Atmospheric Environment 178 (2018) 118–128

Contents lists available at ScienceDirect

Atmospheric Environment

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

Thermo-optical properties of residential coals and combustion aerosols

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ARTICLE INFO

Keywords:
PhotoAcoustic Spectroscopy
Household coal
Laser ablation
Aerosol Angström Exponent
Calorific value

ABSTRACT

In this study, we present the inherent optical properties of carbonaceous aerosols generated from various coals (hard through bituminous to lignite) and their correlation with the thermochemical and energetic properties of the bulk coal samples. The nanoablation method provided a unique opportunity for the comprehensive investigation of the generated particles under well controlled laboratory circumstances. First, the wavelength dependent radiative features (optical absorption and scattering) and the size distribution (SD) of the generated particulate matter were measured in-situ in aerosol phase using in-house developed and customised state-of-the-art instrumentation. We also investigated the morphology and microstructure of the generated particles using Transmission Electron Microscopy (TEM) and Electron Diffraction (ED). The absorption spectra of the measured samples (quantified by Absorption Angström Exponent (AAE)) were observed to be distinctive. The correlation between the thermochemical features of bulk coal samples (fixed carbon (FC) to volatile matter (VM) ratio and calorific value (CV)) and the AAE of aerosol assembly were found to be ($r^2 = 0.97$ and $r^2 = 0.97$) respectively. Lignite was off the fitted curves in both cases most probably due to its high optically inactive volatile material content. Although more samples are necessary to be investigated to draw statistically relevant conclusion, the revealed correlation between CV and Single Scattering Albedo (SSA) implies that climatic impact of coal combusted aerosol could depend on the thermal and energetic properties of the bulk material.

1. Introduction

Atmospheric carbonaceous particulate matter (CPM) is in the focus of scientific interest due its adverse climatic and human health effects (; Andreae and Ramanathan, 2013; Stocker et al., 2013; Penner et al., 1992; Yu et al., 2006; Pope and Dockery, 1996). Ambient aerosol particles emitted from fossil fuel combustion alter the energy budget of the Earth-atmosphere system through scattering and absorbing solar radiation (Bond et al., 2013). Particles that do not absorb, only scatter solar light (e.g. sulfates) produce a cooling effect (Charlson et al., 1991). However, aerosol particles with significant optical absorption in the solar wavelength range cause a remarkable heating effect (Haywood and Shine, 1995). Black Carbon (BC) is the most dominant component of atmospheric light absorbing carbonaceous particulate matter (LAC) (Bond et al., 2013; Rosen et al., 1981). Today, the radiative forcing of BC is one of the biggest uncertainties in climatic models (Bond et al., 2013; Lack et al., 2006). The most important reasons for that are found in the lack of proper knowledge regarding CPM emission rates, lifetimes and optical properties (Bond et al., 2002). Climatic models require the precise and reliable determination of size distribution and the complex optical properties of CPM as input parameters (Bond et al., 2002; Twomey, 1977).

Due to their availability and low price, coal alongside with biofuels have gained new popularity in developing and developed countries as well (Khodaei et al., 2017; Weldu et al., 2017). Carbonaceous particles emitted from domestic coal combustion for both cooking and heating make a significant contribution to the atmospheric concentration of particulate matter (PM) a global and a regional scale as well (Cooke et al., 1999; Bond et al., 2002). According to the most recent estimations, coal burning contributes to almost 50% of CPM emitted from

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https://doi.org/10.1016/j.atmosenv.2018.01.036
Received 24 August 2017; Received in revised form 20 December 2017; Accepted 23 January 2018
1352-2310/

fossil fuel burning and 20% of total global CPM (Liousse et al., 1996. Streets et al., 2001) showed that 45% of CPM originates from coal burning in China, while roughly 55% from residential biofuel combustion. Very recently several studies have reported that under urban wintry conditions, the dominant sources of CPM are traffic and domestic heating (Sandradewi et al., 2008a, b; Favez et al., 2009; Utry et al., 2014; Ajtai et al., 2015a; Salma et al., 2017; Simon et al., 2017). Despites of its importance, neither the climatic nor the adverse health effects of CPM have been adequately investigated yet (Chakrabarty et al., 2014; Titos et al., 2014). Several recent studies have suggested that particles originating from domestic heating pose a more severe threat to both climate and human health than that of other carbonaceous particulate sources like traffic (Chakrabarty et al., 2014; Turóczi et al., 2012; Titos et al., 2014; Sigsgaard et al., 2015; Sandradewi et al., 2008a, b; Favez et al., 2009; Ajtai et al., 2015a; Pintér et al., 2017). The legal regulation of atmospheric CPM emitted from household heating is also among the most concurrent challenges of environmental quality strategies in developing countries to be faced (Waggoner et al., 1981; Weldu et al., 2017; Khodaei et al., 2017; Martinsson et al., 2015; Sigsgaard et al., 2015).

Coal energy is among the most current energy sources used in power plants and for residential heating as well (Werther et al., 2000; Williams et al., 2001; Sami et al., 2001). Moreover, the cofiring of traditional coal types and biofuels have shown promising results regarding CO_2 emission and energetic efficiency (Baxter, 2005; Baxter and Koppejan, 2004). To make coal combustion as economically efficient and environmentally friendly as possible, coal quality, the combustion process and the emission must be continuously monitored and controlled (Jenkins et al., 1998; Majumder et al., 2008). Coal quality is most generally assessed either by pre- or post-combustion approaches (Sheng and Azevedo, 2005). The most commonly utilized laboratory approaches are the determination of the calorific value (CV), proximate and ultimate analysis of the fuel (Werther et al., 2000; Sheng and Azevedo, 2005; Majumder et al., 2008). Nowadays, online analytical methodologies like near-infrared spectroscopy, microwave absorption and most recently laser-induced breakdown spectroscopy (LIBS) are being used for this purpose too (Zhang et al., 2012; Metzinger et al., 2016). However, the routine on-sight application of these methodologies is still not a reality (Gupta, 2007). Therefore, developing novel, online methodologies for the assessment of aerosol quality emitted from coal combustion and revealing the relationship between the bulk and the particulate phase properties are relevant issues both from the perspective of energy industry and protection of the health and environment as well as issues of climate (Metzinger et al., 2016; Gaft et al., 2008).

Recently several studies demonstrated that the segregated spectral response of carbonaceous particulate matter is not only a crucial parameter of climate forcing calculations but also one of the promising candidates for real time source apportionment as well as a possible marker of toxicity (Pintér et al., 2017). Despite of its importance, little information exists neither on the inherent (source specific) nor the apparent (modified by ambient processes) spectral responses of the coal aerosol (Bond et al., 2002, 2013; Bond, 2001; Utry et al., 2014; Ajtai et al., 2015a; Favez et al., 2009; Salma et al., 2017.).

Coal combustion is primarily a combination of volatile matter and elemental carbon ignition consisting of three fundamental stages. At low temperature, the volatile matter is released from the bulk material. At higher (ignition) temperature, the released volatile matter is burned. Following that, at even higher temperature, the remaining elemental carbon fraction is burned too. Although these stages correspond different temperature domains, they might take place simultaneously or subsequently, or even with them taking place in overlapping time domains. CPM is a by-product of coal combustion. CPM evolvement can be described by three distinct but subsequent phases. During the nucleation phase, above ignition temperature, molecules, vapours or fragments are released from the coal sample, that later connect to each other through various type of chemical bonds forming new particulate nuclei in the sub nm size domain. Then, during coagulation phase, these nuclei particles collide and form spherical primary particles up to a few or few dozen nm size domain. Then, finally, these primary spherical particles are bonded to each other creating fractal like aggregates with a complex morphology in the sub um size domain (Gelencsér, 2004).

The most generally used methodology for modelling coal combustion under laboratory circumstances is based on various kinds of stoves (Bond et al., 2002). However, the reproductivity of this approach and its ability for comprehensive investigation of particle formation as well as the complex properties of formed particles are questionable. Recently, a more sophisticated methodology has been introduced for modelling the combustion process of solid fuel based on the nanoablation of a bulk carbonaceous matter (Ajtai et al., 2015b; Smausz et al., 2017). In this set up, pulsed laser energy is responsible for providing the ignition temperature and triggering the combustion process in a controlled and reproductive manner. However, the combustion process and CPM evolvement are equivalent with traditional methods based on stoves. In this approach, laser energy, the composition of gas ambience and its flow rate can be controlled and adjusted independently from each other. Therefore, it can provide a unique opportunity to investigate the inherent features of soot aerosol generated from specific solid fuel targets, under versatile burning conditions. Whilst, fixing the parameters of soot generation at a given value ensures adequate measurement conditions for a comprehensive and comparable analysis of different coal samples.

The most generally used methodology for modelling coal combustion under laboratory circumstances is based on various kinds of stoves (Bond et al., 2002). Recently, more sophisticated methodology has been introduced based on the nanoablation of a graphite target that can provide unique opportunity to investigate the inherent spectral features of soot aerosol in controlled, reproductive and comprehensive manner (Ajtai et al., 2015b). Although the spectral (i.e. optical absorption and light scattering) and microphysical properties like size distribution can be measured on-line or even in-situ, none of them are directly related to chemical compositions. The only real-time measurable spectral parameter that correlates with chemical composition is the wavelength dependency of absorption spectra quantified by so called Absorption Angtsröm Exponent (AAE). However, out of all CPM characteristics, the precise and accurate measurement of optical absorption means the greatest challenge even today (Andreae and Gelencsér, 2006). Photo-Acoustic Spectroscopy (PA) is devoid of the most crucial measurement artefacts associated with other concurrent measurement techniques (Lack et al., 2014). The recent availability of multi-wavelength Photo-Acoustic Spectrometers (PAS) opens novel possibilities for more precise and accurate determination of absorption coefficients and their wavelength dependence as well (Arnott et al., 2005; Ajtai et al., 2010a, b, Ajtai et al., 2011a, b; Schmid, 2006; Utry et al., 2014; Simon et al., 2017). We also experimentally demonstrated earlier that multi-wavelength PAS has exciting potential in the selective identification of CPM with different chemical composition based on the online and aerosol-phase measurement of the wavelength dependence of the optical absorption spectra quantified by the Aerosol Angström Exponent (AAE). (Utry et al., 2014; Ajtai et al., 2015a; Pintér et al., 2017).

In this paper, the thermal and energetic properties of commercially available coal samples and high purity synthetized graphite as reference were determined using traditional offline laboratory methodology (calorimetry and proximate analysis). Our previously developed CPM generator based on laser ablation (Ajtai et al., 2015b) was utilized to generate aerosol from the investigated coal samples. The climate relevant optical (optical absorption and light scattering) and microphysical properties (size distribution (SD)) of the samples were studied online using our in-house developed multi wavelength PAS and supplementary instrumentation. The goal of this paper is investigating the relationship between the online measured climate relevant characteristics of generated model CPM and the offline determined coal