Spectroscopic study of emission coal mineral plasma produced by laser ablation

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Abstract. Spectroscopic analysis of plasma produced by laser ablation of coal samples using 1064 nm radiation pulses from a Q-switched Nd:YAG on different target under air ambient, was performed. The emission of molecular band systems such as C$_2$ Swan System ($d^{3}Π_g$→$a^{3}Π_u$), the First Negative System N$_2$ (Band head at 501.53 nm) and emission lines of the C I, C II, were investigated using the optical emission spectroscopy technique. The C$_2$ molecular spectra (Swan band) were analyzed to determine vibrational temperature (0.62 eV); the density and electron temperature of the plasma have been evaluated using Stark broadening and the intensity of the nitrogen emission lines N II, the found values of 1.2 eV and 2.2 ×10$^{18}$ cm$^{-3}$ respectively.

1. Introduction

Laser-produced plasmas are a topic of interest for different fields of science with applications in medicine, astrophysics and synthesis of new materials. For plasmas produced by laser ablation, light energy to remove a portion of a sample by melting, fusion, sublimation, ionization, erosion and/or explosion. Several laser ablation-based methods have been implemented such as laser induced plasma spectroscopy (LIPS), pulsed laser deposition (PLD) [1]. In the laser ablation most of these molecules are formed in their excited states so that spectroscopic measurements offer a excellent means to investigate their evolution and dynamics [2].

Optical emission spectroscopic (OES) is a technique where light emitted from the plasma by electronically excited species, is collected and transmitted to a grating spectrometer; allow species identification, information about the elemental composition of the sample. In this case the carbon molecules are interesting for their unique and fascinating structural and spectroscopic properties, their importance in astrophysical processes and too role in combustion and soot formation [3].

Investigations recent in coals minerals for determine elemental composition, using technologies based in laser [4, 5], shows than the diagnosis of the plasma of coal can give us valuable information about the reaction mechanism involved in combustion and gasification process for production of synthesis gas under plasmas conditions [6], studies of the influence of sample morphology on laser ablation properties of coal, comparing temperature and electron density of the coal plasma with the different particle size [7, 8].
In this paper we used samples of Colombian coal for produced plasma at environmental conditions, and the spectra are analysed for determined temperature and electron density and vibrational temperature.

2. Experimental setup

We used the Nd: YAG laser that provides pulses in the wavelength of 1064 nm with pulse duration of 9 ns and repetition rate of 10 Hz. The laser beam is focused with an $f = 23$ cm glass lens on the target. The samples were target coal from mines located in Santander, Norte de Santander and Cesar, Colombia. The pressure was atmosphere air environment with a temperature of 26 °C and 55% humidity relative. The laser energy fluence was $7 \, \text{J/cm}^2$ for 10 minutes. The plume is generated by the laser impact of coal samples (figure 1), detecting radiation emission from plasma was performed by means of an optical fiber, which carries the radiation to the spectrometer. Characterization of plasma was performed by optical emission spectroscopy (OES) using a spectrometer model Jobin Yvon Triax 550 of 0.55m, $f = 6.4$ equipped with two gratings of 1200 l/mm and 150 l/mm, coupled to a model 3000 CCD camera cooled air multi-channel and $512 \times 512$ pixels.

3. Results and discussion

Spectral measurements were performed in coal plasma, the electron temperature have been evaluated using the relative intensities of the N II, and electron density of plasma with Stark broadening method, the parameters are available in the literature [10, 11]. In figure 2, carbon plasma produced by laser ablation.

3.1. Temperature and electron density

We report on spectroscopic measurements of plasmas produced by ionization of air at atmospheric pressure using nanosecond laser pulses, obtaining measures consistent with the features observed in nanosecond lasers. The value of electron temperature was $1.2 \, \text{eV}$ assuming the local thermal equilibrium (LTE).

$$\ln \left( \frac{I_{mn}}{A_{mn} \xi_{mn}} \right) = \ln \left( \frac{N}{Z} \right) - \left( \frac{E_m}{kT_e} \right)$$

(1)
LTE is valid if collisional processes are more important than radiative decay; particles will have Maxwellian velocity distribution, in dense plasmas $N_e \geq 10^{16} \text{ cm}^{-3}$ and temperature $kT \leq 5 \text{ eV}$, the velocity distribution of free electrons is almost always Maxwellian [12].(archivo 3) We estimate the number of electron density of plasma by measuring the line width of the individual line of nitrogen. Electron density is related to the line broadening, and for highly ionized and high density plasma, the collisions with charged particles presents a strong electric field that produced a broadening of the transitions between the split atomic levels, these micro electric fields are associated with Stark broadening [13]. The found density was of the $2,2 \times 10^{18} \text{ cm}^{-3}$. In the figure 3, a Lorentz function can be used to fit the line spectra.

Electron density must be sufficiently high, a criterion for LTE necessary but no sufficient is [14].

$$n_e \geq 1.4 \times 10^{14} T_e^{12} (\Delta E_{\text{mm}})^{3} \text{cm}^{-3}$$

(2)

Substituting values for $T_e$ and $\Delta E$ in (2) the value obtain is $9,57 \times 10^{15} \text{ cm}^{-3}$ implying that LTE approximation for these analyses is valid.
3.2. Vibrational temperature

The Swan band of C\textsubscript{2} emission intensities were used for calculated vibrational temperature. The strongest system is well know Swan system in the green, is of special interest for provide an estimation of the plume temperature, and very important in astrophysics. They have been observed in the emission spectra of comets and also in the absorption spectra of stellar atmospheres [15]. The Swan systems arise from transitions between the d'\Pi\textsubscript{g}→a'\Pi\textsubscript{u} electronic states of the C\textsubscript{2} molecules. Band heads Δν =0 (figure 4). The band emission at 510 nm, 515 nm and 520 nm can be utilized to determine the vibrational temperature. These emissions correspond to (0,0), (1,1), (2,2) bands [16].

![Swan Band of C\textsubscript{2}, band heads Δν =0](image)

Using the Boltzmann distribution (ecuacion), for plasmas in LTE, the value for vibrational temperature for C\textsubscript{2} of figure 5 is 0,62 eV. We can see the emission of the nitrogen molecule (figure 4), which emit in the ultraviolet, visible and infrared, in this case the line emission of first negative system attributed to B\Sigma\textsuperscript{g}→X\Sigma\textsuperscript{g}+, occurs readily in a plasma at moderate pressure [17], band head at 501,53 nm.

![Vibrational temperature with Swan System of C\textsubscript{2}](image)
4. Conclusion
The diagnostic of the coal plasmas is very important for analysis parameters such as temperature in the plasma, electron density and the bands system that presents, and this provides information about of the transition and the excited species, incandescence of the carbon particles, and recombination processes and fragmentation. We can observe the formation of the Swan system of C\textsubscript{2} in the visible spectrum as well as the first negative system of nitrogen.

Acknowledgments
The authors (L. P. Vera and J.A. Pérez) wish to express their gratitude for the warm hospitality offered by Dr. Leopoldo Soto, Dr. Felipe Veloso and all the Local Organizing Committee of the ICPP-LAWPP 2010.

5. References

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