

Pollutant gas emissions during the co-combustion of Oil Shales from Uruguay with biomass wastes

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Abstract - The composition of pollutant gases (CO₂, CO and SO₂) during the co-combustion of Oil Shale (OS) and biomass wastes was studied in real time through thermogravimetric analysis (TG) coupled with a Fourier-Transform Infrared Spectrometer (FTIR). OS samples are from Mangrullo Formation (Uruguay). Biomass wastes were mixed with the OS at ratios 25%, 50% and 75% in mass of OS. Results showed that the emissions of pollutants per energy content of the mixture are related with the volatile decomposition and char reacting stages. CO₂ emissions are significant during the volatile decomposition and subsequently combustion stage at the temperature between 400 and 500 °C. The profiles of CO₂ against temperature exhibits one or two peaks, depending on the OS content of the sample and these emissions purely increased with the carbon content in the blends. The concentrations of SO₂ obtained by the TG analysis showed that the amount released increases as the OS content rise. This work showed that the adding of biomass waste to the OS can improve the gas quality as reduces. Generally, the results showed that samples between 0 and 50% of OS-biomass produces lowest total SO₂ emissions.

Keywords: co-combustion, pollutant emissions, TGA-FTIR, Oil Shale, biomass wastes.

1. Introduction

Oil Shales (OS) are sedimentary rocks containing organic matter in their composition. Currently, the OS has applications in Estonia and China. In the case of Estonia, the OS is combusted for energy production, using pulverized firing and a circulating fluidizing bed [1- 5]. In China, OS is used for oil production [6, 7]. OS have different characteristics depending on their origin, not all are suitable for the direct usage for the energy production as the reported for Estonia and China. It is the case of the Uruguayan OS that have a low organic matter content which determine a low heating value [8].

Recent works reported that the co-combustion of OS or bituminous coal with biomass have good potential for energy production, with improved environmental impact [9-12]. The co-combustion of biomass wastes with solid fossil fuels has several advantages with respect to the direct combustion of solid fossil fuel, such as the reduction of the emissions of contaminant gases (e.g. SO_x) in comparison with the combustion of solid fossil fuel and enhancement of the heating value of the blends in relation to the OS [13, 14]. These gases were selected to study because the ratio CO/CO₂ is used as reference of the poison index. On the other hand, the SO₂ emissions are necessary known because at high concentrations can harm trees and plants by damaging foliage, decreasing growth and can contribute to acid rain which harm sensitive ecosystems.

The addition of a certain percentage of biomass to the OS is regarded as a low-cost way for the reduction of the emissions of SO_x. This reduction depends on the OS-biomass mass ratio, the nature and the physicochemical properties of the fuels and the operating conditions (e.g. temperature). Therefore, gas emissions from the co-combustion of OS and biomass are crucial to decide the nature of the biomass and the mass ratio used in the fuel mix. In this sense, thermogravimetric analysis coupled with gas-phase Fourier Transform Infrared Spectroscopy (TG-FTIR) has been successfully used in quantitative analysis of these gaseous products [15-17].

This work aims to perform a systematic study of the CO₂, CO and SO₂ gas emissions by means of TG-FTIR during the co-combustion of Uruguayan OS mixed with three different biomass wastes, and at different mass ratios. The influence of the nature of the biomass and OS-biomass mass ratio with the gas emissions and temperature is presented.

2. Materials and methods

2.1. Fuels selected and sample preparation

The OS sample were supplied by the National oil company of Uruguay (ANCAP) and it was obtained from Mangrullo Formation (northeast). The procedure for its selection and sampling can be seen in [8]. Biomass samples were selected according to the abundance and availability of the biomass wastes generated in Uruguay. The selected biomass are: Grape Pomace (GP), Eucalyptus Grandis Sawdust (EG) and Rice Husk (RH).

GP samples are from a vineyard located in Melilla, Montevideo Department, Uruguay during the grape harvest, and correspond to Tannat type. EG samples come from a 17.5 year-old tree from Piedras Coloradas, Paysandú Department, Uruguay. RH samples were collected from a rice producer located in Rio Branco, Cerro Largo Department, Uruguay and correspond to large seeds of Tacuarí variety. All samples were dried at 105 °C for 24 hours. Dried samples were crushed and sieved to a particle size below 50 mesh [18].

The OS-biomass samples were prepared from the OS powder and the corresponding biomass using a micro rotary mixer for 2 hours. The OS proportions in the different samples were: 100 % (pure OS), 75 %, 50 %, 25 % and 0 % (pure biomass). Samples were characterized by ultimate and proximate analysis, Higher heating values (HHV) of OS and biomass samples were obtained with a bomb calorimeter. For the blends, the HHV was calculated taking in consideration the composition and the HHV of the two components. The methodology employed in these analyses can be seen in [8].

2.2. Co combustion gas emissions analysis

Simultaneous thermogravimetric analysis (TG) was performed on a STA 6000 from Perkin Elmer coupled with a Fourier-Transform Infrared Spectrometer (FTIR) Perkin Elmer model Frontier. Approximately 15 mg of each mix was used per experiment at a heating rate of 5 °C min⁻¹ from 30 to 950 °C. The experiments were conducted in air atmosphere using a gas flow rate of 50 mL min⁻¹. Product gases were pumped into a FTIR spectrometer for analysis using a TG-IR-GCMS interface TL8000 with a flow rate of 50 mL min⁻¹. To avoid the condensation of gases during the transfer line was kept at 573 K during the experiment. Spectra were collected at a resolution of 1.0 cm⁻¹ between 450 and 4000 cm⁻¹. Each test was conducted at least twice to ensure reproducibility. The quantification of the amount of gases released was made with QASoft software, which contains Spectral Libraries for all the gases studied here. In order to compare the gas emission per energy released, the concentration obtained by this analysis (ppm) was divided by the corresponding HHV of the sample.

3. Results and discussion

3.1. Physicochemical characterization

Table 1 summarises the ultimate and proximate analysis performed for the different samples, moreover, the value of HHV is reported. The results showed that the OS present low C content in comparison with the biomass samples and high sulphur and ash content.

Table 1: OS and biomass properties.

Material	Ultimate analysis				Proximate analysis			Calorific Value
	Wt.% (d.b.)				Wt.% (d.b.)			MJ kg ⁻¹ (d.b.)
	C	H	N	S	VM	FC	Ash	HHV
OS	9.3	2.3	0.2	4.0	24.0	3.4	72.6	3.2
GP	48.8	6.0	1.9	0.2	72.7	19.9	7.4	20.6
RH	35.3	4.7	0.3	0.1	64.4	12.8	21.8	14.7
EG	48.2	5.9	0.0	0.0	88.5	11.3	0.24	18.7

VM: volatile matter; FC: fixed carbon; HHV: higher heating value; d.b.: dry basis.

3.2. TG analysis results

The mass loss rate during the heating and combustion processes in TG analysis were shown in Fig.1 as the corresponding corresponding DTG curves. The small peak at 100 °C in all the samples is attributed to moisture loss. Beyond 100 °C, each mass loss rate curve exhibited two or four more characteristics peaks. It is important to highlight that the number of peaks is related to the % OS in the sample. For example, samples with OS content above or equal to 50 % wt. present four distinctive peaks, while samples with OS below 50 % wt. exhibited 2 peaks. The temperature of the first of these peaks depends on the biomass in the mix (ca. 250°C for GP and 300 °C for RH or EG). However, the second peak appears at ca. 400 °C but as the %OS content increases and the volatile matter amount is reducing, an intermediate peak appears between the first and second peak due to the decomposition of the volatile matter from the OS. Furthermore, a fourth peak is exhibited at temperatures close to 600°C and it can be attributed to the decomposition of the inorganic components. Note that an interaction between the different peaks of the different fuels or a peak displacement were not observed during the heating of the samples.

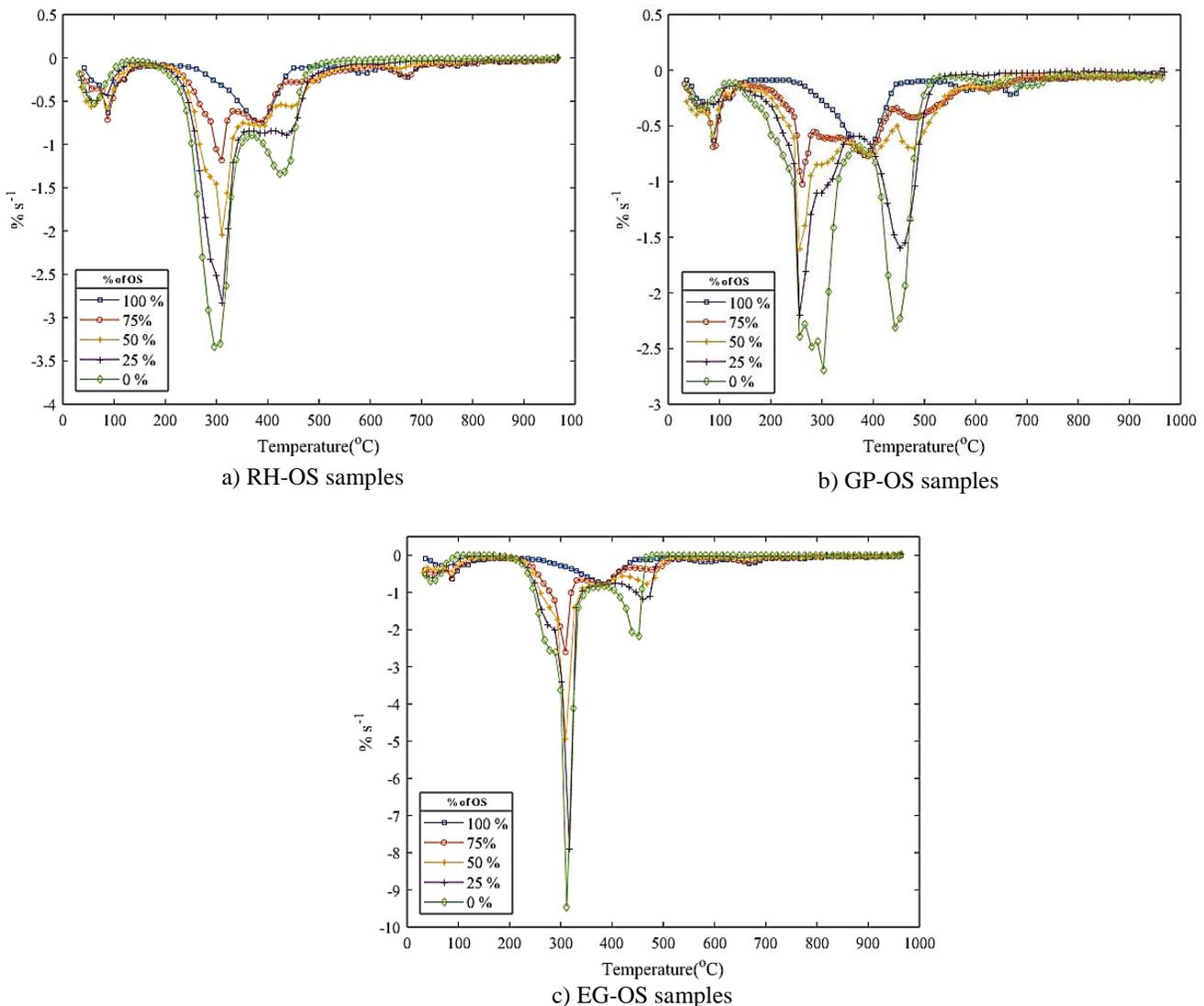


Fig. 1: DTG curves obtained during the heating process by TG analysis.

3.3. CO₂ emission patterns

Fig.2 shows the CO₂ emissions per MJ generated during the heating of the pure samples and their blends. Within the temperature range $265 \leq T < 400$ °C, samples with OS content between 0 and 50 % showed CO₂ emissions less than 1.5×10^{-2} ppm MJ⁻¹, while samples containing 75 to 100% of OS reached values close to 3.0×10^{-2} ppm MJ⁻¹. These emissions are associated to the second stage during the heating of the OS-biomass samples. Subsequently, at 400 °C, the maximum CO₂ emission per unit of energy released is reached for 100 % of OS. This confirms the maximum weight loss due to the volatile matter registered during the TG analysis. As the heating process continues, the trend is the opposite that the observed previously, for samples containing 0 and 50 % of OS the CO₂ released was more significant than on the first range. This fact confirm that the amount of CO₂ released per MJ generated during the devolatilization stage of the biomass was relatively lower compared with the char combustion stage.

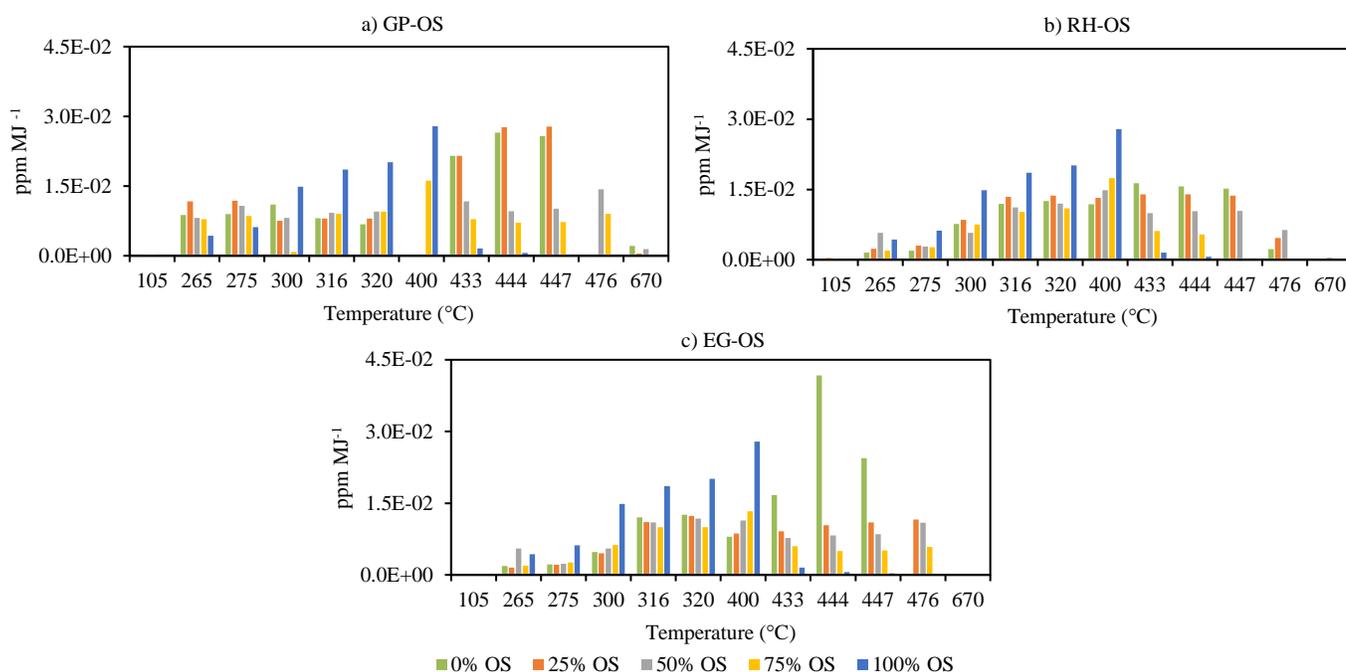


Fig. 2: CO₂ emissions per MJ generated for the different samples and their blends.

The amount of CO₂ released increases significantly when the temperature reached the values of the peaks corresponding to the char combustion of the biomass, because the amount of char from the biomass increases as the OS content decreases. After the char combustion period, a smaller amount of CO₂ was released until the burnout char stage is reached.

3.4. CO₂ emission patterns

Fig. 3 shows the CO₂ emission per MJ generated in the gaseous products for the OS, biomass and their blends. The patterns obtained for this gaseous product has similarities with the observed for CO₂. During the volatile decomposition stage of the biomass, all the blends and pure biomass presents CO emissions per MJ generated less than 1.5×10^{-2} ppm MJ⁻¹. The OS present the higher CO emission peak during this temperature range and it is in agreement with the process observed in the TG analysis due to the volatile decomposition from the OS.

The magnitude of the second emission range (400 – 600 °C) decreases with the increase of the OS content of the blends. Generally, samples with OS content of 100 and 75 % presents similarities on their CO emissions ($\text{ppm MJ}^{-1} < 6.0 \times 10^{-3}$), however, as the biomass content increases (from right to left at each temperature) into the sample the CO emissions too, it is due to the char combustion of the biomass that is taking place on this temperature range. Furthermore, the OS is ending their devolatilization process, the facts mentioned before can explain the behaviour observed on this temperature range.

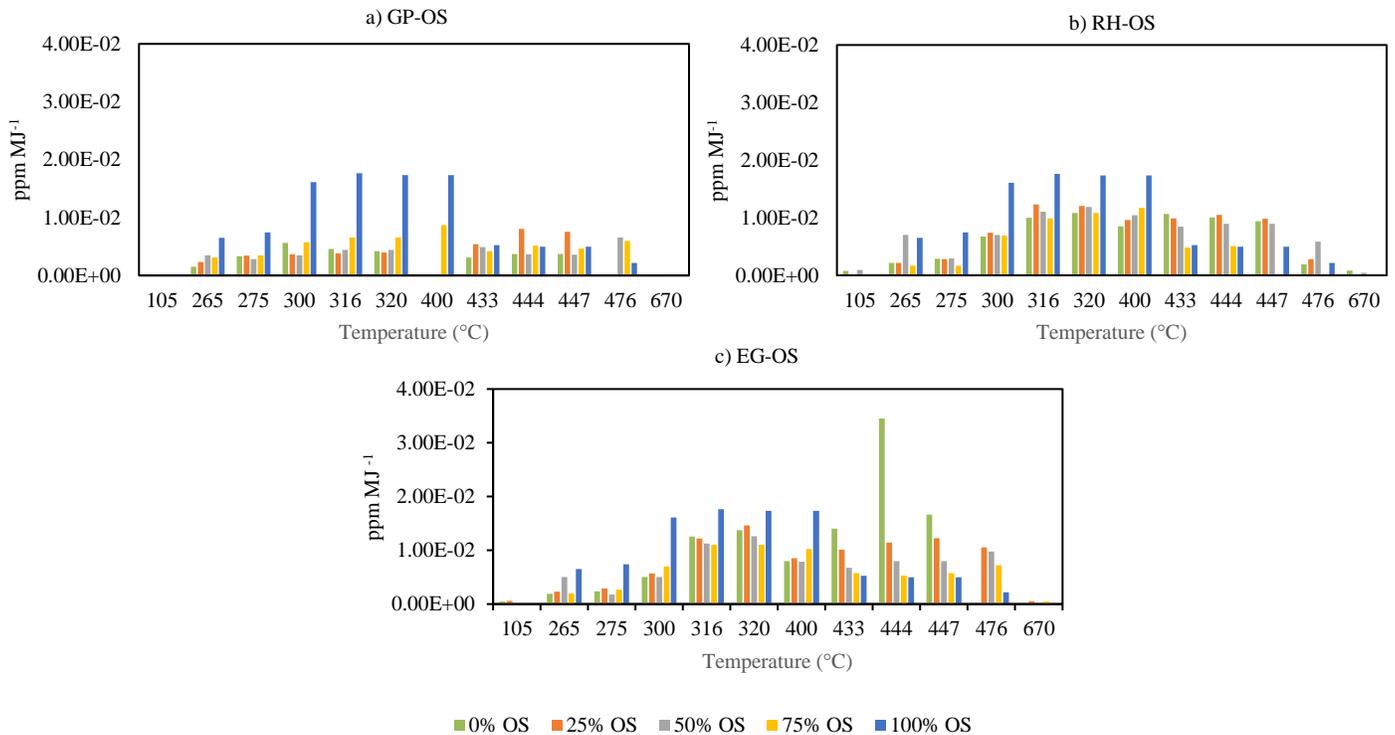


Fig. 3: CO emissions per MJ generated for the different samples and their blends.

3.5. SO₂ emission patterns

Fig.4 shows the SO₂ emission results, the features of the first temperature range (265 - 400 °C) were more strongly influenced by the compositions and the magnitude of the SO₂ emission concentration was higher for the blends with high OS content. The SO₂ generated in this range is from the devolatilization and subsequently combustion of the organic component that contain this element. On the other hand, the magnitude of the second emission range (400 - 670 °C) is more dominant than the first range and it increase of the OS content in the blend, note that for all the cases the maximum SO₂ emissions was registered at 670°C, being in agreement with the process that is taking place at this temperature as for example the decomposition of the pyrite from the inorganic matrix.

The ultimate analysis showed that the amount of S in biomass was less than that in the OS, therefore, the extent of the release and the intensity for SO₂ in the OS was much higher than the value obtained for the biomass.

The second temperature range showed that the SO₂ emission level were reduced with addition of biomass in the blends, such reductions are expected because biomass is a more volatile fuel and has higher oxygen content than OS, which translates into lower sulphur emissions as higher blending ratios of biomass are used. Moreover, note that the value of the SO₂ emissions are lower than the obtained for CO.

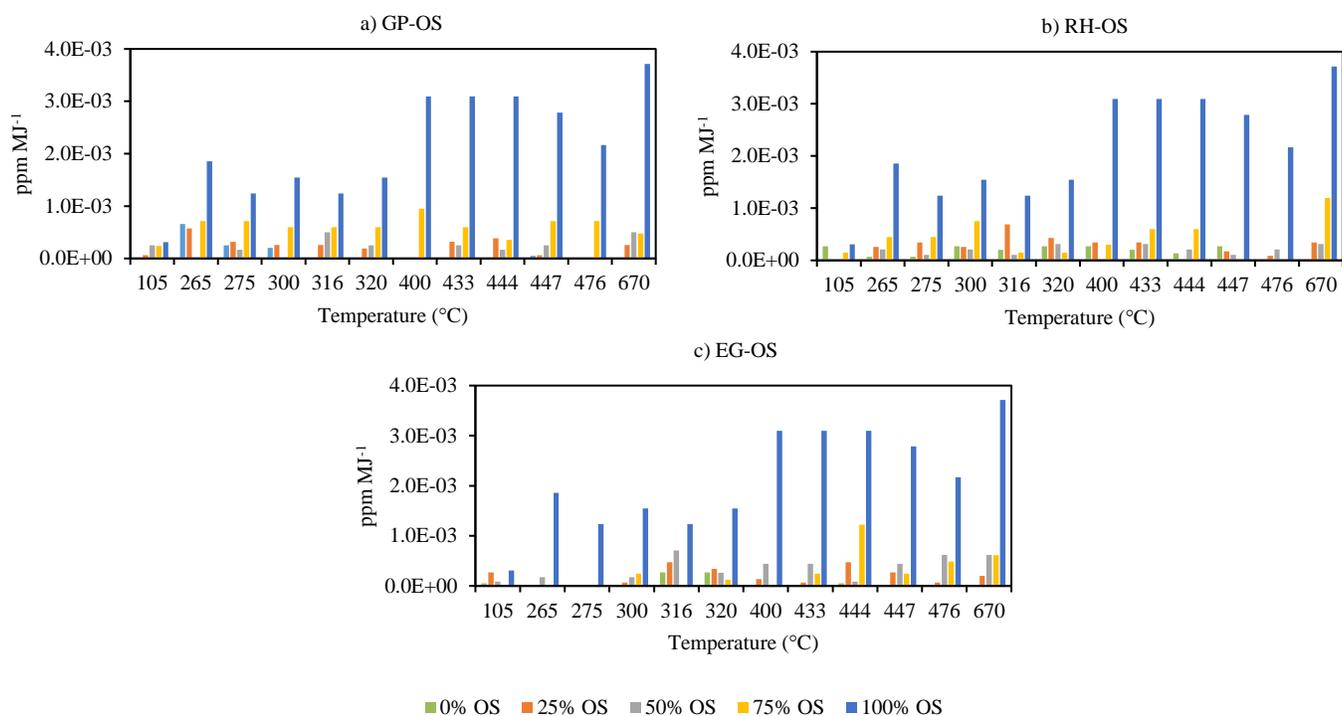


Fig. 4: SO₂ emissions per MJ generated for the different samples and their blends.

4. Conclusion

The emission characteristics of CO₂, CO and SO₂ released per MJ generated from the co-combustion of OS with different biomass were quantified by TG-FTIR. The addition of biomass to the OS diminishes the gas emissions of CO and CO₂ below 400 °C. In the case of SO₂ emission, this diminution, which reached almost 2 orders of magnitude in some cases, is observed at every temperature studied. This study showed that combining the OS with biomass can produce better emission control of SO₂. In addition, to conclude which biomass is the better for burning with OS, a thermal and kinetic analysis should be done which is currently in progress in our research activities.

Acknowledgements

The present work was carried out with the support of Agencia Nacional de Investigación e Innovación (ANII project FSE-1-2016-1-131635). M. Torres thanks the Uruguayan ANII for the grant received (POS-NAC-2016-1-129893), to the PEDECIBA-QUIMICA and CSIC-Udelar for the economic support gave to performing the research internship at the University of Queensland and to ANCAP for the OS samples provided for the research.

Moreover, the authors thank to the Sociedad Anónima Molinos Arroceros Nacionales (SAMAN) for the rice husk sample, to the vineyard Amendola Hnos.y Boido S. for the grape pomace sample and to UPM Forestal Oriental for the eucalyptus grandis sample.

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