Optical Characterization of Biomass Soot Samples

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Abstract. Soot from different biomass sources is investigated to develop absorbent coatings for use in solar cookers. Soot samples were analysed by spectral and solar reflectance in the range 280-2400 nm, by its organic elemental composition and through Raman spectroscopy. The soot was obtained from biomass burning of sugarcane, pine resin and firewood in a hearth. The averaged spectral reflectance for sugarcane soot is 3.5%, for wood-stove soot is 2.7% and the lower value corresponds to pine resin soot at 1.4%. Likewise, the lowest value of the solar reflectance was of 14.8 Wm⁻² for pine resin soot. In addition, elemental composition analysis showed that pine resin also has the highest carbon content. Raman spectroscopy measurements were performed to find the structure and the degree of disorder in the graphite structure.

1. Introduction

Solar energy is a source of clean environmental energy that has been proposed as a viable solution to counter the global climate crisis. Solar energy is harnessed through various processes, including mainly the solar photothermal conversion that occurs through the photoexcitation of the absorbent material to produce heat [1]. The heat generated is used in different applications, such as cleaner water [2], solar cookers [3-5], dryers water heaters [6], among others.

A critical factor in determining the thermal efficiency of a solar thermal system is the absorbent coating that converts light into heat. Absorbent coatings must have several characteristics such as efficient response in the range of the solar spectrum and high absorbance with minimum reflectance for wavelengths shorter than 3 μm. It has been reported that semiconductors, noble metals and organic materials have an excellent thermal conversion efficiency [7-9]. Organic materials such as carbon-based materials have the advantage of being cheaper, abundant, with an excellent light absorption and efficient thermal conversion [10, 11].

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Biomass materials are a rich source of sustainable carbon for efficient photothermal applications. Different biomass sources have been carbonized at high temperatures to produce absorbent coatings for water evaporation and to cook food with a high thermal performance and low cost [12-14]. The use of biomass material residues, such as soot deposited in fireplaces of rural wood stoves, has been an ecological and sustainable alternative for the manufacture of selective absorbent coatings. Soot from biomass combustion have been proposed as a selective absorber coating for low-cost solar cookers since they are untreated materials from rural areas [15]. In a previous work [16,17], selective absorbent coatings based on biomass soot for solar cookers were optically and thermally analyzed [16,17]. Results showed that the thermal parameters and optical properties increased using soot-based biomass coatings compared to a commercial black paint.

In this work, soot from different biomass sources were investigated to develop absorbent coatings for solar cookers. For this purpose, the spectral and solar reflectance of different types of soot were determined within the range of 280-2400 nm. Besides, an organic elemental analyzer was employed to determine the amount of total carbon present in the samples. Finally, Raman spectroscopy was used to obtain the degree of disorder of the graphite present in the employed samples.

2. Materials and Methods

2.1. Materials Preparation

The raw materials used in this work were three kinds of soot produced by the burning of pine resin, sugarcane and pine from a wood-burning stove. The soot preparation process begins by collecting the raw material. Pine resin was obtained from natural exudation of pine tree, which is then burned in a cylindrical metal container with various metal meshes where the soot is deposited. Finally, the material is collected with a spatula. For the other two types of soot the process is simpler. The soot from the wood stove and the soot from the sugarcane are the waste from chimney cleaning in rural houses and from a sugar mill in the region. In addition to the analyzed soot samples, graphite powder with a purity of 99.95% and a grain size of less than 45 μm was taken as a reference.

Images of the graphite and soot samples are shown in Figure 1. These images were obtained with an optical microscope where variations in sizes, structures and even coloration are observed among the materials used.

![Graphite, Pine Resin, Wood-stove, Sugarcane](image)

Figure 1. Optical images of graphite and three types of soot.

2.2. Methods

The analysis of the three types of soot was carried out by Diffuse Reflectometry, Organic Elemental Analyzer and Raman Spectroscopy. Diffuse reflectance was measured by an UV-VIS-NIR spectrophotometer (Agilent Technologies, model Cary 5000) attached to an integrating sphere (DRA2500); a highly reflective standard (PTFE) was employed as a reference. On the other hand, the elemental content of total carbon and nitrogen was obtained using a Perkin Elmer 2400 Series II elemental analyzer. Finally, the Raman spectra analysis was obtained by using a micro Raman system (Thermo Scientific Nicolet, model Almega XR) coupled to an optical microscope and a laser emitting at 532 nm as the excitation source. Light emitted by the laser was focused over the sample and the employed exposure time was 10 s.
3. Results

3.1. Diffuse Reflectometry

For an efficient photothermal conversion solar absorber surfaces must have a low reflectance at wavelengths shorter than 3 μm at the operational temperature [7]. Thus, to select the most suitable material for the elaboration of a solar coating, three types of soot were evaluated through its reflectance.

Figure 2. Reflectance curves for different types of soot (a); Solar-reflected irradiance of wood-stove soot, sugarcane soot and pine resin soot (b).

Figure 2(a) shows the obtained results for the reflectance curves (diffuse and specular) as a function of wavelength in the range of 280-2400 nm. As can be seen in the figure, the pine resin and wood-stove powders have a similar behavior. For both samples, an increase in the spectral reflection is observed with the wavelength and both curves remain almost constant in the infrared region. However, for sugarcane soot, the reflectance response is markedly different and a gradual increase in reflectance is observed throughout the analyzed spectral region. This difference in reflectance behavior for sugarcane soot could be related to the elemental composition of this sample. The averaged spectral reflectance for sugarcane soot is 3.5%, for wood-stove soot is 2.7% and the lower value corresponds to pine resin soot at 1.4%. Therefore, pine resin soot has the highest absorbance of the three investigated samples. This result agrees to the performance of a resin soot coating where it was reported to have the best thermal performance for solar thermal applications [17].

To analyze the performance of soot powders for solar applications, it is necessary to consider the solar irradiance. For this purpose, the solar-reflected irradiance of soot samples was calculated by multiplying the reflectance (see Fig. 2(a)) by the solar irradiance function. Figure 2(b) shows the results obtained for the solar-reflected power per unit area in the range of 280–2400 nm. As can be qualitatively observed the pine resin soot has the overall lowest value for the reflected irradiance. The integration of Fig. 2(b) traces gives the solar-weight reflectance which is a measure of the total reflectance of samples under Sun irradiation. The obtained results were: 14.8 Wm-2 for pine resin soot; 25.1 Wm-2 for sugarcane soot; and 25.4 Wm-2 for wood-stove soot. As expected, pine resin soot has the lower integrated reflectance with a reflectance value of 1.8% of the total solar irradiance while the value obtained for the other two types of soot was 2.8%.
3.2. Elemental Composition
Since the reflectance properties of a material could be related to its chemical composition, an elemental composition analysis for carbon and nitrogen was performed and the obtained results are shown in Table 1. Pine resin soot contains the highest percentage of carbon with a value of 85.23\% while sugarcane soot contains 49.46\%. The different percentages of carbon are in agreement with the values obtained from the reflectance curves. The resin soot has a higher absorbance and in turn a higher carbon content.

Table 1. Elemental analysis obtained by combustion.

| Sample             | C (%) | N (%) |
|--------------------|-------|-------|
| Pine resin soot    | 85.23 | 0.15  |
| Wood-stove soot    | 61.32 | 4.08  |
| Sugarcane soot     | 49.46 | 0.39  |

3.3. Raman Spectroscopy
To further investigate the structure and the degree of disorder present in the graphite for the different investigated soot samples, Raman spectroscopy measurements were performed. Besides, soot powders were compared to graphite, which was taken as a reference. Graphite exhibits only one first-order band, the G band ("Graphite") around 1580 cm\(^{-1}\), which is related to a highly oriented polycrystalline or single graphite crystals. As the material presents disorder in its crystalline structure, the D bands ("Defect") appears, growing in intensity as the disorder in the graphitic structure increases. The D1 band (around 1360 cm\(^{-1}\)), which is usually of higher intensity than the other D bands and corresponds to a graphitic lattice vibration mode with A\(_{1g}\) symmetry. Another first-order band that indicate structural disorder is the D2 band at 1620 cm\(^{-1}\) and corresponds to a graphite lattice mode with E\(_{2g}\) symmetry. Depending on the degree of disorder in the crystal structure, more bands appear (D1, D2, D3, D4) [18]. The ratio of intensities between G and D bands (AD/AG) gives information about the graphitization degree [19].

Figure 3(a) shows the normalized intensity of Raman spectra observed for the different analyzed samples. The trace of the graphite sample exhibits two bands; one first-order band, the G band at around 1580 cm\(^{-1}\) and the first-order band D1 around 1360 cm\(^{-1}\) with a much lower intensity compared to the G band. The colored traces correspond to the different analyzed soot powders. All samples exhibit two broad and strongly overlapping peaks with a maximum intensity at 1356 cm\(^{-1}\) and 1600 cm\(^{-1}\). As discussed above, the location of these peaks is related to the D and G bands. However, the peak in 1600 cm\(^{-1}\) includes not only the G band but also the D2 band related to graphite lattices [18].

Figure 3. Raman spectra of graphite and different types of soot with \(\lambda_0=532\) nm (a) and curve fit of the first-order Raman spectra for sugarcane soot (b).
Afterwards the spectral parameters were obtained by fitting the experimental curves through Lorentzian profiles. Figure 3(b) shows the obtained peaks for the sugarcane soot sample. Curve centers were kept fixed during the fitting process at $G = 1580$ cm$^{-1}$, $D_1 = 1350$ cm$^{-1}$, $D_2 = 1620$ cm$^{-1}$, $D_3 = 1500$ cm$^{-1}$ and $D_4 = 1200$ cm$^{-1}$.

The obtained parameters are summarized in Table 2. The values of the areas ($A$) of $G$ and $D_1$ bands allow to determine the degree of graphitization by means of the ratio between $AD_1$ and $AG$. The quotient obtained for the graphite sample has the lowest value as expected. Besides, the values calculated for the sugarcane, pine resin and wood-stove soot were 4.13, 2.77 and 2.22 respectively. These results indicate that the carbon present in soot has essentially an amorphous structure.

### Table 2. Spectral parameters of soot samples and graphite.

| Sample            | Area ($A$) [a.u.] | G Band Width (w) [cm$^{-1}$] | Area ($A$) [a.u.] | D1 Band Width (w) [cm$^{-1}$] | AD1/AG |
|-------------------|-------------------|------------------------------|-------------------|-------------------------------|--------|
| Graphite          | 33.45             | 20.99                        | 1.83              | 57.45                         | 0.05   |
| Sugarcane soot    | 64.57             | 70.86                        | 266.74            | 195.74                        | 4.13   |
| Pine resin soot   | 44.78             | 56.50                        | 123.99            | 147.77                        | 2.77   |
| Wood-stove soot   | 68.00             | 66.77                        | 150.90            | 162.21                        | 2.22   |
| Soot              |                   |                              |                   |                               |        |

### 4. Conclusions

In this work, three types of soot have been investigated as raw materials to be used as solar radiation-absorbent coating. Results shows that pine resin soot has a higher absorbance than sugarcane and wood-stove soot in the 280-2400 nm spectral range. The solar-weight reflectance of pine resin samples is 35% lower than the other investigated samples. Besides it was obtained that pine resin has also a higher carbon content. On the other hand, Raman spectroscopy analysis has shown that all three types of soot contain amorphous carbon, and the highest value of AD1/AG (degree of graphitization) was for sugarcane soot. Based on the results obtained, pine resin soot is the best candidate for use in solar absorption coatings.

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