to pass directly through the filter and be measured with detectors placed in different angles. The energy spectra of the interaction products provide information on the sample's elemental composition and the areal density (atoms/cm^2) of the carbon deposit (Ferrer et al., 2014; Gurbich, 2014). Among the numerous IBA methods, proton elastic scattering analysis (PESA) and particle-induced gamma emission (PIGE) are governed by rules of nuclear reactions and appropriate kinematic relations (Schmidt & Wetzig, 2013) and are the most common to study atmospheric aerosols (Cohen, Stelcer, Hawas, & Garton, 2004). Both methods are well suited for studying air pollution because they are quick, non-destructive, require little or no sample preparation, and are capable of investigating microscopic samples.

The main goal of this article is to characterize soot particles emitted by wood burning cook stoves. A microstructure and morphology study of soot was carried out with high-resolution transmission electron microscopy (HRTEM) and HRTEM images of soot aggregates to calculate its perimeter fractal dimension (PFD). The chemical composition on surface and carbon bonding is explored with X-ray photoelectron spectra (XPS) of soot samples deposited directly over aluminum foils. Additionally, soot particles deposited onto quartz (SiO_2) filters were analyzed by backscattering elastic protons at 150° and PIGE using deuterons. In the latter case, the carbon useful γ-radiation comes from nuclear reactions.

2. Methodology

2.1. Cook stoves and wood used as fuel

The soot particles analyzed were directly sampled from the chimney of two wood burning cook stoves. Patsari cook stove CS-1 (Fig. 1a) was developed by the Center for Ecosystems Research (CIECO), Universidad Nacional Autónoma de México