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Determination of Extraction Efficiency of Different Solvents for Organic Carbon Content in Biomass Combustion Aerosols

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ABSTRACT

Biomass combustion is a major source of organic carbon (OC) aerosols found in the atmosphere. In this study OC generated from biomass combustion was sampled and treated with different solvents to determine their extraction efficiency. Commonly used biomass fuels (wood and dung cake) were combusted in a temperature controlled chamber and the generated aerosols were sampled on Quartz filter paper. The dried filter paper pieces were analysed for their OC content in **Total Carbon and Nitrogen Analyzer (PrimacsSNC, Skalar). From the obtained OC data extraction efficiencies were determined.** The extraction process was repeated with four different solvents viz. deionised water, hexane, acetone and methanol. The extraction efficiency of each solvent was determined using difference in OC of filter paper before and after extraction. Extraction efficiency for OC samples obtained from wood combustion in water, hexane, acetone and methanol were 54, 30, 83 and 92 % respectively. And for dung cake, it is observed as 20, 37, 76 and 80 % respectively. The extraction efficiency depended on the polarity index of the solvent used.

I. INTRODUCTION

Carbonaceous aerosols are ubiquitous in troposphere with biomass combustion as one of its major source [1]. Various types of organic carbon and black carbon are components of carbonaceous aerosol. Carbonaceous aerosols are important in direct Radiative forcing because of their prevalence in the ambient atmosphere and the ability of BC and some OC to absorb solar radiation which could warm the atmosphere [2]. From the combustion of biomass, 60% of the primary BC and 91% of primary OC are emitted globally. Biomass combustion includes biofuel combustion (biomass used for heating or cooking) and open vegetative burning (uncontrolled combustion of forests, croplands and grasslands) [3]. estimated the global annual emissions of BC and primary OC as 8 Tg (10^{12}g) and 34 Tg respectively. The contribution of biofuel and open vegetative burning are 19% and 74% respectively to total primary OC, and 19% and 41% to total primary BC.

Black carbon (BC) is the refractory and most strongly light-absorbing component of soot, which is mainly emitted from the incomplete combustion of fossil fuels and biomass burning [4]. Airborne BC is the most significant particulate absorber of solar radiation in the atmosphere and an important contributor to both global and regional-scale climate forcing [5]. While, OC accounts for a large fraction of atmospheric aerosols and has profound effects on air quality, atmospheric chemistry and climate forcing [6]. OC is 3-12 times greater than BC by mass [7] and in atmosphere it accounts for 10-70% of total dry mass [8]. Mostly OC compounds absorbs IR & UV radiation strongly but are relatively transparent to visible and near-IR wavelength. However, certain types of OC absorb radiation efficiently in near-UV visible ranges. For such type of OC, a new term "brown carbon" (BrC), has emerged [9]. Primary sources of BrC are forest fires & biomass burning, residential heating of wood, coal & biogenic release of fungi, plant debris & humic matter [10]. The magnitude of BrC contribution to radiative forcing of climate by absorption of incoming solar radiation on a planetary scale is estimated to be in the range of 0.1-0.25 w/m^2, which is approx. 25% of the radiative forcing by BC (1.07 w/m^2) [11]. Humic like substance (HULIS) and Tar ball found an important component of BrC. Atmospheric HULIS formation occurs during cloud processing of smoke from biomass burning, these are also produced through multiphase chemistry of organic constituents derived from other anthropogenic & natural sources such as vehicle exhaust, fossil fuel combustion in urban areas, biogenic & marine emission. [6] While Tar ball, commonly detected in smoke emission from smoldering burns of biofules. And these are the most absorbing and refractory BrC material that can be easily observed under the vacuum condition of an electron microscope [13]. Although OC could have an important contribution to radiative forcing, its treatment in global models to date has been simplistic; it has been treated as a compound that primarily scatters light and has invariant properties [14]. In fact, chemical and optical properties of OC may differ due to the nature of the OC source [15]. The present paper aims to contribute to understanding the variable behaviour of BrC regarding its polarity. BrC constituents exhibit characteristic of polar molecules and contain both water soluble & insoluble components. For that purpose, in current study four different solvents used for qualitative study of brown carbon composition.

II. METHODS

Sample generation

The OC aerosols are often studied using filter paper based method in which the OC are sampled on filter paper and extracted using suitable solvent for further analysis. For that purpose, OC aerosol samples were generated at lab scale by pyrolyzing small pieces of biomass in an adjustable, electrically-heated enclosed combustor. The combustor created a temperature-controlled environment using resistive heating principle. The dimension of the combustor was 13 cm X 13 cm X 24 cm. The combustor contains no flame source and formation of BC can be avoided by preventing flames when no oxygen enters the combustor. A nitrogen carrier gas (7 lpm) kept the combustor at a slight positive pressure. Smoke escaped through combustor and was sampled. The combustor simulates the release of volatile matter at realistic biomass temperatures. The schematic diagram of experimental setup is shown in figure 1.

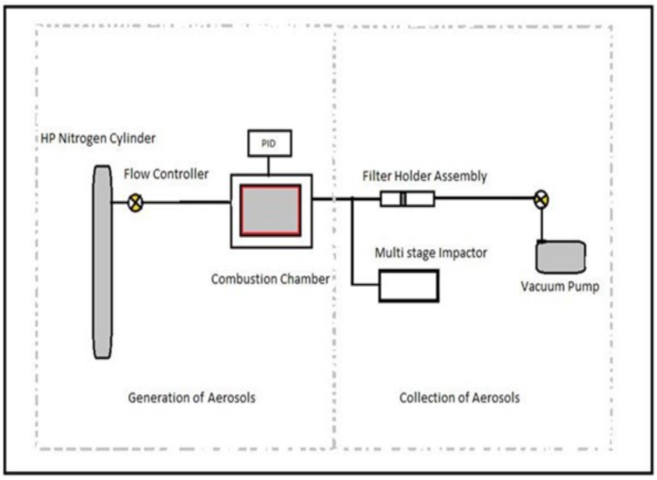

Figure 1. Schematic diagram of experimental setup

The sampling unit consisted of filter holder casing to house quartz filter and multi stage impactor. A vacuum pump constantly maintained negative pressure for aerosols collection. Prior to start of experiment the combustor was continuously flushed with nitrogen gas for 30 minutes to ensure nitrogen environment. Biomass samples were placed in the bottom centre of the combustor, and temperature was measured near the exterior of the biomass pieces. The measured temperature represents the temperature of the biomass surface. The internal temperature of the biomass would be lower than the surface temperature when it was just put into the combustor [16]. modelled the heat transfer into biomass (wood) and found that under smoldering conditions for the biomass size, the internal temperature can reach the surface temperature in less than 10 minutes. The time is relatively short compared with a normal overall test which generally lasted for 1-2 hours. It was observed that combustor took some time to reach the set temperature at the rate of 10°C/min.

Filter holder assembly collected total organic carbon aerosols escaping from the combustor chamber at the outlet. Then filter papers were stored in Petri dishes lined with baked aluminium foil prior to sampling. At the end of the sampling period, the filters were returned to the dishes immediately and stored in a freezer (-4 °C) until further analysis.

Sample extraction:

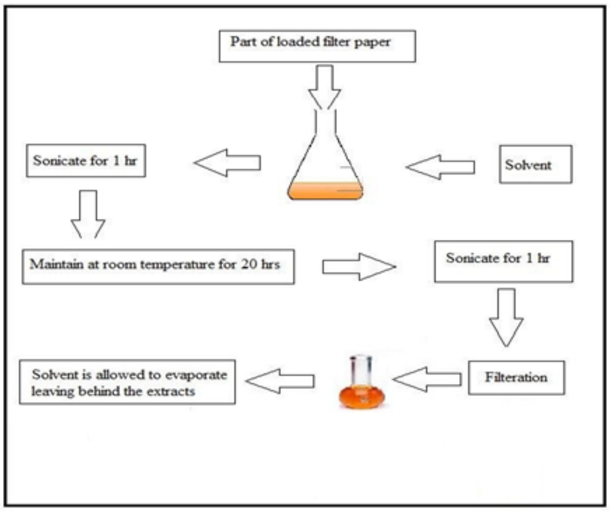

Figure 2. Schematic diagram of extraction procedure for organic carbon

Sampled quartz filter paper was extracted with 20mL deionized water and organic solvents: methanol (A.C.S. certified, Fisher Scientific), hexane (Fluka) and acetone (A.C.S. certified, Fisher Scientific). A punch (1/8th) of filter paper and solvent were sonicated (Ultrasonic Cleaner, Cole Parmer 8892) for 1 hour, kept at room temperature for 20 hours to let the solution reach equilibrium, and sonicated for 1 additional hour [17]. reported that sonication increases extraction efficiencies by 10-15%. All extracts were filtered by syringe through a 25mm diameter filter with a 0.2*m*m pore size (Whatman, Anotop* Disposable Syringe Filters, Fisher Scientific) to remove impurities during the extraction process. Residual filters were taken out of the solutions, dried in a fume hood and then kept in the freezer for further analysis. Schematic diagram of extraction setup shown in figure 2.

III. RESULT AND DISCUSSION

Sample collected on quartz filter paper showed brownish colour as shown in figure 3, which ensures the presence of BrC in the collected samples.

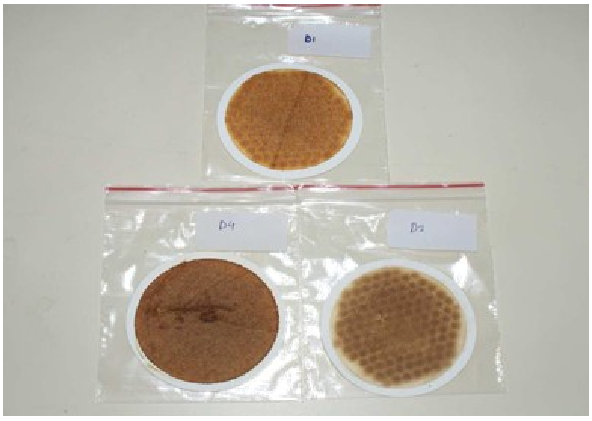

Figure 3. Brown carbon loaded quartz filter paper

Total organic carbon was analysed in **Total Carbon and Nitrogen Analyzer (PrimacsSNC, Skalar make), which consists a** Combustion furnace, Peltier cooler, Halogen scrubber, and NDIR (Non Dispersive Infrared detection). For organic sample TC direct method was used in which sample initially passes through combustion furnace where carbon is completely oxidized to CO_2, by continuously circulating the sample through the combustion furnace. The CO_2 is measured by (NDIR) for Total Carbon. The instrument was calibrated with the standard result in which EDTA taken as standard, which contain 41% of carbon. Absolute carbon value was calculated before and after extraction to calculate solubility of wood and dung cake sample obtained on fillter paper in water, hexane, acetone and methanol. Figure 4 shows typical spectra of carbon analysis.

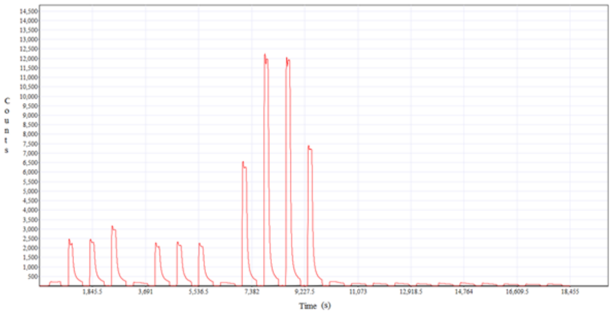

Figure 4. A typical Carbon analysis spectrum in TC analyser

Extraction Efficiency:

Based on polarity index, solvents with extreme and mid values were chosen for sample extraction (for water, hexane, acetone and methanol polarity index values are 10.2, 0.1, 5.1 and 5.1 respectively).

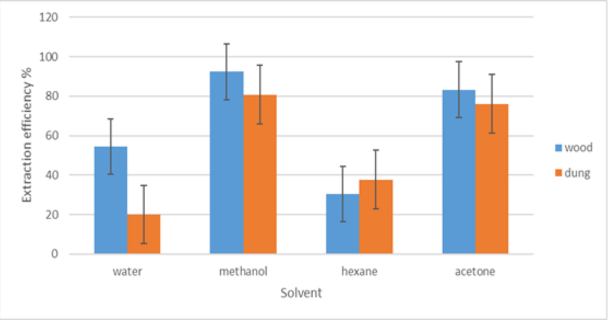

Figure 5. Extraction efficiency of solvents (%)

After calculation of absolute carbon value before and after extraction, efficiency of all four solvents was calculated. For wood and dung cake sample maximum extraction efficiency was obtained with methanol and least extraction efficiency for wood sample obtained in hexane whereas for dung cake sample lowest efficiency was observed in water. This shows that BrC constituents behave differently towards polarity on the basis of their source (fig. 5).

Dependance of Extraction efficiency on relative polarity:

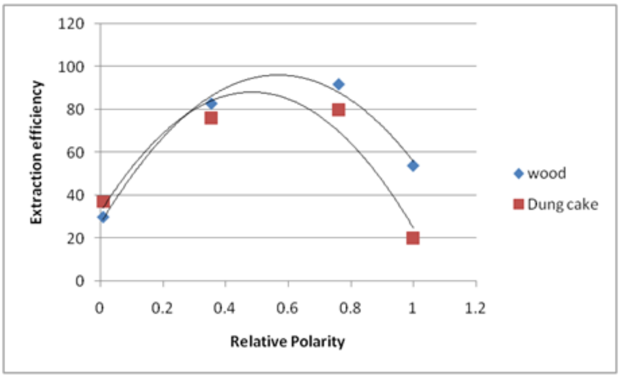

Figure 6. Extraction efficiency of solvents w.r.t. relative polarity (%)

The extraction efficiency depends on the polarity of the solvents. The extraction efficiency increased with increasing polarity, reached maxima and then decreased. As seen in fig 6, the extraction efficiency can be stated to be maximum in the relative polarity range of 0.4 to 0.8. This polarity dependence behaviour of OC is related to the nature of compounds present in the OC samples. It has been shown that OC aerosols generated from biomass combustion are mixture of fused polycyclic aromatic hydrocarbons, HULIS, tar, and other high molecular weight organic compounds.

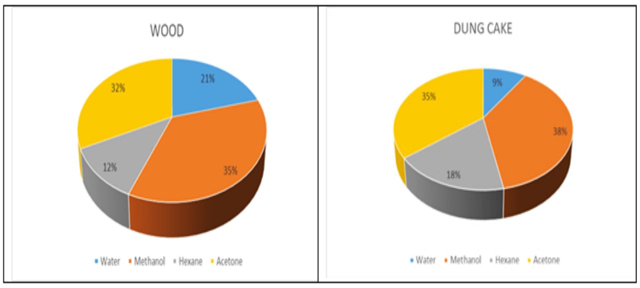

Figure 7. Absolute soluble carbon value for wood and dung cake (%)

Many studies have been done to know water soluble and water insoluble fraction of brown carbon. Chen, Y et al [17] observed that water soluble fraction of BrC is usually less (below 70%) than polar solvents (nearly 90%). In the present study, as shown in fig. 7, it is observed that Methanol has maximum relative extraction contribution amongst all the used solvents. Both Methanol and acetone shared maximum relative extraction efficiency in both the fuels. However water showed more relative efficiency in wood than in dung cake.

IV. CONCLUSIONS

Acetone and Methanol whose polarity index is in range of 5-6. showed highest efficiency for both fuels. The extraction efficiency showed an increasing trend with increase in relative polarity initially up to the value of 0.8 and then decreased with further increase. This shows that the BrC component in the biomass have a mid-polarity characteristic.

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