Semivolatile and volatile compounds evolution during pyrolysis and combustion of Colombian coffee husk

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ABSTRACT

Thermal characterization of coffee husk (*Coffea arabica*) from Colombian coffee has been studied. Different products, mostly volatile and semi-volatile compounds, were analyzed paying special attention to 16 polycyclic aromatic hydrocarbon classified by *Environmental Protection Agency* (EPA) as priority pollutants, frequently used for checking toxicity in environmental samples. Fixed amount of raw material was exposed to different excess air ratios (λ: 0-2.33) and nominal temperature of 1123 K in a horizontal quartz reactor. The results show that coffee husk is a promising biomass for energetic exploitation with reduced formation of PAH in low air excess ratio. This implies reduction of carcinogenic potential in limited presence of oxygen, demonstrated by calculating the carcinogenic potential (KE) for each experimental condition. Most volatile and semi-volatile compounds followed different trends with the oxygen presence prevailing their decomposition with increasing the air excess ratio.

1. INTRODUCTION

A great part of world economy relays on petroleum and its byproducts. The finding of energy alternatives will be boosted in coming years after the historic Paris Climatic Change Conference where more than 180 nations signed an agreement to combat climatic change. Basically, developing countries must gradually stop using the most polluting fossil fuels. Under this context, alternative sources of energy plays an important role to replace traditional fossil fuels. This challenge requires a shared effort aiming to acquire scientific and technological development to diversify energy sources and control the massive emission of greenhouse gases into atmosphere [1].

Biomass is considered as potential source of renewable energy that provide higher advantages than fossil fuels. This is especially true in terms of greenhouse emissions, since it is considered a CO_2 neutral option energy generation[2-4]. The agricultural Colombian sector generates an important amount of biomass that partly becomes waste with great disposal problems. It is known that the accumulation and improper disposal of residues from forestry and agriculture generates multiple environmental problems like contamination of soil and groundwater[5].

Some countries that with agriculture as the main economy sector have taken advantage of such potential for using clean energy from agricultural and forestry crops[6].

Fifty years ago, Colombia initiated an effort to increase coffee quality, and as a result now has the reputation as the best coffee in the world. Colombia produced 720.000 tons of coffee in 2014, with data of the International Coffee Organization, which

represents the third country worldwide as higher producer of coffee bean (*Coffea arabica*). A 97 % of the coffee produced was exported. In this context, coffee farming contributes widely to Agricultural Gross Domestic Product from Colombia[7].

The wet coffee fruit consists of a smooth outer skin or pericarp, which covers the soft yellowish berry. This is followed by a translucent, thin, viscous and highly hydrated layer of mucilage (called pectin layer) and another thin layer of endocarp, yellowish in color called husk or parchment [8]. The coffee grains can be managed by two ways, dry and wet processing. Less than 5 % of the biomass generated is used for drink preparation, remaining an important fraction that corresponds to leaves, lambs, steam, pulp and husk. Coffee generates significant amount of agricultural waste ranging from 30% to 50% the weight of the total coffee produced, depending on the type of processing[9]. Coffee husk corresponds to an unexplored biomass and represents around 4.5 % of weight on wet basis coffee. Colombia alone produce around 0.6 million tons/year of coffee husk [10], which because of its thermal energetic properties it is frequently used as fuel on drying process of the bean but great part of this material is accumulated as waste[11].

Coffee husk has been partially studied. A recent work from Oliveira and Franca[9] shows different attempts for determine the potential uses of coffee husk as biofuel. Their principal conclusion shows that it constitutes a promising alternative, but there still is a need for significant research to make it both technically and economically viable.

Mentioned by Saenger et al. [12] one of the reasons for the low level of usage of coffee husks as fuel for direct combustion is the lack of sufficient information concerning

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the combustion and emission characteristics of these residues. In this way, just some works have been focused on flash pyrolysis of coffee husk with tar characterization [13] including elemental analysis[5].

Other authors have used torrefaction processes to evaluate coffee husk's energetic potential[2]. Thermal degradation and kinetic parameter has been also analyzed[14]. Concerning the coffee husk from Colombia, a study on co-gasification with coal for determining the syngas generation has been reported[11]. Gas produced from co-combustion was found to be rich in hydrogen and a higher proportion was observed with increasing biomass percentage. Others produced gases were CO, CH_4 and different hydrocarbons (tars). According to Dominguez et al.[15] pyrolysis of coffee husk produces mainly H_2, CO, CO_2,CH_4,C_2H_4 and C_2H_6 under different temperatures analyzed.

Despite of polycyclic aromatic compounds are priority compounds to be expected in a biomass combustion[16], in literature there is a lack of research focused on PAH determination in combustion of coffee husk an even less considering different oxidation conditions.

In this context, with the purpose of continuing effort for improving the knowledge on biomass and its implications for energetic usage, the present work reports new experimental data on coffee husk (*Coffea arabica*) by a comprehensive gas characterization, and paying special attention on polycyclic aromatic hydrocarbons (PAHs) formation[17, 18]. United States Environmental Protection Agency (U.S. EPA) has classified sixteen PAHs as priority pollutants (EPA−PAH): naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene,

pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, indene(1,2,3-cd)pyrene, dibenzo(ah)anthracene, and benzo(g,h,i)perylene. Additionally, the carcinogenic equivalence sum (KE) has been determined in different experiments and an attempt has been made to evaluate the influence of different oxidative environments on the harmful effect for health.

Experiments were carried out by using a horizontal plug flow reactor in pyrolysis and combustion conditions of 0.3 g of coffee husk, under different excess air ratio (ʎ: 0.1, 0.25, 0.6, 1.4, 2.33) at a fixed nominal temperature (1123 K) and atmospheric pressure. Additional semi-volatile branch aromatic hydrocarbons, and others containing oxygen and/or nitrogen, were quantified.

2. MATERIALS AND METHODS

2.1 Raw material

Coffee husk was collected at Los Naranjos farm (2°35´0.5" N, 76°32´57" O) at 1700-1900 meters above sea level in Cajibio (Cauca, Colombia). The location is about 14 km north of Popayán and is property of SUPRACAFÉ Company and "Parque Tecnicafe". Samples correspond to specie *Coffea arabica* and mixture of subspecies Bourbon, Typica, Castillo and Caturra. Samples were collected using simple random sampling.

Samples were ground by using a Dinko laboratory blender, by time intervals for avoiding the overheating of samples and consequently the devolatilisation of compounds from coffee husk, which can occur at low temperatures[12]. All the

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experiments presented in this paper were carried out with dried samples. To achieve the sample homogeneity, material went through screening with mesh of 1 mm. Table 1 shows the characterization values of raw material. Elemental analysis of the major components was carried out in a Perkin Elmer 2400 apparatus. The net calorific value (NCV) was determined in an AC-350 calorimetric bomb from Leco. Ash percentage and moisture content were determined according to European Standards UNE-EN 14775 and UNE-EN 14774-1, respectively. Each parameter was developed in triplicated for assuring the validity of the results.

Ultimate analysis results are similar to those reported by other authors in previous work by using coffee husk from different species (eg.[5, 19]). By means of theoretical procedures, described by Dorge et al. [20] and Friedl et al. (2005) [21], it was established that the husk net calorific value is 4000 Kcal/Kg, which is similar to the experimental value measured in the present work.

As recommended by the standard UNE-EN 15290, a semi-quantitative analysis of element weight percentages from coffee husk by X-ray fluorescence, with an automatic sequential spectrometer (model PW2400, Philips Magix Pro Philips Co., Ltd.) was also determined (Table 2). As mentioned by the above regulation, a detailed description of element concentration from potential biofuels should be reported for determining the values of some toxic elements or its possible additional usage of its sub-products.

In general, elements present in coffee husk are the typical ones found in agricultural biomass with the unique difference of a major presence of K and Ca, that match information from other authors [15]. Due to major presence of these metals, the coffee

husk is frequently used and applied to soil as fertilizer, rather than energy source [5].
This fact, at the same time, gives an opportunity to use ashes produced after thermal
conversion process as manure for coffee crops.

High amounts of calcium/potassium in thermal processes should be taking into
notice due to combustion process. These metals are released into the atmosphere
as inorganic particles and cause problems of agglomeration, fouling, slagging and
corrosion[16]. This must be an important fact to be considered in the appropriate
design of burners. As mentioned by Jones et al.[16], potassium could react in favorable
conditions to form KCl in the gas stream of combustion or condense on the K_2SO_4
nuclei forming a high concentration of fine aerosols which may cause pollution and
potential risk for human health. In this case, burners should be equipped with
efficient particles control system. Nevertheless, this precaution has to be taken in all
combustion systems independent if the fuel employed is biomass or not.

2.2 Experimental set-up

Seven experiments of pyrolysis and combustion were done in a batch laboratory
scale horizontal tubular reactor placed inside of an electric furnace. Experimental
setup is described in detail elsewhere[22]. The reactor temperature was fixed at 1123
K and excess air ratio (λ), calculated as in Conesa and Domene[3], was varied
between 0 (pyrolytic conditions, in nitrogen) and 2.33, by varying the linear velocity
of introduction of sample[22]. Fixed sample weight of 0.3 g was introduced into reactor
at a constant speed. The carrier gas flow, nitrogen or synthetic air, was 300 mL/min.
The total time of each experiment was fixed in 16 min. It is worth mentioning that
gases/semi-volatile collection line is only connected during this time.

After that time the sample holder was isolated from the furnace. The color and the aspect of the residue formed at the end of the experiments depended on the atmosphere used; in this way, the residue from pyrolysis presented a black and solid tarry appearance, whereas the residue formed at combustion experiments had the aspect of white ash. Elemental analysis of these residues showed a 78 % of carbon for pyrolysis compared to approx. 2 % in combustion runs. Other elements such as nitrogen, hydrogen and sulphur where negligible.

2.3 Determination of gases and semivolatile compounds

Gas fraction was collected in 5 L Tedlar® bags and analyzed by two gas chromatographs (GC) equipped with thermal conductivity detector (TCD) to determine mainly CO and CO_2 (Agilent 7820A GC) and flame ionization detector (FID) for light hydrocarbons between C1 and C6 together with benzene and toluene (Shimadzu GC-17A).

Semivolatile compounds including EPA-PAH in the gas phase were collected at the exit of reactor by trapping them in a thin-tube of 100 mm in length and an external diameter of 10 mm packed with XAD-2 resin. Advantages of using XAD-2 resin compared to other adsorbents were shown in previous works[23, 24].

Extraction of resin was done with solvent in accordance with the EPA Method 3545C by using a DIONEX ASE 100 accelerated solvent extractor and analyzed with gas chromatography coupled to mass spectrometry (GC-MS by the isotope dilution method for the PAHs). Internal standard containing 6 compounds were used (Dr. Ehrenstorfer-Schafers, Augsburg, Germany), namely: 1,4-dichlorobenzene D4,

acenaphthene D10, chrysene D12, naphthalene D8, perylene D12 and phenanthrene D10, additionally a standard containing the sixteen EPA-PAH was also used to determine the calibration curves.

A fixed amount of 5 µL of internal standard (Anthracene D10) was added to each sample before of extracting process. Subsequently, the solvent with the analytes was reduced to approximately 3 mL by rota-evaporation. The extract then underwent micro-concentration using a nitrogen stream (Pasvial sample vial concentration JSD) to give a final volume of 1.0 mL. EPA-PAH/semivolatile analyses were carried out immediately after each experiment to avoid any loss of compounds during storage.

Analysis of concentrated extract was carried out by gas chromatography coupled to mass spectrometry (GC-MS). A 6890N Agilent gas chromatograph model with a 5973N Agilent mass detector, equipped with a 30 m long HP-5Ms Phenyl Methyl Silox capillary column (0.25 mm ID,0.25 mm film thickness), was used. Samples were injected in split mode (1:25) with split flow of 25 mL/min using Helium as the carrier gas. All analyses were performed in SCAN mode of the MS in order to determine the presence of a wide fraction of semivolatile compounds, which was done comparing unknown mass spectra with NIST database reference spectra. A semi-quantitative estimation of the yields was calculated with the response factors of the deuterated internal standards with the nearest retention time, according to the EPA 8270D method.

3. RESULTS AND DISCUSSION

The present section includes outcomes from thermal characterization of coffee husk from Colombian coffee (Coffea arabica) and the influence of different air excess ratios in the formation on most abundant gases such as H_2, CH_4, CO, CO_2 and C_2 – C_8 and other semivolatile compounds, but paying special attention to EPA-PAH detected by gas chromatography coupled to mass spectrometry. The concentrations of the different species are given on dry basis.

In a first stage the influence of pyrolysis and combustion under different oxygen environment on lighter gases amount formed will be analyzed. The atomic C balance closed better at combustion conditions (between 96 and 100 %) respect to pyrolysis condition where the C balance was found to close on 81 %.

3.1. Evolution of gas composition

Figure 1 shows the concentration of different gases at 1123 K formed under a number of excess air ratio conditions (λ: 0 – 2.3), compounds were organized according their levels. Concentration of hydrocarbons was negligible at λ> 1.4, this is why x-axis in figures 1b-1d is shorter than in Figure 1a.

The compounds with higher concentration were CO_2 and CO even in samples/tests under pyrolytic conditions, due to the high amount of oxygen present in the material. As expected, an increase in oxygen presence causes a rise in CO_2 concentration and a gradual decreasing of CO (Figure 1a). High concentration of H_2, CH_4 and C_2H_4 was also observed, which is consistent with thermal characterization of different biomass e.g.[25] . Couto et al.[26], in their experimental and numerical studies on gas formation from coffee husk, described that the most important fraction, accounting for more than 70 % (w), is formed of light gases, namely, CO, H_2, CH_4, and CO_2,

what coincides with the results of present work. This is an important issue to consider the energetic potential from coffee husk.

In all cases (Figures1a-1d), hydrocarbons diminished as the presence of oxygen is increased, except for acetylene where a slight maximum at λ: 0.1 is observed (Figure 1b), exhibiting a different trend than the rest of hydrocarbons. This can be explained since it could be formed from ethylene in a first step as mentioned by [23], what could be slightly accelerated by low oxygen presence. This reaction competes, at the same time, with aromatic formation catalyzed by presence of oxygen radicals at λ>0.1[16]. Subsequently, decreasing of acetylene could be explained by predominance of oxidation reactions. Ethane, 1,3-butadiene, n-hexane and iso-octane show a marked similar behavior for decreasing with the rise of oxygen presence.

Evolution of organic compounds was discussed by Conesa et. al. [27] in pyrolysis and combustion of different wastes. According to their results, compounds such as volatile hydrocarbons (e.g. methane, ethane, benzene), semivolatile aliphatic compounds and monoaromatic hydrocarbons (e.g. toluene, benzene) decreased their presence with increasing oxygen. This trend coincides with organic compound evolution in the present work, total gas pollutant analyzed in Figure 1 (except for CO_2 and C_2H_2) decreased until be completely oxidized at the λ≥0.6. This means that the pollutant emissions during the coffee husk combustion could be reduced considerably in low presence of oxygen.

3.2. Evolution of PAH and semivolatile compounds

Figure 2 shows the concentrations of 16 individual PAH as a function of oxygen presence. The confidence interval (CI) is presented from a duplicated experiment in

λ: 0.25 by using a confidence level of 95% and Student T distribution. Previous work, using the same experimental device and equipment[3], noted that duplicated runs cannot exactly be done. This is because small changes in the disposal of the sample can produce changes in the uptake of oxygen for runs planned with the same experimental operating conditions. However, despite of this fact, the present work showed a good repeatability and the CI is considered as acceptable. As shown in previous studies[3], a possible error between 10 and 12 % should be considered for the yields of gases, volatiles and semivolatiles retained with the XAD.

As it can be observed in Figure 2, the most abundant compounds were naphthalene and acenaphthylene, which correspond to the lighter PAHs. Increasing the oxygen presence led to decrease concentration of all PAHs. Contrary to this results, Sanchez et al. [23] and Frenklach et al. [28] mentioned that PAHs seem to be encouraged by the presence of low oxygen ratio compared to the pyrolysis conditions. This is probably due to the different characteristics of the fuel and also to the higher temperatures used in the mentioned works, much higher than the one used in the present work.

The descending order of predominance of individual EPA-PAH for the cases evaluated is naphthalene> acenaphthylene> phenanthrene, the rest compounds depends on the oxidative environment, except for dibenzo(a,h)anthracene that has lower concentration in all cases. This behavior coincides with that observed by McGrath et al. [29] in their studies on different biomass pyrolysis, as they found that the majority of PAH under most pyrolysis conditions had two to four aromatic rings. In the Figure it can be also observed that even in low air excess ratios (>0.25) the

formation of PAH is limited. Precisely the change in λ: 0.25 to 0.4 reduces substantially the PAH concentration, that could be explained by important oxygen contained in the coffee husk.

3.3. Toxicity of emissions

PAH has been widely analyzed mainly in environmental samples due to their carcinogenic potential. In particular, benzo(a)pyrene has been identified as highly carcinogenic. Thus, the health risk associated with inhalatory exposure to PAH either in the occupational atmosphere or in outdoor air is commonly assessed on the basis of benzo(a)pyrene concentration, which is an indicator of human PAH exposure [30].

This way, a parameter called the toxicity equivalent factor (TEF defined by Nisbet and Lagoy [31]) with the aim of helping to characterize more precisely the carcinogenic properties of PAH-priorities, comparing every compound with benzo(a)pyrene, which has the highest TEF value. Using the TEF values, it is possible to determine a KE value, which is a parameter that determines the inhalative carcinogenic potential caused by airborne PAH. The KE value is calculated as the sum of the different TEF values of each PAH-priority multiplied by its concentration found for each PAH, as is shown in Eq. (1), where it corresponds to the 16 PAH-priority compounds.

$$KE = \sum_{i}^{16}[PAHs]_i * TEF_i \quad \text{Eq (1)}$$

Figure 3 shows the carcinogenic equivalence sum (KE) for different air excess ratio. Increasing λ causes a clear lineal decreasing of both PAH and KE. KE values from coffee husk are significantly lower than conventional diesel fuels [32], maybe the

presence of a low amount of sulphur and/or metals in the biomass feedstocks avoids the production of carcinogenic species.

Blomqvist et al. [33] obtained a maximum value of KE of ca. 100 μg/g in the combustion of wood board under-ventilated conditions, that is similar to the level found in the present study in the pyrolysis runs. Levels in well ventilated ambient were reported to be reduced to 0,01 μg/g. On the other hand, Hedberg et al.[34] studied the emissions from birch wood combustion in a wood stove and found levels of 60 μg/MJ wood burned, that is equivalent to ca. 1,09 μg/g, pointing out very good combustion conditions.

KE from different liquid fuels (REF: reference fuel from diesel, RSM: methyl esters of rapeseed oil, WCOM: biodiesel from waste cooking oil, WCOE: ethyl esters of waste cooking oil) was determined by Ballesteros et. al.[32]. The PAH characterization was done in combustion ($\lambda \approx 0.9$) of these real samples in a diesel engine under two different operating modes, urban and extraurban modes. The highest KE values, considering pure fuel, were observed in urban mode for all cases (REF$\approx$5 µg/g, WCOM$\approx$1 µg/g, RSM$\approx$ 0.8 µg/g and WCOE$\approx$ 0.3µg/g). Comparing these factors with those in the present work is possible to determine that under similar combustion conditions coffee husk did not present PAH, and in the same extent KE. This provides additional evidence on the feasibility to use biomass instead of conventional fuel, in terms of toxicity potential.

In the present work the gas chromatography was operated by Scan mode, this allows to detect other semivolatile compounds, which are shown in Table 3. The majority

compounds correspond to branch PAHs, oxy- and nitro-PAHs. According to previous work[27], different compounds created from a numbers of materials presented 3 different behaviors in dependence of change in oxidative environment, which match observations of this present work. Most compounds decreased with oxidative environment, but other compounds exhibited a maximum value or rise on their concentration, i.e., these compounds were formed in pyrolytic conditions, but they were consumed in the presence of oxygen. On the other hand, compounds presenting a maximum with increasing oxygen ratio were partially oxidized compounds or compounds formed by decomposition of oxygenated compounds such as aldehydes or ketones. Three compounds are found to increase their presence with increasing air ratio: 5H-Dibenzo[a,d]cycloheptene, 11H-Benzo[a]fluorene and 4-methyl-Chrysene. All of them are intermediate compounds with high resistance to oxygen under working conditions but in more aggressive conditions (higher temperature or residence time) these compounds should present a maximum of concentration.

4. CONCLUSIONS

Thermal characterization of biomass from *Coffea arabica* production (coffee husk) have been determined in pyrolysis and combustion (λ: 0.25, 0.4, 0.6, 1.4, 2.3) conditions at temperature of 1123 K by using a quartz horizontal reactor.

Ultimate analysis results from coffee husk are similar to those reported by using coffee husk from different varieties of the coffee plant. Determination of element weight percentages by using X–ray shows a safe biomass with energetic potential

without significant percentage of elements which can become toxics, the unique concern constitutes high presence of Na and K that could form inorganic particles which are then exhausted into the atmosphere as pollutants or cause problems of agglomeration, fouling, slagging and corrosion in combustion chambers. In general terms, lighter compounds decreases as oxygen presence increase, until completely oxidized at the $\lambda \geq 0.6$, where the unique compound observed was CO_2.

Concerning to EPA-PAHs, naphthalene and acenaphthylene were the compound with higher concentration under all cases evaluated. Lighter gases prevailed on the heavier ones. This causes a lower carcinogenic potential than some fossil fuels and other biomass feedstocks, representing an important advantage as energy alternative source. Semivolatile compounds present three trends: 1) Decreasing with excess air ratio increasing, 2) A maximum value in different excess air ratio and 3) increasing as the air presence increased. The evolution of EPA-PAH corresponds to first trend for coffee husks.

ACKNOWLEDGEMENTS

LITERATURE CITED

1.   Protásio, T. P.; Bufalino, L.; Tonoli, G. H. D.; Guimarães Junior, M. G.; Trugilho, P. F.; Mendes, L. M., Brazilian lignocellulosic wastes for bioenergy production: Characterization and comparison with fossil fuels. *BioResources* **2013,** 8, (1), 1166-1185.
2.   Granados, D. A.; Velásquez, H. I.; Chejne, F., Energetic and exergetic evaluation of residual biomass in a torrefaction process. *Energy* **2014,** 74, (C), 181-189.
3.   Conesa, J. A.; Domene, A., Synthesis Gas Production from Various Biomasses. *AIMS Energy* **2013,** 1, 17-28.
4.   Ohlström, M.; Mäkinen, T.; Laurikko, J.; Pipatti, R., New concepts for biofuels in transportation biomass-based methanol production and reduced emissions in advanced vehicles. In *VTT Tiedotteita - Valtion Teknillinen Tutkimuskeskus*, 2001; pp 3-94.
5.   De Oliveira, J. L.; Da Silva, J. N.; Graciosa Pereira, E.; Oliveira Filho, D.; Rizzo Carvalho, D., Characterization and mapping of waste from coffee and eucalyptus production in Brazil for thermochemical conversion of energy via gasification. *Renewable and Sustainable Energy Reviews* **2013,** 21, 52-58.
6.   Wright, L., Worldwide commercial development of bioenergy with a focus on energy crop-based projects. *Biomass and Bioenergy* **2006,** 30, (8-9), 706-714.
7.   Arana, V. A.; Medina, J.; Alarcon, R.; Moreno, E.; Heintz, L.; Schäfer, H.; Wist, J., Coffee's country of origin determined by NMR: The Colombian case. *Food Chemistry* **2015,** 175, 500-506.
8.   Esquivel, P.; Jiménez, V. M., Functional properties of coffee and coffee by-products. *Food Research International* **2012,** 46, (2), 488-495.
9.   Oliveira, L. S.; Franca, A. S., *Coffee in Health and Disease Prevention*. Elsevier Inc.: 2015.
10.   Gordillo, G.; Rodriguez, C., Adiabatic gasification and pyrolysis of coffee husk using air-steam for partial oxidation. *Journal of Combustion* **2011,** 2011.
11.   Vélez, J. F.; Chejne, F.; Valdés, C. F.; Emery, E. J.; Londoño, C. A., Co-gasification of Colombian coal and biomass in fluidized bed: An experimental study. *Fuel* **2009,** 88, (3), 424-430.
12.   Saenger, M.; Hartge, E. U.; Werther, J.; Ogada, T.; Siagi, Z., Combustion of coffee husks. *Renewable Energy* **2001,** 23, (1), 103-121.
13.   Bok, J. P.; Choi, H. S.; Choi, Y. S.; Park, H. C.; Kim, S. J., Fast pyrolysis of coffee grounds: Characteristics of product yields and biocrude oil quality. *Energy* **2012,** 47, (1), 17-24.
14.   Jeguirim, M.; Bikai, J.; Elmay, Y.; Limousy, L.; Njeugna, E., Thermal characterization and pyrolysis kinetics of tropical biomass feedstocks for energy recovery. *Energy for Sustainable Development* **2014,** 23, 182-193.
15.   Domínguez, A.; Menéndez, J. A.; Fernández, Y.; Pis, J. J.; Nabais, J. M. V.; Carrott, P. J. M.; Carrott, M. M. L. R., Conventional and microwave induced pyrolysis of coffee hulls for the production of a hydrogen rich fuel gas. *Journal of Analytical and Applied Pyrolysis* **2007,** 79, (1-2 SPEC. ISS.), 128-135.

16.   Jones, J. M.; Lea-Langton, A. R.; Ma, L.; Pourkashanian, M.; Williams, A., *Pollutants Generated by the Combustion of Solid Biomass Fuels*. Springer: 2014.

17.   Doel, R.; Jørgensen, R.; Lilley, L. C.; Mann, N.; Rickeard, D. J.; Scorletti, P.; Stradling, R.; Zemroch, P. J.; Heinze, P.; Thompson, N. D.; Hall, D. E., Evaluation of automotive polycyclic aromatic hydrocarbon emissions. *CONCAWE Reports* **2005,** (4).

18.   Sánchez, N. E.; Salafranca, J.; Callejas, A.; Millera, Á.; Bilbao, R.; Alzueta, M. U., Quantification of polycyclic aromatic hydrocarbons (PAHs) found in gas and particle phases from pyrolytic processes using gas chromatography-mass spectrometry (GC-MS). *Fuel* **2013,** 107, 246-253.

19.   Wilson, L.; John, G. R.; Mhilu, C. F.; Yang, W.; Blasiak, W., Coffee husks gasification using high temperature air/steam agent. *Fuel Processing Technology* **2010,** 91, (10), 1330-1337.

20.   Dorge, S.; Jeguirim, M.; Trouve, G., Thermal degradation of Miscanthus pellets: Kinetics and aerosols characterization. *Waste and Biomass Valorization* **2011,** 2, (2), 149-155.

21.   Friedl, A.; Padouvas, E.; Rotter, H.; Varmuza, K., Prediction of heating values of biomass fuel from elemental composition. *Analytica Chimica Acta* **2005,** 544, (1-2 SPEC. ISS.), 191-198.

22.   Conesa, J. A.; Domene, A., Gasification and pyrolysis of Posidonia oceanica in the presence of dolomite. *Journal of Analytical and Applied Pyrolysis* **2015,** 113, 680-689.

23.   Sánchez, N. E.; Callejas, A.; Millera, Á.; Bilbao, R.; Alzueta, M. U., Influence of the oxygen presence on polycyclic aromatic hydrocarbon (PAH) formation from acetylene pyrolysis under sooting conditions. *Energy and Fuels* **2013,** 27, (11), 7081-7088.

24.   Chuang, J. C.; Hannan, S. W.; Wilson, N. K., Field comparison of polyurethane foam and XAD-2 resin for air sampling for polynuclear aromatic hydrocarbons. *Enviromental Science and Technolgy* **1987,** 21, (8), 798-804.

25.   Conesa, J. A.; Urueña, A.; Díez, D., Corn stover thermal decomposition in pyrolytic and oxidant atmosphere. *Journal of Analytical and Applied Pyrolysis* **2014,** 106, 132-137.

26.   Couto, N.; Silva, V.; Monteiro, E.; Brito, P. S. D.; Rouboa, A. In *Experimental and numerical analysis of coffee husks biomass gasification in a fluidized bed reactor*, Energy Procedia, 2013; 2013; pp 591-595.

27.   Conesa, J. A.; Font, R.; Fullana, A.; Martín-Gullón, I.; Aracil, I.; Gálvez, A.; Moltó, J.; Gómez-Rico, M. F., Comparison between emissions from the pyrolysis and combustion of different wastes. *Journal of Analytical and Applied Pyrolysis* **2009,** 84, (1), 95-102.

28.   Frenklach, M.; Clary, D. W.; Yuan, T.; Gardiner, W. C., Jr.; Stein, S. E., Mechanism of Soot Formation in Acetylene-Oxygen Mixtures. *Combustion Science and Technology* **1986,** 50, (1-3), 79-115.

29.   McGrath, T.; Sharma, R.; Hajaligol, M., An experimental investigation into the formation of polycyclic-aromatic hydrocarbons (PAH) from pyrolysis of biomass materials. *Fuel* **2001,** 80, (12), 1787-1797.

30.   Petry, T.; Schmid, P.; Schlatter, C., The use of toxic equivalency factors in assessing occupational and environmental health risk associated with exposure to airborne mixtures of polycyclic aromatic hydrocarbons (PAHs). *Chemosphere* **1996,** 32, (4), 639-648.

31.   Nisbet, I. C. T.; LaGoy, P. K., Toxic equivalency factors (TEFs) for polycyclic aromatic hydrocarbons (PAHs). *Regulatory Toxicology and Pharmacology* **1992,** 16, (3), 290-300.

32.   Ballesteros, R.; Hernández, J. J.; Lyons, L. L., An experimental study of the influence of biofuel origin on particle-associated PAH emissions. *Atmospheric Environment* **2010,** 44, (7), 930-938.

33.   Blomqvist, P.; McNamee, M. S.; Stec, A. A.; Gylestam, D.; Karlsson, D., Detailed study of distribution patterns of polycyclic aromatic hydrocarbons and isocyanates under different fire conditions. *Fire and Materials* **2014,** 38, (1), 125-144.

34.   Hedberg, E.; Kristensson, A.; Ohlsson, M.; Johansson, C.; Johansson, P. A.; Swietlicki, E.; Vesely, V.; Wideqvist, U.; Westerholm, R., Chemical and physical characterization of emissions from birch wood combustion in a wood stove. *Atmospheric Environment* **2002,** 36, (30), 4823-4837.

Table 1. Ultimate analysis of raw coffee husk

Moisture (% wt)	9.3 ± 0.05
NCV (Kcal/Kg)	4362 ± 28
Ash (% wt)	3.2 ± 0.1
Element (% wt)	
N	1.1
C	44.0
H	6.1
S	0.3
O (by difference)	45.3

Table 2. X ray analysis of coffee husk*

Element	Dry weight percentage (%)
Ca	3.01
K	2.67
Fe	0.68
Mg	0.33
S	0.30
Al	0.22
Si	0.15
Cl	0.08
P	0.07
Ti	0.04
Mn	0.04
Sr	0.03
Rb	0.01
Zr	0.00

* limit of detection of the equipment ca. 0.02-0.05 %

Table 3. Emission of semivolatile compounds (mg/Kg) during the pyrolysis and combustion of coffee husk.

Compounds	Oxygen ratio (λ)						Type
	0	0.25	0.4	0.6	1.4	2.33	
benzene 1-3 dimethyl[a]	260	93	28	-	-	-	D
Phenylacetylene[a]	171	199	17	-	-	-	M
Styrene[a]	1338	783	58	-	-	-	D
Cyclohexanone[a]	125	65	15	27	25	29	D
Benzaldehyde[a]	16	43	8	-	-	-	M
Phenol[a]	1258	697	33	-	-	-	D
Benzonitrile[a]	393	584	57	-	-	-	M
Benzofuran[a]	588	424	47	-	-	-	D
Benzyl alcohol[a]	13	6	2	4	3	4	D
Indene[a]	2459	1186	46	-	-	-	D
Benzaldehyde, 3-ethyl-[a]	24	15	2	-	-	-	D
Isoquinoline[b]	233	244	18	-	-	-	M
Indole[a]	367	227	12	-	-	-	D
1-methylnaphthalene[a]	693	300	12	-	-	-	D
1H-Indene, 1-ethylidene-[a]	456	202	10	-	-	-	D
Diphenyl[a]	280	211	18	-	-	-	D
Naphthalene, 1-isocyano-[a]	93	114	8	-	-	-	M
Naphtho[2,1-b]furan[a]	110	128	0	-	-	-	M
Diethyl Phthalate[a]	-	-	23	-	10	9	D
1H-Phenalene[a]	155	86	-	-	-	-	D
2-methyl anthracene[b]	73	46	1	-	-	-	D
Carbazole[b]	57	50	-	-	-	-	D
1H-Indene, 1-(phenylmethylene)-[a]	72	52	-	-	-	-	D
Phenanthrene, 1-methyl-[b]	92	49	-	-	-	-	D
Phenanthrene, 4-methyl-[b]	87	51	-	-	-	-	D
6H-Cyclobuta[jk]phenanthrene[a]	226	174	4	-	-	-	D
2-Phenylnaphthalene[b]	112	131	5	-	-	-	M
5H-Dibenzo[a,d]cycloheptene, 5-methylene[a]	32	52	-	-	-	-	I
7H-Benzo[c]fluorene[b]	149	78	-	-	-	-	D
11H-Benzo[a]fluorene[a]	52	63	-	-	-	-	I
Triphenylene[b]	115	84	-	-	-	-	D
Chrysene, 4-methyl-[b]	61	63	-	-	-	-	I
Total	10160	6500	424	31	38	42	

^a Calculated by Forward value (forward value) (100×,[∑(LIB × UKN)1/2]2/∑ LIB × ∑ UKN where LIB refers to the intensity of the spectrum of the proposed compound at a given mass and UKN refers to the intensity of the unknown spectrum at a given mass higher than 80 and quantification using internal standard. ^b Different Lee Index less than 1% and quantification using internal standard. And the quantification is done using internal standard. Type indicates the behavior of compound with rise of excess air ratio, I: increase, D: decrease and M: maximum.
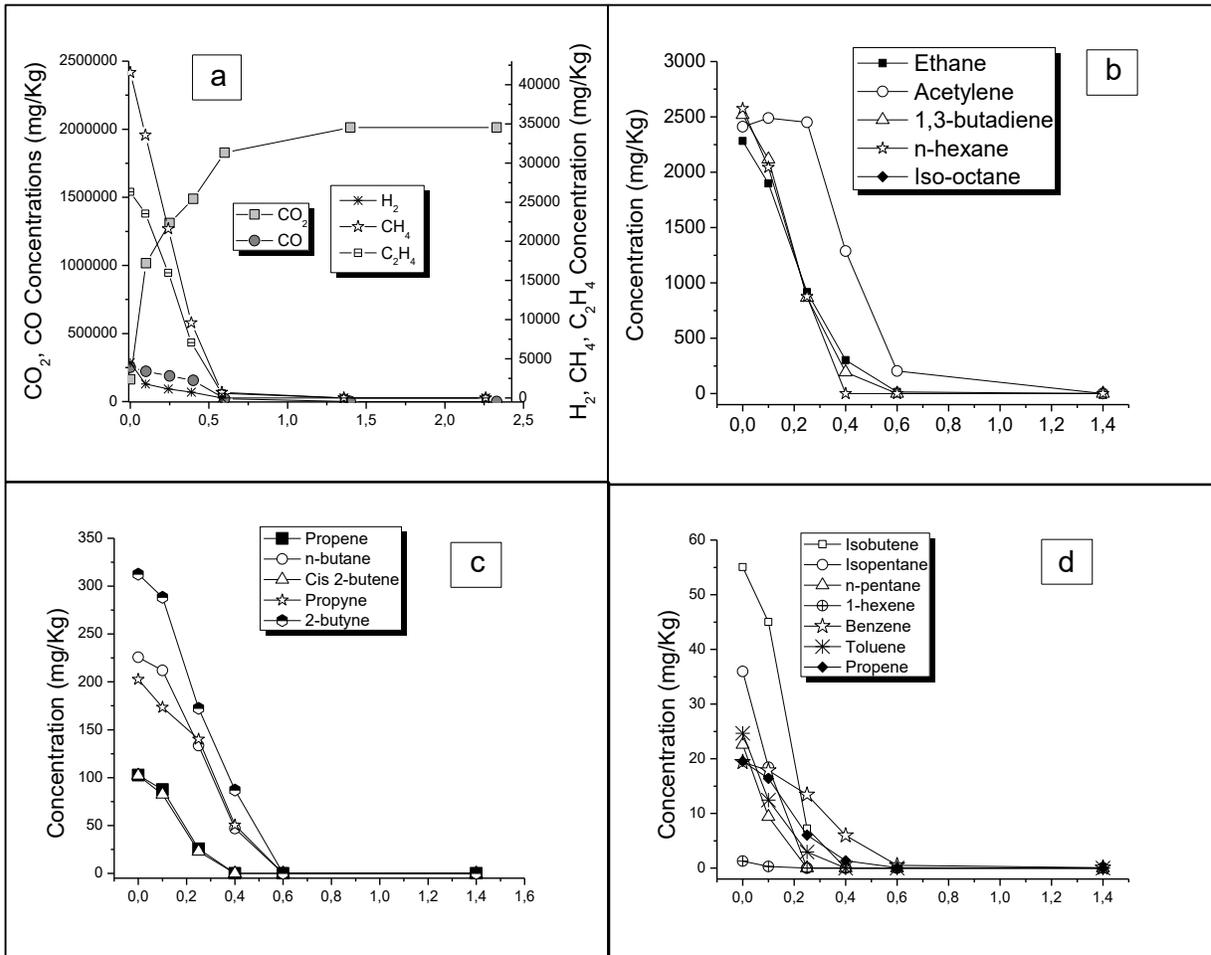
Figure 1. Emissions of different compounds from pyrolysis and combustion of coffee husk at 1123 K. X-axis corresponds to oxygen ratio (λ)
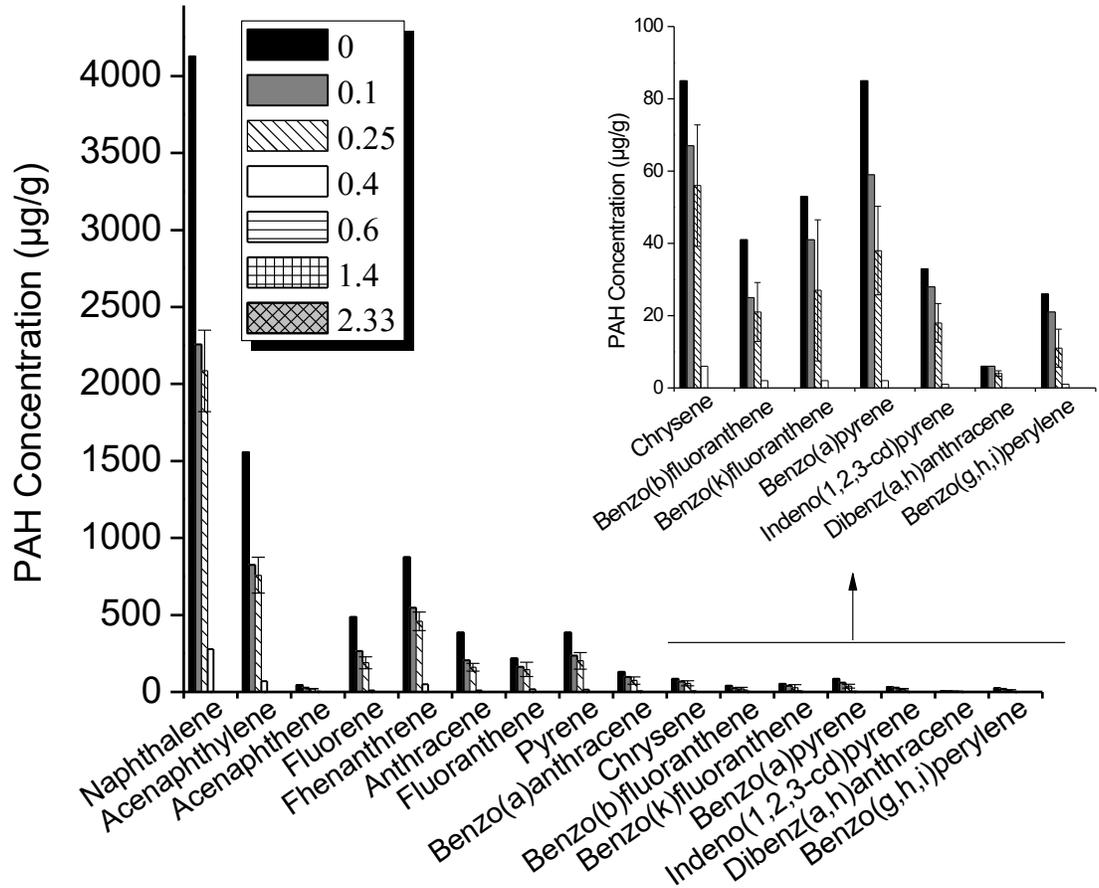
Figure 2. EPA-PAH concentration as a function of oxygen ratio under pyrolysis and combustion of coffee husk. Confidence interval (CI) was observed to λ=0.25
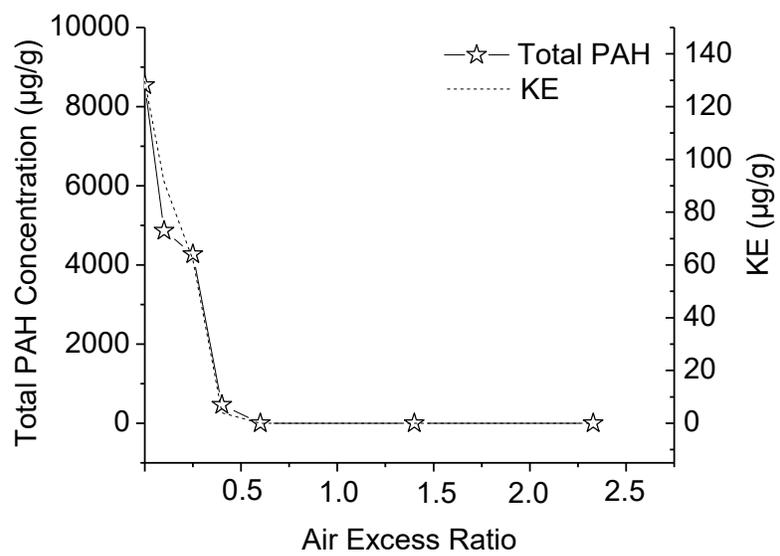
Figure 3. Total PAHs and Carcinogenic potential vs air excess ratio during thermal decomposition of coffee husk.