Biofuels and biomaterials from primary and activated sludge.

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Keywords: Sewage sludge, pyrolysis, biofuels, bio-oil, biochar

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ABSTRACT

Sewage sludge has become an environmental challenge because it is produced in a large scale and still has an uncertain final destination. The process of pyrolysis is a sustainable and innovative way of managing this residue mainly because turn a waste into useful bi~~l~~o-oil and a sterile carbon char. The products formed in the reaction depend on a myriad of factors, such as the diversity of metals present in the *in natura* sludge; the contents of carbon, hydrogen, nitrogen and oxygen; the temperature, heating rate; and the residence time; among other factors. This study proposes the pyrolysis of primary and secondary sludge at 450 °C and the analysis of formed biochars and bio-oils oils. The complex crystallographic profile, absent of potentially toxic metals and the increase of superficial area of biochars grant the use as a biomaterial. The bio-oil analysis shows the displacement of carbonyl groups probably related to the degradation of the fatty acids during the reaction, also seen in NMR spectra, which can lead them to be used as biofuels.

Introduction

The wastewater treatment occurs through physical and biological processes[2], which will inevitably produce large amounts of sludge. For instance, about 30 million tons of sludge are produced in China every year [6], while in Brazil, about 372,000 tons are generated[7] and leans to increase as much as universalisation of sanitation occurs. The primary sludge arises from the removal of suspended solids, organic matter, oils and greases. The secondary sludge arises from the removal of organic matter and macronutrients such as N and P by microorganisms[3]. The current final disposal of the sludge is mostly done by landfilling, land spreading, or incineration[4]. Those methods are potentially hazardous to the environment and not economically optimized since the cost of managing the sludge represent up to 50% of the total cost of treatment of the effluent itself[8].

There are many challenges regarding bringing the traditional sludge management techniques up to date with modern stands of sustainability and effiency. The pyrolysis, a thermochemical treatment carried out in the absence of oxygen at moderate to high temperatures (300-700 °C)[13], of the sludge is a technological solution to this problem, since it presents the main advantages of the incineration (the destruction of pathogens, the recovering of mineral resources and the reduction in volume[11]) and has substantial energy and environmental advantages,[12] like the reduction of Greenhouse Gases (GHG) and the recovery of energy. The resulting products achieved in this process are a solid called biochar and a liquid product known as bio-oil[14], which has properties analogous to petroleum diesel. The reaction conditions and the characteristics of the feedstock sludge determine the physicochemical properties of both the formed biochar and the bio-oil, such as composition, particle size, distribution and also regularity of the internal structure of micro, meso and macropores[15].

In this work we have studied the pyrolysis of a primary and a secondary sludge collected from Norte Sewage Treatment Station in Brasilia, Brazil. After the pyrolysis it was obtained a biochar and a bio-oil, which were characterized in order to identify potential uses for them.

Materials and Methods

The primary and secondary sludge were collected from Norte Sewage Treatment Station in Brasilia, Brazil, dried at 105 °C and their total content of fat, oil and grease (FOG) was measured by *n*-hexane extraction with the aid of a Soxhlet apparatus using standard methods[16]. The solvent mixture with the lipidic material was then subjected to filtration, evaporation and drying under vacuum. The pyrolysis reaction was carried out with 10 g of dry sample in alumina crucible in a stainless steel horizontal tubular furnace, from room temperature to 450 °C, with a heating rate of 10 °C/min, residence time of 90 min under inert atmosphere- N_2 (g). The bio-oil formed was collected from the outlet of the furnace and was solubilized in dichloromethane, which was later evaporated at 40 °C. The dried sludge feedstock and the biochars were analyzed through Scanning Electron Microscopy with Dispersive Energy Spectroscopy (SEM-EDX) on a Jeol 840a microscope, with a tungsten capillary filament and electric potential difference of 0.2 to 40 kV with a take-off angle of 49.57°and voltage of 15,000kV acceleration. The elementary analysis of Carbon, Hydrogen, Nitrogen (CHNO) were made in Perkin Elmer EA 2400 Series II equipment, with thermal conductivity detector. The X-ray diffraction (XRD) analysis were made on a RIGAKU model ULTIMA-IV, operating with a copper tube and nickel filter, under a voltage of 35 kV and a current of 15 mA, the scan speed was

0.05 °/min and 2θ angle ranged from 2 to 80°. The Analysis of the pore volume was performed on a Quanta Chrome Nova Win apparatus at -195,85 °C.

The oils extracted and bio-oils ^{1}H and ^{13}C spectra were obtained from 20 mg of sample dissolved in 0.5 mL of deuterated chloroform ($CDCl_3$) and with TMS (tetramethylsilane) as internal standard, using a Mercury Plus 7.05T spectrometer (300 MHz), with a 5 mm diameter probe. The infrared spectra (FTIR) were acquired on a Shimadzu IR Prestige 21 spectrometer, with an attenuated total reflectance (ATR) cell. The spectra were acquired after the accumulation of 32 interferograms, covering the region between 400 and 4000 cm^{-1}.The acidity essay of the oils were made according to American Society for Testing and Materials[17].

Results and Discussion

The of reaction yield analysis (Figure 1) indicates a bigger volatilization of the organic fraction present in the Primary Sludge (PS). The Elemental analysis of hydrogen, oxygen and carbon of the sludges (Figures 2 and 3) shows there is carbon and nitrogen fixation after the thermal process in the Primary Sludge (PS) and Primary Sludge Biochar (PSB) and losses of hydrogen (probably in the gas fraction). Regarding the Secondary Sludge (SS) and Secondary Sludge biochar (PSB), it was possible to observe a high fixation of oxygen in the produced char. The nitrogen percentage of this sludge feedstock (compared to PS) is much higher due to the presence of nitrogen compounds in the biological flake. The H/C and O/C ratios show low aromaticity and high content of oxygenated functional groups.

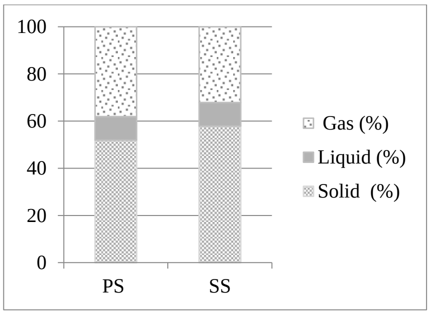

Figure 1- Yield of Pyrolysis Reaction of PS and SS

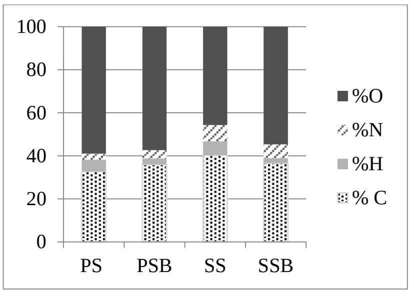

Figure 2- Analysis CHNO of PS (Primary Sludge), PSB (Primary Sluge Biochar), SS (secondary Sludge), SSB (Secondary Sludge Biochar)

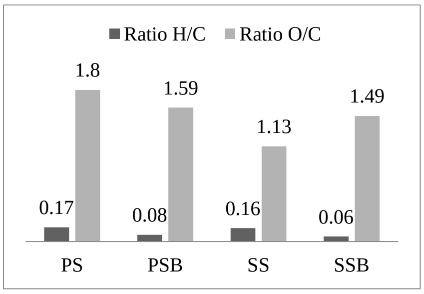

Figure 3- Ratio H/C and O/C of PS , PSB , SS and SSB

The analysis of the images generated by the scanning electron microscope (SEM) (Figure 4) indicates both dried *in natura* sludges have a very irregular structure, with asymmetric cavities and a surface full of granules but the SS image also shows the presence of flakes, arising from the activated sludge. After the thermal process, both biochars seems to be have a more simetric structure, with a continuous network, also seen in EDX and XRD analysis.

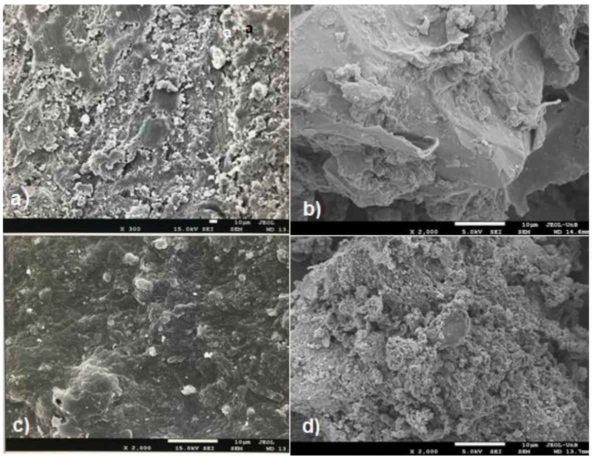

Figure 4- SEM microscopy a) PS (300X), b) PSB (2000X), c) SS (300X), d) SSB(2000X)

The PS samples have higher crystallinity and a greater number of peaks, as seen in the the X-Ray diffractogram (Figure 5). The intense peak at 26° is related to the crystallographic plane of SiO_2 in the form of quartz (c) the peak near 35° (peak d) is relative to calcite ($CaCO_3$), at 21° associated to kaolinite- $Si_2Al_2O_5\,(OH)_4$ (peak a), which is clearer after the reaction. In the SS samples the a large band between an intense signal of SiO_2 in the form of quartz in 26 ° (c signal) and a broad band in 22° (peak b) is relative to cellulose type I, which is decomposed in thermal process. The detailed profile of metals is seen in the analysis of X-ray fluorescence (EDX) data (Table 1) which reveals the absence of potentially toxic metals and a higher percentage of aluminum, iron, silicon and calcium in the PS samples. In contrast, the SS samples present high phosphorus content (removed from the effluent and precipitated in the sludge). BET analysis indicates irregular internal mesoporous and an increase of surface area after heat treatment, mainly on PSB, consistently to sludge biochars.

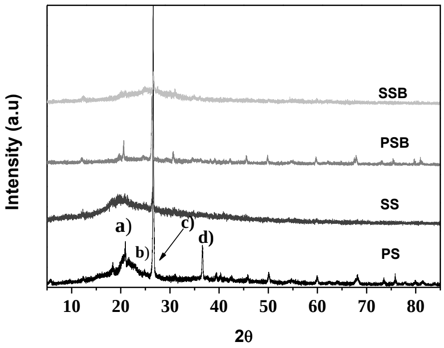

Figure 5- XRD of PS, SS, PSB, SSB. Peaks refers to a)kaolinite, b)cellulose type I, c) quartz and d) calcite**.**

Table 1- EDX of PSB and SSB

Element	PSB		SSB	
	Mass %	atomic %	Mass %	atomic %
Oxygen	38,17	56,81	33,6	51,18
Magnesium	0	0	3,88	3,89
Aluminum	14,95	13,19	10,51	9,49
Silicon	14,56	12,35	8,67	7,52
Phosphorus	5,03	3,87	17,45	13,73
Potassium	2,69	1,64	8,56	5,33
Calcium	9,93	5,9	7,54	4,58
Iron	14,67	6,25	9,79	4,27
Total	100	100	100	100

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Table 2- Specific Superficial Area and Porus Volume

Sample	Specific Superficial Area (m^2g^{-1})			Porus Volume ($cm^3.g^{-1}$)		
	BET[a]	Microporous[b]	External	$V_{0,98}$[c]	Microporous[b]	Mesoporous
PS	0	0	0	3,4	0	3,4
PSB	18,89	9,89	9,00	13,08	6,3	6,78
SS	0,55	0	0,55	3,08	0	3,08
SSB	2,59	0	2,59	3,9	0	3,9

[a]- BET Method (Brunauer, Emme and Teller). [b] *t-plot* method, [c]adsorbed volume at $p/p_0=0{,}98$

Characterization of liquids

The fatty, oils and grease (FOG) extracted from the primary sludge has a disagreeable smell and dark color, whereas the one from the secondary sludge has a more yellowish tone which shows different levels of oxidation. The FOG from the PS presents acidity of 107.69 mg KOH/g while the one from the PS has 80.57 mgKOH/g. The carboxylic acid and triacylglyceride profile shown by the infrared and nuclear magnetic resonance analyzes are quite similar. In the ^{13}C NMR spectrum of both oils (Fig 10 and Fig 11) there is a small band around 180 ppm relative to C=O carbonyl (of carboxylic acid or ester) and a reduced signal at 130 ppm relative to C=C. Relative bands between 16 and 37 ppm relative to sp^3 carbon and the multiplet between 22 ppm and 34 ppm refers to sp^2 carbon. The spectra of ^{1}H indicate the presence in all samples of peaks related to aliphatic hydrogens (2.48 ppm, singlet, 2.30 ppm, 0.98 ppm), terminal CH$_3$ hydrogens (triplet at 80 ppm) and CH$_2$ (intense singlet at 1.3 ppm) but did not present H associated with acid groups and no triacylglyceride related hydrogens (multiplet at 4.5 ppm). ^{1}H spectra indicate the presence in all samples of peaks related to terminal CH$_3$ hydrogens (triplet at 0.80 ppm) and CH$_2$ (intense singlet at 1.3 ppm). The modifications on carbon and hydrogen structure before and after the thermal process are also seen in Table 3 and 4, demonstrating the increase of alkanes and short aliphatic products after the thermal process of PSO while the SSO lead to form long and branched aliphatics and olefins. To better understand the formation of acid groups, the analysis of Infrared Spectra because the influence of the solvent CDCl$_3$ affect the chemical shift of carbonyl groups on 13C NMR spectra and OH from carboxylic acids on ^{1}H NMR spectra.

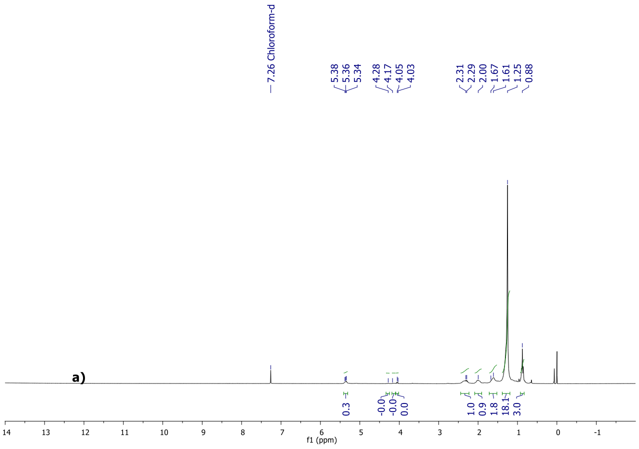

Figure 6- ^{1}H NMR spectra of PSO

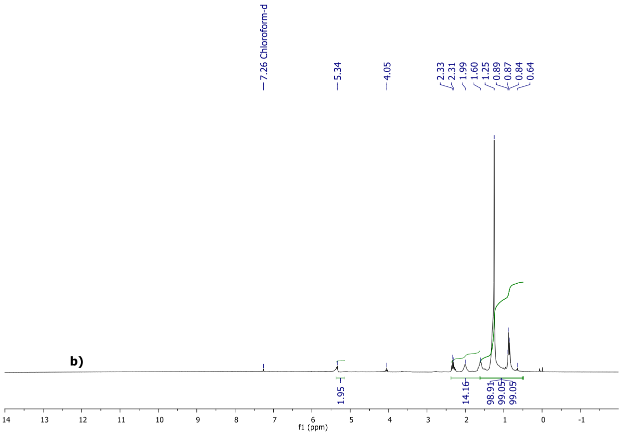

Figure 7- 1H NMR spectra of SSO

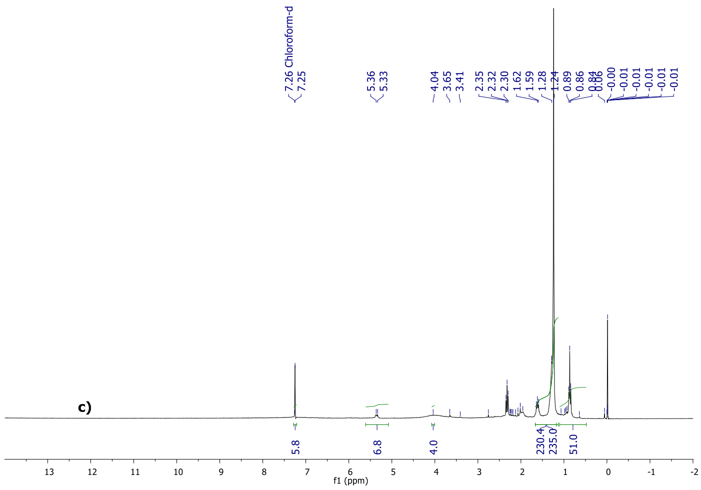

Figure 8- 1H NMR spectra of PSB

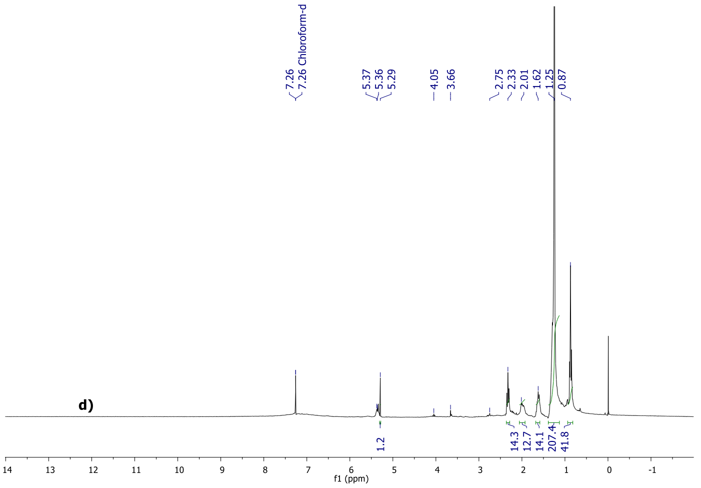

Figure 9- 1H NMR spectra of SSB

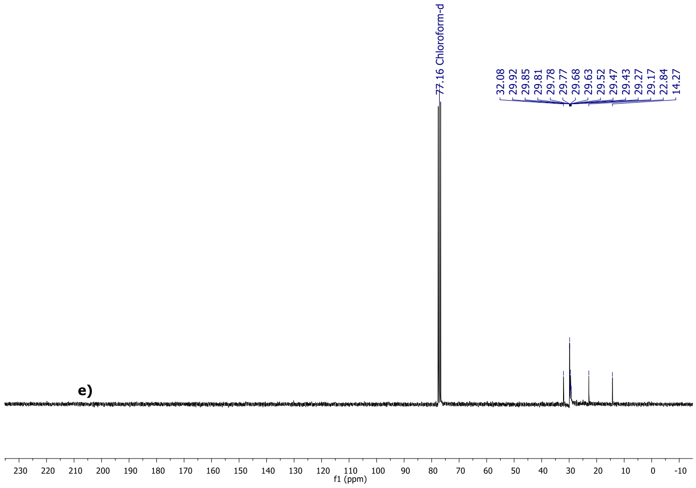

Figure 10- 13C NMR spectra of PSO

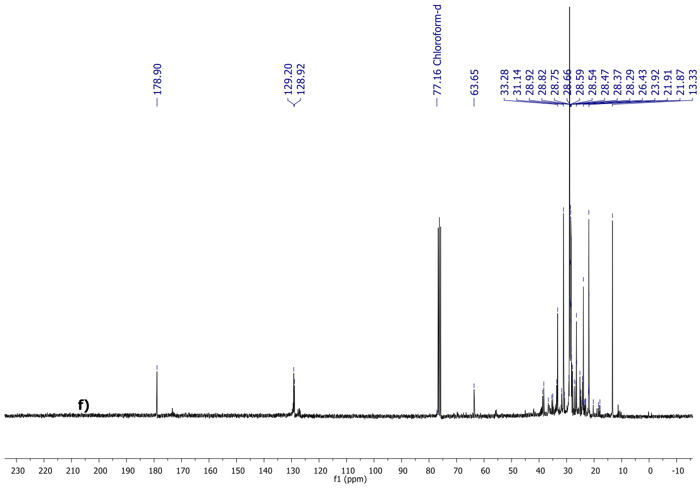

Figure 11- 13C NMR spectra of SSO

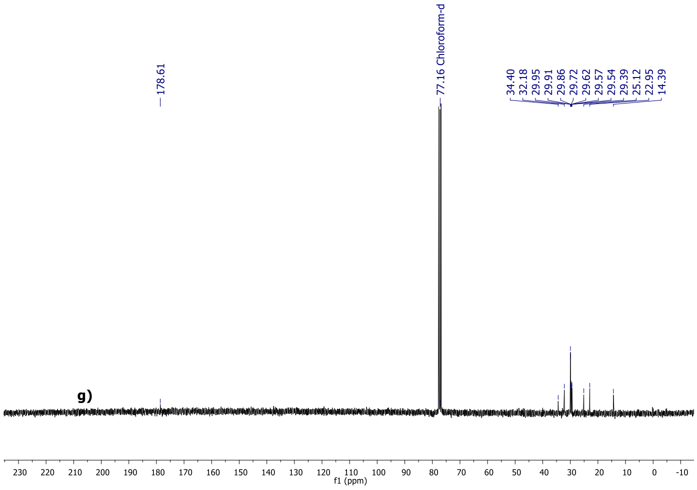

Figure 12- 13C NMR spectra of PSB

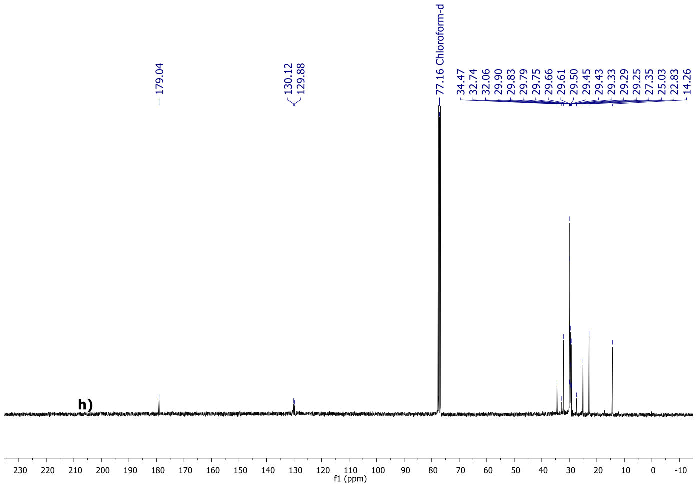

Figure 13- 13C NMR spectra of SSB

Table 3- Chemical shift on^{13}C NMR spectra.

δ (ppm)	Carbon assignments	PSO	SSO	PSB	SSB
0-28	Short aliphatics	7,14%	59,26%	21,43%	21,05%
28-55	long and branched aliphatics	92,86%	22,22%	71,43%	63,16%
55-95	alcohols, ethers, phenolic-methoxys, sugars, carbohydrates	0,00%	3,70%	0,00%	0,00%

95-165	aromatics, olefins	0,00%	7,41%	0,00%	10,53%
165-180	esters, carboxylic acids	0,00%	3,70%	7,14%	5,26%

Table 4- Chemical shift on ^{1}H NMR spectra

δ (ppm)	**Proton Assignment**	**PSO**	**SSO**	**PSB**	**SSB**
0,5-1,5	alkanes	16,67%	45,45%	37,50%	20,00%
1,5-3,0	aliphatics α-to heteroatom or insaturation	41,67%	36,36%	50,00%	40,00%
3,0-4,4	alcohols, methylene-dibenzene	16,67%	9,09%	0,00%	20,00%
4,4-6,0	methoxyl, carbohydrates	8,33%	9,09%	12,50%	20,00%

Infrared spectra of the two oils (Fig 14 and Fig 15) presented a broad band between 2500 and 3500 cm^{-1} relative to the presence of O-H of acid groups. The infrared spectra of the two oils show the widening of the bands between 2500 and 3500 cm^{-1} relative to the presence of acid groups. The C = O draw of carboxylic acids appears less displaced than the C = O groups of esters (1710 cm^{-1} and 1740 cm^{-1}, respectively). In the sample, along the C = O stretch, the C-O-H bond deformation appears around 1800 cm^{-1}. At 1420 cm^{-1}, there is presence of the band referring to the angular deformation O-H and axial stretching O-C-C.

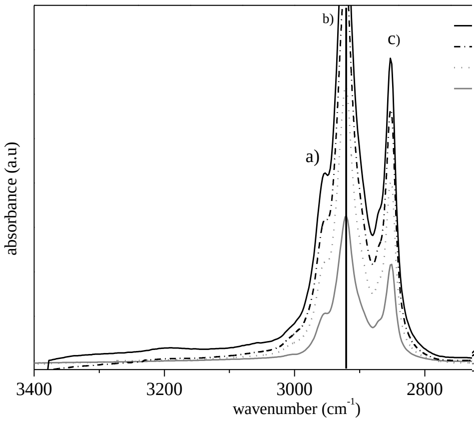

Figure 14- Infrared spectra of Primary Sludge Oil (PSO), Secondary Sludge Oil (SSO), Primary Sludge Bio-oil (PSB) and Secondary Sludge Bio-oil (SSB)

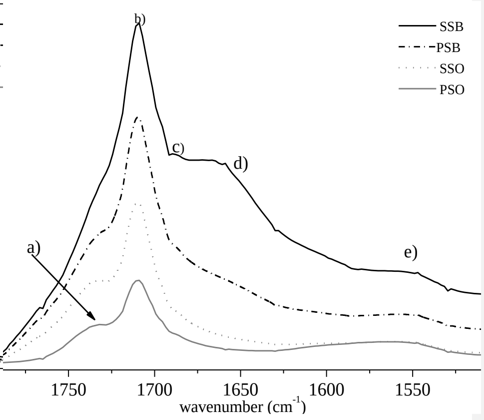

Figure 15- Infrared spectra of Primary Sludge Oil (PSO), Secondary Sludge Oil (SSO), Primary Sludge Bio-oil (PSB) and Secondary Sludge Bio-oil (SSB)

Conclusion

In this study primary and secondary sludge were pyrolyzed at 450 °C and the analysis of formed biochars and bio-oils oils. The sludge generated in the Primary treatment presents peaks related to a regular and diversified crystalline network, with the presence of silicates. In the SS samples the a large band between an intense signal of SiO_2 in the form of quartz in 26 ° and a broad band in 22°, related to cellulose type I is decomposed in thermal process. Scanning Electron Microscopy (SEM) and BET analysis denote the presence of irregular internal mesopore and an increase of surface area after heat treatment, mainly on PSB, consistenly to sludge biochars. There is also the increase of alkanes and short aliphatic products after the thermal process of PSO while the SSO lead to form long and branched aliphatics and olefins. In summary, the pyrolysis seems to be an excellent alternative for managing sludges. We are currently studying potentials uses for the bio-oil and the biochar obtained in the process.

Acknowledgments

The authors are in debt with CAESB, CNPq, CAPES and FAPDF for financial support of this work.

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