23rd ABCM International Congress of Mechanical Engineering
December 6-11, 2015, Rio de Janeiro, RJ, Brazil

DETERMINATION OF EMISSION FACTOR OF METHANE AND NON-METHANE HYDROCARBONS FROM FOREST BIOMASS COMBUSTION

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Abstract. *Biomass combustion releases several compounds into the atmosphere, among them are hydrocarbons. These compounds can be classified as methane and non-methane hydrocarbons (NMHC). Hydrocarbons are emitted in low concentration, but nevertheless, they significantly affect the biogeochemical cycles in the atmosphere. Non-methane hydrocarbons, for example, play a very important role as precursors of O_3 and particulate matter. NMHCs emissions are little known, since they require more complex analytical procedures for its determination. Thus, the objective of this study was to determine the emissions of hydrocarbons, methane and non-methane, generated during forest biomass combustion. In the laboratory, Araucaria and Amazon biomass were burned. The gas generated during combustion was stored and subjected to analysis by Gas Chromatography coupled with Flame Ionization Detector method. The burning of Amazon biomass resulted in higher emissions. Emission factors for Amazon biomass (g/kg) were of 2.24±0.59, 0.56±0.16, 0.21±0.07, 0.18±0.05, 0.13±0.06 and 0.20±0.09, respectively for CH_4, (C_2H_2 +C_2H_4), C_2H_6, C_3H_6, C_3H_4 and C_3H_8. The method of Gas Chromatography showed good sensitivity in the detection of hydrocarbons from biomass combustion.*

Keywords: *Gas Chromatography, methane, non-methane hydrocarbons, forest biomass, combustion.*

1. INTRODUCTION

Amaral *et al.* (2014a) described that the biomass combustion is one of the best way to reduce the consumption of fossil fuels. Wood is one of the important renewable resources and its use provides substantial benefits as far as the environment is concerned. Biomass absorbs carbon dioxide during growth, and emits it during combustion. Therefore,

biomass helps the atmospheric carbon dioxide recycling and does not contribute to the greenhouse effect. Biomass consumes the same amount of CO_2 from the atmosphere during growth as is released during combustion (Demirbas, T. and Demirbas, C., 2009). For Cieslinski *et al.* (2015), this material provide utility, flexibility, cleanliness and economy, when it is used as fuel. However, use of forest biomass as an energy source is only sustainable when renewable biomass is used. This mainly consists of waste from forest harvesting and lumber mills (Amaral *et al.*, 2014b).

Even though it is a renewable source of energy, the forest biomass combustion emits into the atmosphere, numerous polluting compounds. Williams *et al.* (2012) described the biomass combustion consists of the heating-up and drying, devolatilization to produce char and volatiles, where the volatiles consist of tars and gases, combustion of the volatiles and combustion of the char. Emission components can be grouped in two general categories according to the type of reaction: components from a complete combustion and components from an incomplete combustion. A complete combustion process takes place when all biomass components react with sufficient oxygen from the air (Villeneuve *et al.*, 2012). When complete combustion is achieved, carbon (C) and hydrogen (H) are respectively oxidized to carbon dioxide (CO_2) and water (H_2O), producing energy as heat at elevated temperatures (Demirbas, T. and Demirbas, C., 2009).

According to Villeneuve *et al.* (2012), other compounds released from the complete combustion include nitrogen oxides (NO_x, mainly nitrogen monoxide (NO) and dioxide (NO_2)), nitrous oxide (N_2O), sulfur oxides (SO_x, mainly sulfur dioxide (SO_2)), hydrogen chloride (HCl), particulate matter (PM) and heavy metals.

An incomplete combustion of the fuel results from an overall lack of available O_2, an insufficient mixing of air and fuel in the combustion chamber, a low combustion temperature, or a short residence time. The components emitted to the atmosphere as a consequence of incomplete combustion include CO, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), PM, methane (CH_4) and other hydrocarbons and small amounts of ammonia (NH_3) (Villeneuve *et al.*, 2012; Neto, *et al.*, 2009; Demirbas, 2004). In studies of Lobert *et al.* (1990), involving the biomass burning in laboratory, the main compound issued was CO_2, followed by 10 % of CO and approximately 2% of CH_4 and other hydrocarbons.

Hydrocarbons are emitted in low concentration, but nevertheless, they significantly affect the biogeochemical cycles in the atmosphere (Neto, *et al.*, 2009). Non-methane hydrocarbons (NMHCs), for example, play a very important role as precursors of O_3 and particulate matter. According to Barker *et al.* (2007), the contribution of CH_4 as a greenhouse gas is 21 times that of CO_2.

Gas Chromatography coupled with Flame Ionization Detector (GC-FID) is used for non-methane hydrocarbons monitoring. CO_2, NO_x and CO concentrations are, in general, well reported (Amaral *et al.*, 2014b; Njenga *et al.*, 2014; Wei *et al.*, 2012; Burling *et al.*, 2010; Gonçalves *et al.*, 2012; Neto *et al.*, 2011), but not the ones of individual NMHCs which require more complex analytical procedures (Alves *et al.*, 2010). For all these reasons is substantially important to correct, complete, and enlarge the existing long-term databases in order to report reliable mixing ratios of individual NMHCs species. Neto *et al.* (2009) highlighted that the quantification of such emissions is essential to predict environmental impacts.

Thus, the objective of this study was to determine the Emission Factor (EF) of hydrocarbons, methane and non-methane, generated during forest biomass combustion. Hydrocarbon analysis was made through by Gas Chromatography coupled with Flame Ionization Detector (GC-FID). The following components were evaluated: CH_4 (Methane), C_2H_2 (Ethyne), C_2H_4 (Ethene), C_2H_6 (Ethane), C_3H_6 (Propene), C_3H_4 (Propyne) and C_3H_8 (Propane).

2. MATERIAL AND METHODS

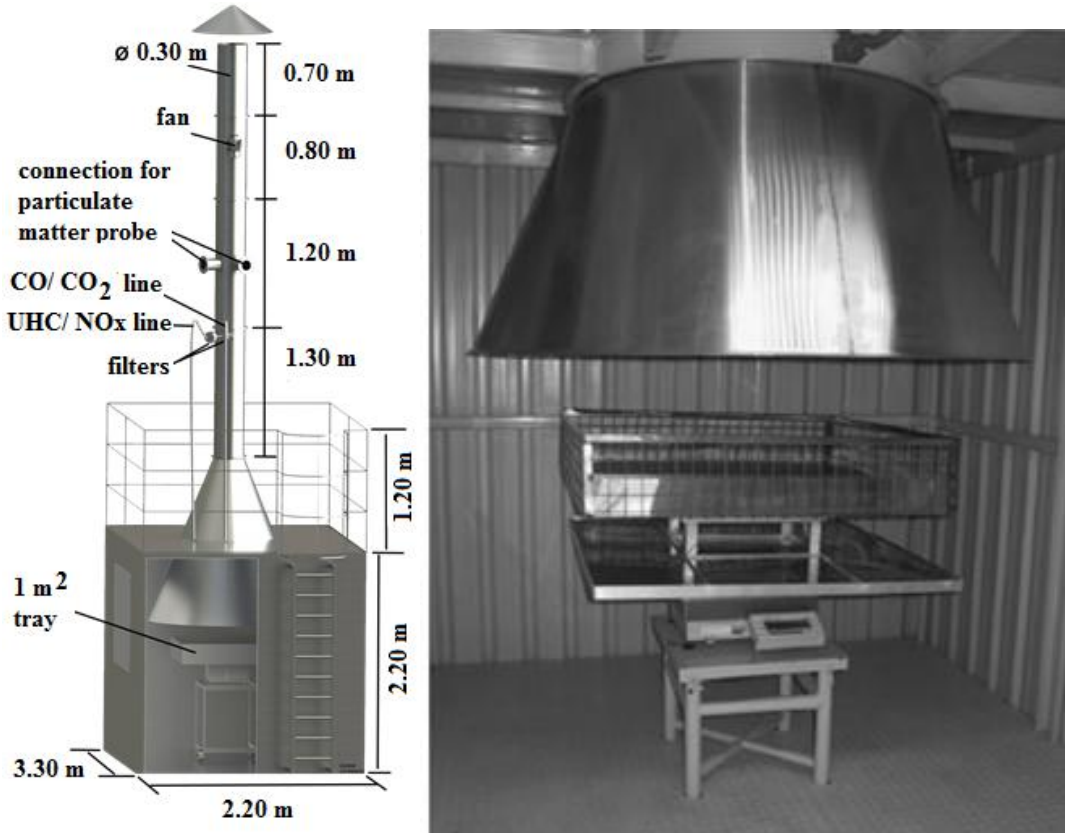
2.1 Biomass fuels and experimental setup

For the burn experiments, conducted in this study, the forest biomasses of Araucaria and Amazon were employed. The moisture content of biomass was approximately 12 %. Four experimental repetitions were performed for the burning of Araucaria biomass, and five repetitions for Amazon biomass. In each experimental repetition, approximately 1.5 kilogram of biomass was burned. The biomass was composed of 90 % branches, with a maximum of 2 cm^2 cross-section. The remaining material was composed of thin branches and leaves.

The burning experiments were conducted at INPE of Cachoeira Paulista, SP, Brazil. In the center of a container, a tray (1 m^2) was placed on a balance for measuring the fuel mass variation along the combustion process. The balance showed response time of 1s and was coupled to a microcomputer, which through the LabView platform, made the signals acquisition. The ignition of combustible material was carried out with the aid of a torch, with Liquefied Petroleum Gas.

The gases generated in combustion process were directed up a chimney. The targeting of the gas was done with the aid of an axial exhaust fan. A diaphragm pump was used to suck the gas samples through probes installed inside the chimney, and these were conducted for filters and thermal baths. In the filters were retained the particles, and in the thermal baths, moisture and tar were removed.

An illustration of the combustion device can be visualized in Fig. 1.



(a) (b)

Figure 1. (a) Scheme of combustion equipment; (b) details inside the container.

Additional details about the experimental setup can be found in the work of Neto *et al.* (2011).

After gases filtration, a system for collection of samples, for analysis in Gas Chromatograph, has been adapted (Fig. 2). In this adapted system samples were stored in canisters and subsequently transported to the laboratory for analysis.

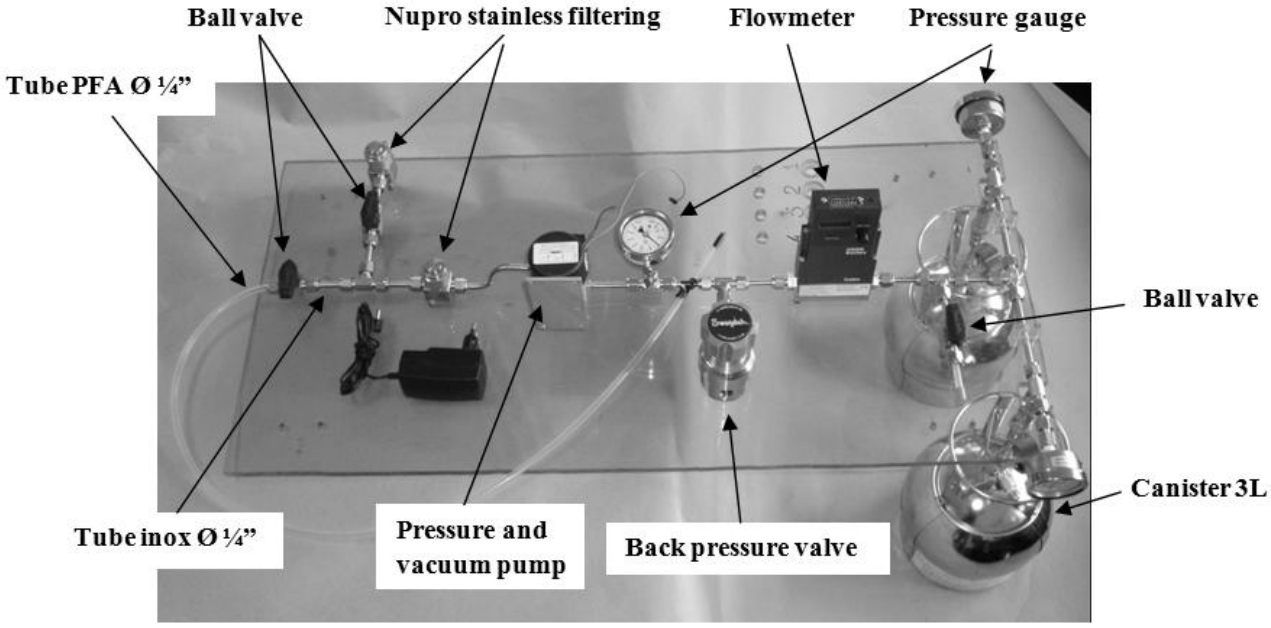


Figure 2. System of gas sampling mounted and fixed in acrylic table.

2.2 Chromatographic analysis

The methane and non-methane hydrocarbons, contained in the gases from the combustion of forest biomass, were determined in chromatograph Auto System Model, PerkinElmer.

Initially, the column of the chromatograph was enabled through heating. This procedure was used to prevent impurities adsorbed on column interfere with the separation of combustion products. The column used was the type packed (Haye Sep; 12 ft).

After heating, chromatographic analysis, of three standards of known concentrations, certified by Air Liquide, were held. Standards analysis allows obtaining from the area of each species that you intend to analyze.

After obtaining the area, gas samples were injected into the chromatograph, through a system adapted. This system contained a quick coupling, for fitting the canister into the chromatograph and a needle valve. The needle valve was used to control the flow of the sample entry in the loop side of the injection valve gas chromatograph.

The chemical species, of the samples analyzed, were separated on column. After the separation of the species in the column, the same were burned and quantitatively detected in a Flame Ionizing Type detector (FID).

The gas chromatograph contained an automated system. In this system it was possible to control the several parameters that influence on chromatographic analysis, including time, temperature of the injection chamber, chamber temperature of the column, column type, the gas flow of drag, etc.

For control of process variables was selected the EMI method, contained in the software of the gas chromatograph, and whose values are specified in Table 1.

Table 1. Values used in gas chromatography (EMI Method).

Factors	Values
Haye Sep Column	12 ft
Analysis time	53 min
Flow of Helium carrier gas (He)	30 ml/min
Injector temperature	250 °C
Detector temperature	350 °C
Flow of H_2 at the FID	45 ml/min
Flow of air at the FID	450 ml/min

After detection of the chemical species, their concentrations were determined through calculations. These calculations were made taking into account the standards areas, which were obtained in the gas chromatograph, and their concentrations. With these values were plotted area curves in function of the concentration, which were referred to as calibration curves. Through the standard calibration curve it was possible to determine the concentrations of gases in the samples analyzed.

2.3 Emission factor calculation

After the tests, the data obtained in the analyses by Gas Chromatography were used for the calculation of Emission Factors of hydrocarbons.

The emission Factor is a parameter that is widely used in the study of biomass combustion emissions. EF corresponds to the mass of a gas emitted in grams per kilogram of dry biomass consumed during the combustion process, according to Eq. 1:

$$EF_X = \frac{V_{Total-chimney}}{m_{fuel(dry\ basis)}} \cdot \frac{[\ ]_{X-gas}}{V_{X(1\ mol\ at\ 1\ atm\ and\ 0°C)}} \quad (1)$$

In the Eq. 1, EF_X is the emissions factor of species X (g of species x per kg of dry fuel burnt); $V_{Total-chimney}$ is the total gaseous volume of the chimney during the burn (m^3); $[\ ]_{x-gas}$ is the average concentration of species X (ppm); M_X is the molecular mass of species X (g/mol); m_{fuel} (dry basis) is the quantity of dry fuel consumed (kg); and V_X is the molar volume of the gas at STP. V_X is 0.0224 m^3.

3. RESULTS AND DISCUSSION

The chromatographic analysis allowed the detection of methane and non- methane hydrocarbon. Among the non-methane were evaluated the C_2H_2+C_2H_4, C_2H_6, C_3H_6, C_3H_4 and C_3H_8.

Figure 2 illustrates the percentage of methane and non-methane compounds in the total of hydrocarbons analyzed in the flue gases. Methane accounted for about 64 % of total hydrocarbons analyzed in the gases from the forest biomass burning. The 36 %, of the remaining hydrocarbons, are assigned to non-methane.

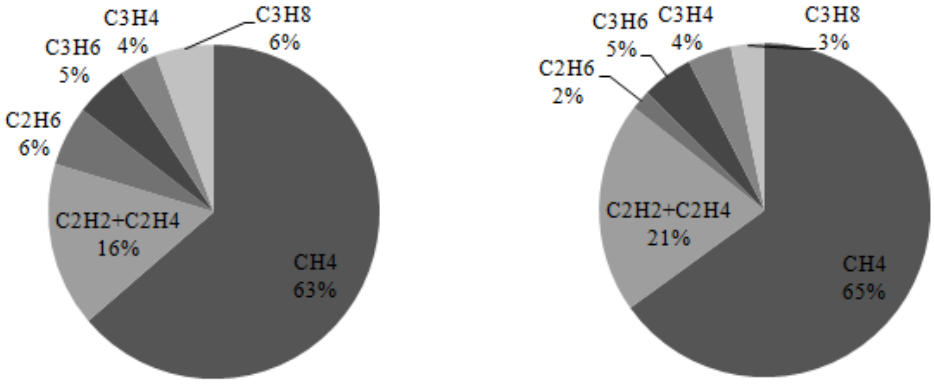


Figure 2. Percentage of methane and non-methane hydrocarbons in the flue gases: (a) Amazon biomass; (b) Araucaria biomass.

During Amazon biomass burning, C_2H_6, as well as the C_3H_8, represented 6% of hydrocarbons analyzed. For Araucaria biomass, the percentage of these compounds was lower than Amazon biomass.

Despite the high sensitivity and comprehensiveness of the Gas Chromatography in the detection of hydrocarbons, this equipment is not able to separate the compounds ethene and ethyne. The percentage of ethene and ethyne in Araucaria biomass, was 21%, while in gases from Amazon biomass burning this value was 16%.

In the case of emission factors (g/kg) for Amazon biomass, were of 2.24±0.59, 0.56±0.16, 0.21±0.07, 0.18±0.05, 0.13±0.06 and 0.20±0.09, respectively for CH_4, C_2H_2+C_2H_4, C_2H_6, C_3H_6, C_3H_4 and C_3H_8.

The emission factor (g/kg) of CH_4, C_2H_2+C_2H_4, C_2H_6, C_3H_6, C_3H_4 and C_3H_8, for Araucaria biomass, was 1.29±0.38, 0.41±0.11, 0.04±0.03, 0.10±0.03, 0.08±0.01 and 0.07±0.01, respectively.

The total emission factor of non-methane hydrocarbons was of 1.28 g/kg, for Amazon biomass, and of 0.69 g/kg, for Araucaria biomass.

In General, higher emissions of methane (2.24±0.59 g/kg) and non-methane hydrocarbons (1.28 g/kg) were observed during the burning of Amazon biomass.

As discussed in section 1, the potential polluter of methane is 21 times that of CO_2 (Barker *et al.*, 2007). In this way, Amazon biomass burning has a potential polluter, higher than of the Araucaria biomass.

Alves *et al.* (2010) and Neto *et al.* (2011) described that the methane emissions are higher for fires with low combustion efficiency. In studies of Amaral *et al.* (2014b), it was observed that during the Amazon biomass burning the carbon dioxide emission, that is responsible for increased combustion efficiency, was lower than Araucaria biomass. In this way, the higher emission of hydrocarbons, in the Amazon biomass burning, is related to with its lower combustion efficiency.

In Table 2, the emission factors found in the literature, for the burning of forest biomass, are showed.

Table 2. Emission factors values (g/kg) of methane and non-methane hydrocarbons, found in the literature, for the forest biomass burning.

CH_4	NMHC	Type of measurement	Reference
1.29 ± 0.38	0.69 ± _	Laboratory	Araucaria biomass
2.24 ± 0.59	1.28 ± _	Laboratory	Amazon biomass
3.40 ± _	2.56 ± _	Ground, flaming	Neto *et al.* (2009)
7.30 ± _	4.72 ± _	Ground, intermediate	Neto *et al.* (2009)
13.10 ± _	7.49 ± _	Ground, smoldering	Neto *et al.* (2009)
6.80 ± 2.00	_ ± _	Review	Andreae and Merlet (2001)
14.20 ± 5.90	_ ± _	Laboratory	Neto *et al.* (2011)
3.20 ± 0.50	_ ± _	Laboratory	Amorim *et al.* (2013)

The emission factor values found in the literature, for gases emitted during the burning of forest biomass, were higher than those obtained in this work.

In studies of Neto *et al.* (2011), the NMHC emission factor ranged between 2.56 and 7.49 g/kg. However, these values have been obtained from the combustion of biomass in the field. The biomass burning in the field can be less efficient than that carried out in the laboratory, which leads to increased hydrocarbon emissions. Methane emissions, found in the literature, ranged from 3.40 to 14.20 g/kg.

4. ACKNOWLEDGEMENTS

Funding for this study was provided by the State of São Paulo Foundation for the Support of Research (FAPESP) Brazil (Thematic Project number 2008/04490-4 and 2013/21231-0).

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