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Experimental Determination of Emission Factors of Vocs from Burning Commonly Used Biomass Fuels in India

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ABSTRACT

Biomass fuel is the prime fuel for cooking purpose especially in the developing countries like India. The fuels used in India are mainly biomass fuels in rural area and LPG in urban areas. Burning of domestic fuels emits gases such as CH_4, CO_2, CO, VOCs and some other trace compounds. The co-emission of VOCs has got attention in recent times due to their proved toxicity and carcinogenicity. Quantity and quality of VOCs in indoor environment depends on the choice of household fuels and combustion conditions. Apart from their health hazards, VOCs in environment also lead to the formation of ozone, secondary organic aerosol and other photo oxidants.

A lab-scale experiment was carried out for analysis of combustion generated VOCs by burning the common domestic fuels in India. Three types of fuels viz. wood, dung cake and LPG were used in this study. The fuels were burned in a specially designed setup and the generated exhaust gases were collected in special bags known as tedlar bags. The method of whole air sampling with Solid Phase Micro-extraction (SPME) technique followed by detection with Gas chromatography coupled with Flame Ionisation Detector (GC-FID) was developed and the concentrations of different VOCs in the sampled gases were determined. Major Volatile organic compounds which were present in gaseous samples were benzene, Toluene, cis-1,2- Dichloromethane, Ethyl benzene, o- Xylene, m- Xylene, p- Xylene, Styrene etc. CO and CO_2 concentrations were determined with special sensors. Emission Factors (EF) for NMHC in wood, dung cake and LPG were calculated by using Carbon mass balance methods. And the value obtained were 5.6, 17.5, 0.68 g/kg of dry mass for wood, dung cake and LPG respectively.

Keywords: Whole Air sampling; SPME; GC-FID; MCE, CE, EF, NMHC

I. INTRODUCTION

Globally, almost 3 billion people rely on biomass (wood, charcoal, crop residue, and dung) as their primary source of domestic energy [1, 2]. Smoke generated due to biomass burning contains a large number of pollutants including particulate matter, carbon monoxide, nitrogen dioxide, sulfur oxides and volatile organic compounds [3, 4]. Exposure to indoor air pollution (IAP) from the combustion of solid fuels has been implicated, with varying degrees of evidence, as a causal agent of several diseases including acute respiratory infections (ARI) and otitis media (middle ear infection), chronic obstructive pulmonary disease (COPD), lung cancer (from coal smoke), asthma, cancer of the nasopharynx and larynx, tuberculosis, perinatal conditions and low birth weight, and diseases of the eye such as cataract and blindness [4, 5]. VOCs and their public health impacts are drawing increasing concern from the environmental health research community, environmental regulatory agencies, industries, as well as the public. Adverse health effects of VOCs include headache, nausea, eye/throat/nose irritation,damage to liver, kidney and central nervous system. Benzene, toluene, ethylbenzene, o-, m- and p-xylene (BTEX) form an important group of aromatic VOCs. Among these, Benzene is classified by the International Agency for Research on Cancer as Group 1 human carcinogen. Toluene, ethylbenzene, o-, m-, and p- xylenes have been found to develop adverse health impacts on respiratory and neurological effects [6].

VOCs include a variety of chemicals, some of which may have short- and long- term adverse health effects. The quantity and quality of VOCs in indoor environment depends on the choice of household fuels and combustion conditions. The co- emission of VOCs along with other trace gases from combustion of biomass may further degrade the indoor air quality. As per census 2011, in India 67.2% households are using biomass and coal as a fuel for cooking. Dependency on biomass as cooking fuel is very much high in rural area as compared to urban area. Due to awareness and availability of other fuels like biogas and LPG, rural area people are encouraged to use LPG as cooking fuel. The figures from census 2001 and 2011 shows that the most significant increase in absolute number in LPG/PNG is at 109.6 percent followed by figures for no cooking with 26.5 percent. As per census 2011, use of firewood for cooking purposes by households is highest at 49.0 percent followed by LPG/PNG occupying a percentage share of 28.5 percent in the country. [7]

This paper focuses on determination of emission factor for volatile gases which are emitted from burning of wood, dung cake and LPG. Also a comparative study about modified combustion efficiency (MCE), of biomass and LPG combustion has been carried out.

II. MATERIALS AND METHODS

Firewood, dung cake and LPG fuels were purchased locally from Trombay, Mumbai.All solid samples were oven dried to reduce their moisture content at 60^0 C for one hour prior to experiment (Fig.1). The carbon percent in each fuels were determined using TC analyser (PrimacsSNC, Skalar). The carbon percentage obtained for dung cake, wood and LPG was 39, 50 and 82.44% respectively.

Figure 1. Photographs of collected fuels viz. firewood, dung cake and LPG stove

2.1 Experimental setup design

A combustion chamber was specially designed so that sufficient oxygen was available during burning of fuels.

The experiment was repeated five times for each fuel type for correct estimation of the emission. The combustion chamber (Fig. 2) was designed in three parts A, B, and C. Part A having a volume 0.0243 m3 was used for keeping the cooking stove, few holes were provided in wall for continuous availability of air during combustion of fuel. Part B, an upper cut pyramidal shape of volume 0.0130 m3was designed to provide dilution of gaseous emission prior to analysis. Part C a cylindrical shape of volume 0.0018m3was designed to sampleaportion of smoke for analysis and stack out the remaining. Sampling point was drawn from part C at a height of 0.90 m which is the breathing height in squatting posture. Sampling was forced through part C with using motor.

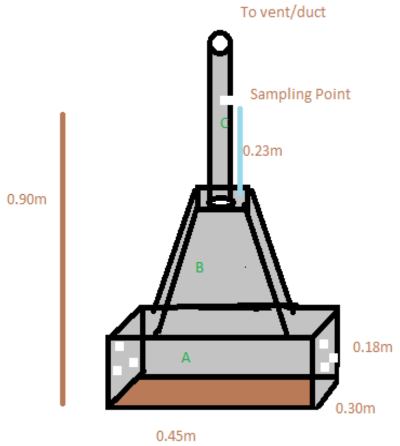

Figure 2. Combustion chamber design: part (A) of setup design to contains stove, part (B) was provide a space to combustion emission gases get cool and dilute prior to analysis while part (C) contain sampling point.

The experimental setup for collection of gas samples in tedlar bag from sampling point of combustion chamber is shown in Figure 3. Gas sample which are coming out from sampling point of combustion chamber are allowed to pass through the filter paper.

Filter papers were used to separate particulate matter from gas sample. After removal of particulate matter gas samples were passed through dilution chamber and then from dilution chamber filled in tedlar bag with the help of pump.

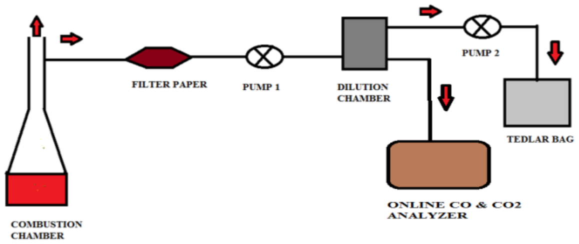

Figure 3. Experimental set up for collection of gas sample

Purposes for providing dilution chamber was to lower down the temperature of gaseous emission and also to make homogenous mixture. Inlets for CO & CO$_2$ monitor were directly taken from dilution chamber.

2.2 Extraction and sampling

After collecting the gas sample in Tedlar bag, SPME technique was used for extraction and sampling of gases from tedlar bags. Solid-phase micro extraction (SPME) is a simple and effective adsorption and desorption technique, which eliminates the need for solvents or complicated apparatus, for concentrating volatile or non-volatile compounds in liquid samples or headspace. SPME is compatible with analyte separation and detection by Gas chromatography [8]. This method was invented by Pawliszyn in 1989 [9]. In this technique, sampling, extraction and pre concentrations are incorporated into a single step and the use of solvents, where possible environmental pollutants may reside, is eliminated. A fused-silica fibre, coated with a polymer, is exposed to the gaseous sample or immersed in an aqueous sample to extract the analytes. The fibre is then injected into the gas chromatography injection port for thermal desorption and analysis. 50/30µm, DVB/CAR/PDMS (Divinylbenzene/Carboxen/Polydimethylsiloxane) SPME fibre was used in this study due its high response for volatile organic The Analytical detail of SPME fibre are given in Table 1.

Table 1. Analytical information about SPME (DVB/ CAR/ PDMS)

Fiber coating	**DVB/CAR/PDMS(Divinylbenzene/Carboxen/ Polydimethylsiloxane)**
Fiber core	Stable Flex(1cm)
Hub description	Gray/plain
Film Thickness	50/30μm
Maximum temperature (◦C)	270
Recommended Operating Temperature(◦C)	230-270
Exposure time(min)	5
Desorption time(min)	2

2.3. Analysis of VOCs using GC-FID

Analytical gas standards were prepared using volumetric injection. A known amount of VOCs standard gas mixture (DW-VOC Std. #2 200 μG/ml, P&T Methanol,) from RESTEK was loaded into 300ml glass container through a septum using a gas-tight syringe. After the sample preparation, the SPME syringe needle was inserted into glass container filled with standard gas mixture through a septum. The DVB/CAR/PDMS SPME fiber was then lowered into the standard gas by depressing the plunger. Target VOCs were partitioned into the polymeric coating of the fiber until equilibrium was reached. The plunger was then withdrawn, and the needle was removed from the standard gas container. After exposing for 5 min, the fiber was directly injected into GC inlet port with desorption for 2min at 250 ◦C in the GC injector. The gas samples collected in Tedlar bag were extracted using the same procedure followed in SPME extraction from a standard gas glass container. Analysis were carried out on a Gas chromatograph model GC- 2010 plus, Shimadzu make which was connected to a Flame Ionization Detector. The GC injection port was maintained at a temperature of 250◦C for thermal desorption. Separation was carried out on a 60 m × 0.25 mm × 0.25 μm capillary column while column oven temperature was initially held at 50 ◦C for 1 min, programmed to 280 ◦C at a rate of 15◦C/min. High-purity helium (99.995%) was used as a carrier gas at a flow-rate of 1 mL/min. In FID H_2 flow rate, air flow rate and make up gas (helium) flow rates were 30ml/min, 400ml/min, 30ml/min respectively.

2.4. CO and CO_2 measurements

For carbon dioxide and carbon monoxide, sample was taken directly from the dilution chamber. Both Carbon monoxide and dioxide were measured by using individual online monitors which are coupled with Non Dispersive Infra Red (NDIR) detector.

III. RESULT AND DISCUSSION

Samples of exhaust gases generated from burning of biomass and LPG were collected in tedlar bags. Samples were classified based on phase of combustion (flaming and smoldering). Concentrations of carbon dioxide, carbon monoxide, methane, and non-methane hydrocarbons (VOCs)were determined in the collected samples. On the basis of this analysis data, emission factors for individual VOCs emitted in the combustion were calculated for each fuel (wood, dung cake and LPG).

Combustion efficiency (CE) is defined the as the ratio of carbon (C) emitted as CO_2 to the total amount of carbon emitted. By definition the combustion efficiency is the fraction of fuel carbon emitted by the fire that is completelyoxidized to CO_2. Modified combustion efficiency is defined as ratio of CO_2 to the sum of CO plus CO2 concentration [10].

Modified combustion efficiency depends only on the CO_2 and CO concentration in gas sample. Due to complete combustion Modified combustion efficiency (MCE) value was maximum in LPG as compared to other fuels. (As shown in figure 4). Dung cake was having least MCE due to incomplete combustion of dung cake and impure quality.

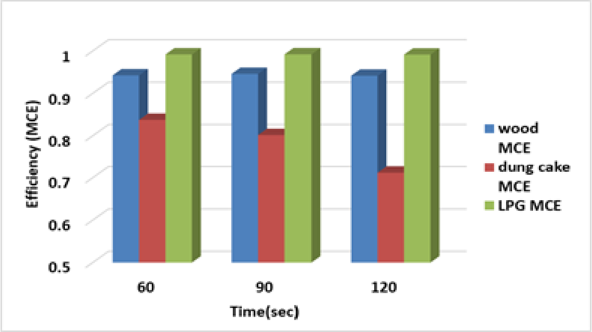

Figure 4. modified combustion efficiency of fuels

Burning of biomass takes place in 4 stages: Dehydration, Pyrolysis and gasification, flaming and smoldering. In this study only flaming and smoldering cases are discussed. The CO_2 and CO Concentrations for wood, dung cake and LPG are shown in Figure 5. In wood, CO_2 showed increasing trend up to flaming phase and after that due to prevailing of smoldering phase over flaming CO_2 value started decreasing. While in case of CO the concentrations showed increasing trends throughout burning of fuels. In dung cake smoldering phase prevails during the entire combustion. Due to incomplete combustion in dung cake, carbon monoxide (CO) value was high compared to wood and LPG. In LPG, due to complete combustion only flaming phase exists during entire combustion. It was found that in LPG, Carbon monoxide concentration was 100 to 200 times lower than CO_2 concentration.

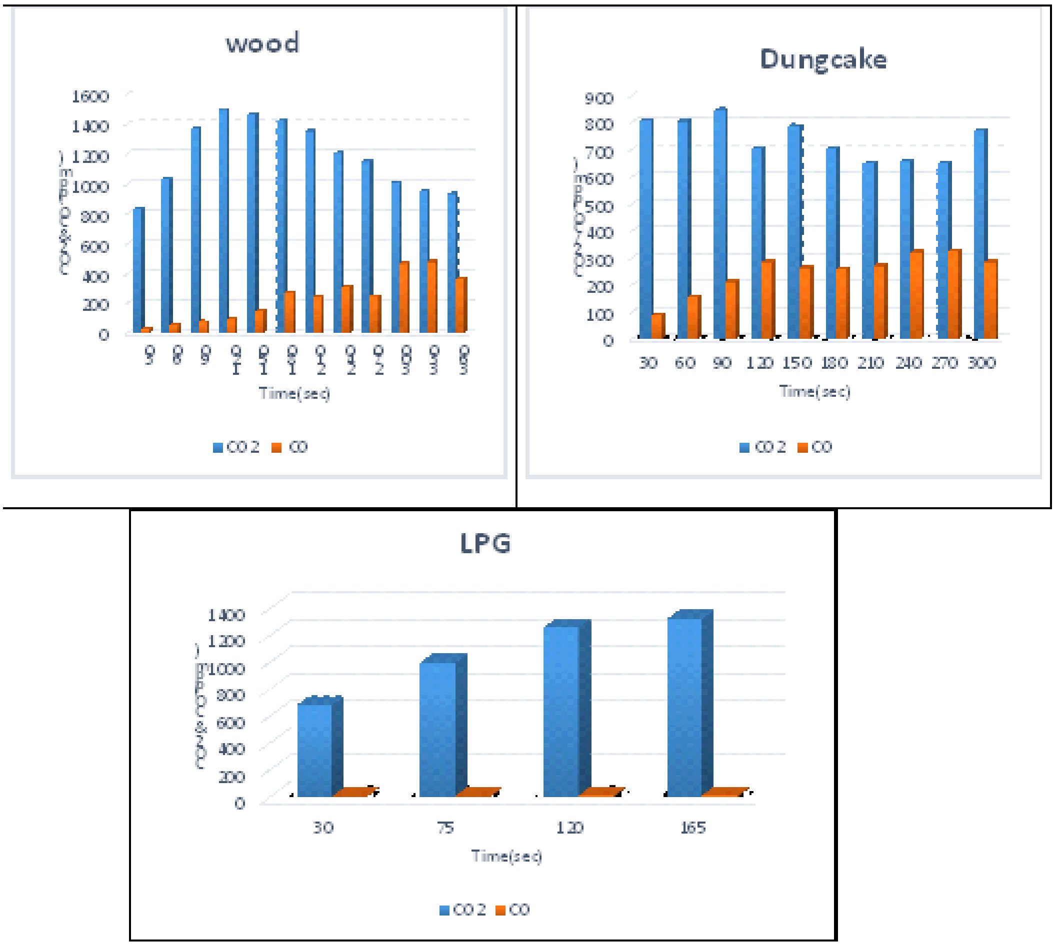

Figure 5. Carbon monoxide and carbon dioxide concentration for wood, dung cake and LPG

Emission factor is determined by Carbon Mass Balance (CMB) method. The underlying premise of this method is that all of the carbon combusted in a fire is emitted into the measurable portions of a smoke plume in five forms: CO2, CO, CH4, non-methane hydrocarbons, and particulate carbon in smoke particles. The emission factor of a species, *n*, is then calculated from the ratio of the mass concentration of that species to the total carbon concentration emitted in the plume [10]

$$\mathrm{EFn} = \frac{[\mathrm{n}]}{[\mathrm{C}]\mathrm{CO2} + [\mathrm{C}]\mathrm{CO} + [\mathrm{C}]\mathrm{CH4} + [\mathrm{C}]\mathrm{NMHC} + [\mathrm{C}]\mathrm{PC}} \qquad (1)$$

Where, the subscript CO2 is for carbon dioxide, CO is for carbon monoxide, CH4 is for methane, NMHC is for non- methane hydrocarbons, and PC the particulate carbon emitted. The emission factor is expressed in units of mass of species n emitted per unit mass of carbon burned. To convert this emission factor to the more commonly used grams n produced per kg dry matter burned, EFn is multiplied by the mass fraction of carbon in the fuel.

Table 2. Emission factor (g/kg of dry mass) for gaseous compounds

Fuel type	Cis-1,2-Dichloroethene	Toluene	Chloro benzene	Ethyl benzene	P&m Xylene	o-Xylene + Styrene	Benzene	NMHC
Wood								
Flaming	0.1140	1.0336	0.0688	0.1574	0.1739	0.2971	0.0008	1.8459
Smoldering	0.1160	4.3768	0.6668	0.68669	1.8819	1.0042	0.0023	8.7350
Dung cake flaming	0.1804	5.9428	1.2981	2.01908	5.2225	2.8001	0.0017	17.4648
LPG smoldering	0.0042	0.2002	0.1664	0.07565	0.1574	0.0709	0.00003	0.6749

In Eq. (1) <EF$_n$> needs to be a mass average over the entire life of the fire. However, emission factors are typically determined at instantaneous measurements. A carbon budget is formulated from specific samples as opposed to being constructed from a continuous measurement. Since flaming and smoldering combustion are the two distinct phases of combustion, <EF$_n$> could be weighted by emission factors for these two distinct components (EF$_{nf}$ and EF$_{ns}$, for flaming and smoldering combustion, respectively) by the fraction of biomass consumed by each process. [10]

Emission factor for gaseous compounds depends upon the combustion efficiency of fuels. According to experimental data given in Table 2 emission factor for VOCs in dung cake was 25 times larger than LPG. This shows that combustion efficiency for LPG is more as compared to dung cake. As given in Table 2 emission factor for VOCs in smoldering phase of wood burning was 5 times more than the flaming phase, it shows that in smoldering phase, the combustion efficiency is less compared to flaming phase.

IV. CONCLUSION

It was observed that emission factor for NMHC depends upon type and quality of fuels. In dung cake, emission factor for NMHC was maximum. It showed that dung cake is not good fuels for household purposes. LPG showed very low Emission factor for

NMHC as compared to wood and dung cake. It shows that LPG is safest and environmental friendly fuel for household purposes.

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