
Evaluation of forest fire biomass for energy production: pyrolysis versus combustion

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ABSTRACT

This thesis concerns the evaluation of biomass remaining after forest fires occurring in Portugal for energy production purposes. It involves the study of post-fire remains of *pinus pinaster* by investigation and characterization of bio-char, bio-oil obtained from pyrolysis.

Pyrolysis trials were performed at temperatures ranging from 400 to 500°C for 15 min. Next, pyrolysis of samples mixed with catalysts at 475°C was made. Catalysts used were: CaCO₃, Na₂CO₃, Li₂CO₃, limestone and zeolite Y. Lastly, carbonization at temperatures between 250-300°C was performed.

Methods used to investigate the composition of the obtained solid and liquid material included: Raman spectroscopy and Fourier-transform infrared spectroscopy.

Results of pyrolysis at different temperatures indicated that the amount of bio-char tended to decrease with temperature increase. Yields of bio-char, bio-oil and bio-gas showed that in most cases the dominating pyrolysis product is bio-gas. Comparison between two samples affected and not affected by direct fire revealed that when samples were subjected to fire they produced more bio-char during pyrolysis, while the ones not affected by fire were producing more bio-oil. Pyrolysis with catalysts showed that catalysts promote gasification and decrease the bio-oil yield, except for Y zeolite, which slightly increases the bio-oil and decreases the bio-gas yield.

Keywords: Forest fires, burned biomass, pyrolysis, bio-oil, bio-char, FTIR.

1 INTRODUCTION

Biomass which remains after forest fires is a resource which gains more attention, especially considering the Iberian Peninsula region where wildland fires are a problem increasing each year. In Portugal between July and September during years 2003-2012, there were 31 forest fires larger than 5 000 ha (including 12 fires on an area bigger than 10 000 ha) [1].

Main reasons standing behind forest fires, besides human-induced acts of vandalism are atmospheric conditions during the summer season and the Mediterranean type of climate [2]. Almost the whole Portuguese territory has a long hot and dry season which can last from three to five months [3].

Wildfires drastically change the structure of the forest, reduce the biomass vegetation and in a short amount of time significantly transform the landscape and affect the ecological and economical value of the forests.

On Portuguese territory as visible in Figure 1, forests are dominating type of land use and they contribute to more than 1/3 of total territory.

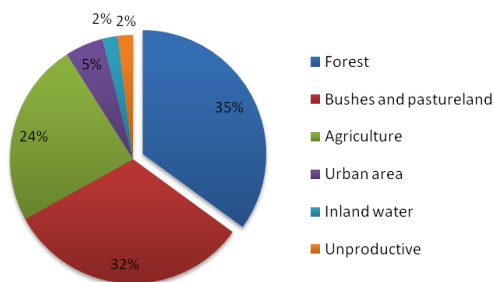


Figure 1 – Land use distribution in mainland Portugal. Adaptation of [4]

Forest fires wasn't considered key problem in the past, however after 1970, when Portuguese population transitioned from agriculture to more industrial, lands which were previously used for productive farming became abandoned or converted into forests [5]. This lead further to ecological succession and accumulation of big amount of biomass on this regions which made them susceptible to the occurrence of large fires. Nowadays, according to European Forest Fire Information System, Portugal is the country most affected by fire incidences [6]. As it can be seen on Figure 2 fire events are distributed irregularly in terms of the area burnt with biggest accumulation on north of the country



Figure 2 - Spatial distribution of fire events between 2001–2013 [6]

2 MATERIALS AND METHODS

2.1 FOREST FIRE DERIVED BIOMASS

Materials used in experiment were parts of Pine tree (*Pinus Pinaster*) from burned areas of the forest. Pine tree is of great importance in Portugal and Galicia, because it is one of the main resource and supply chain element in the wood-based industry.

Samples provided for research were mostly burn only in thin surface layer of bark and cambium.

2.2 PYROLYSIS

Pyrolysis trials were performed in one of laboratories belonging to Chemical department of the Instituto Superior Tecnico. Equipment used was cylindrical oven Eurotherm and fixed bed vertical reactor which is long, glass column to which glass wool, inert material and sample were introduced. The reactor was installed in a temperature controlled oven and connected to, condenser to collect water and other humid substances which may appeared during process and gas chromatograph

Obtained products were bio-char and bio-oil with acetone which was used as a carrier to transfer bio-oil from reactor to container. Later acetone was removed by rotating evaporator.

2.3 CARBONIZATION

Raw biomass was subjected to carbonization process in 250, 275 and 300°C temperature. Later, one of carbonized biomass sample, 250°C was used for 15 min pyrolysis in 475°C.

2.4 RAMAN SPECTROSCOPY

Raman spectroscopy was performed on the equipment belonging to one of the laboratories belonging to Informatics department of IST. The instrument had spectral range of 600 – 2000 cm⁻¹ and measurement was performed at room temperature, with laser energy at 532 nm wavelength as the excitation source.

Bio-char samples from pyrolysis of all raw biomass and one burned biomass sample (from 400°C pyrolysis) were measured.

2.5 FTIR

Bio-oil samples investigation by Fourier-transform Infrared spectroscopy was performed using Perkin-Elmer Spectrum Two FT-IR Spectrometer, a horizontal attenuated total reflectance equipment, with a ZnSe crystal and ATR accessory.

3. RESULTS AND DISCUSSION

Results from pyrolysis trials included yields of bio-char, bio-oil and gas obtained without catalysts for temperatures ranging from 400 to 500°C and for temperature 475°C with addition of catalysts such as CaCO₃, Na₂CO₃, Li₂CO₃, limestone or zeolite Y (detailed results in Table 1 and 2). Also the amount of bio-char as function to temperature was represented for raw and burned biomass sample.

3.1 Raw biomass pyrolysis yields

The pyrolysis results (Figure) indicated that in case of raw biomass, bio-char amount was decreasing with the temperature increase and more oil and gas was produced as visible in Figure 3.

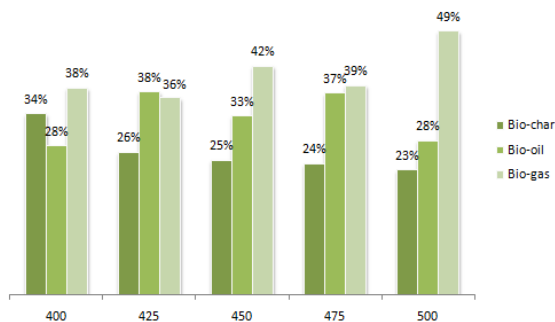


Figure 3 – Raw biomass bio-char, bio-oil and bio-gas pyrolysis yields

On Figure 4 it can be seen that when catalysts were used during process, gas yields increased at all trial temperatures and the bio-char amount was smaller in each case. All catalysts except Y zeolite increased the gas yield by few percent, however, Y zeolite as only increased the bio-oil yield. The best catalyst for obtaining highest amount of bio-char was Li₂CO₃ and Na₂CO₃. Highest bio-oil yield was obtained with Y zeolite and bio-gas when Na₂CO₃ was used.

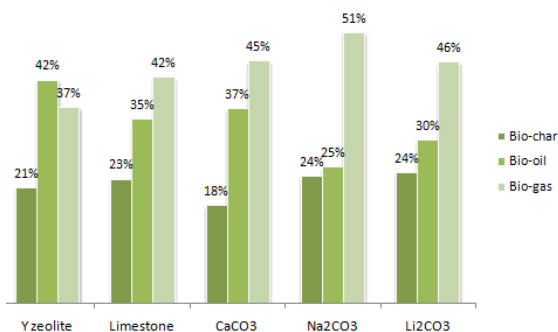


Figure 4 – Raw biomass with addition of various catalysts pyrolysis yields

3.2 Burned biomass pyrolysis yields

For burned biomass represented in Figure 5, the biggest char yield was obtained for the smallest pyrolysis temperature, 400 °C. and its amount was decreasing with temperature increase. Bio-oil yield was increasing simultaneously with temperature and gas yield except for 400^o remained on similar level with only few percent variation through the trials.

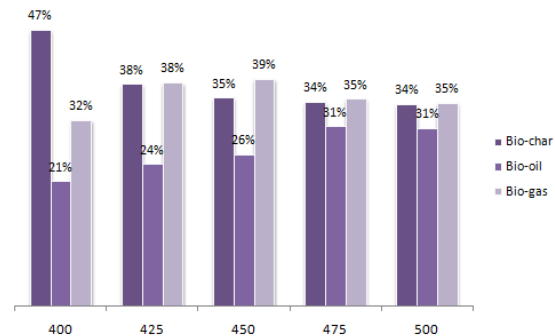


Figure 5 – Burned biomass bio-char, bio-oil and bio-gas pyrolysis yields

With addition of catalysts, the bio-char amount was similar in each case and corresponded to the value without catalyst at the same temperature. Bio-oil yield was the highest for limestone and lowest for Li₂CO₃ as it can be seen in Figure 6. Carbonate-based catalysts showed lower results of bio-oil and bio-char and dominance of gas yield among other products was observed for Na₂CO₃ and Li₂CO₃.



Figure 6 – Burned biomass with addition of various catalysts pyrolysis yields

3.2 Carbonized biomass

Carbonized biomass data was included in raw and burned biomass pyrolysis comparison to serve as an additional reference point.

Table 1 - Raw biomass char, bio-oil and bio-gas yield results

Sample no.	Mass [g]	Temp. [°C]	Time [min]	Catalyst	Catalyst mass [g]	Char yield [%]	Bio-oil yield [%]	Gas yield [%]
1	10,1	400	15	-	-	34	28	38
2	10	425	15	-	-	26	38	36
3	10	450	15	-	-	25	33	42
4	10	475	15	-	-	24	37	39
5	10	500	15	-	-	23	28	49
6	10	475	15	Y zeolite	2	21	42	37
7	10	475	15	Limestone	2	23	35	42
8	10	475	15	CaCO ₃	2	18	37	45
9	10	475	15	Na ₂ CO ₃	2	24	25	51
10	10	475	15	Li ₂ CO ₃	2	24	30	46

Table 2 - Burned biomass with catalysts char, bio-oil and bio-gas results

Sample no.	Mass [g]	Temp. [°C]	Time [min]	Catalyst	Catalyst mass [g]	Char yield [%]	Bio-oil yield [%]	Gas yield [%]
1	10	400	15	-	-	47	21	32
2	10	425	15	-	-	38	24	38
3	10	450	15	-	-	36	26	39
4	10	475	15	-	-	35	31	35
5	10	500	15	-	-	34	30	35
6	10	475	15	Limestone	2	38	29	34
7	10	475	15	CaCO ₃	2	35	28	37
8	10	475	15	Na ₂ CO ₃	2	35	23	42
9	10	475	15	Li ₂ CO ₃	2	35	20	44

3.3 Comparison of raw and burned biomass pyrolysis yields

From comparison analysis (Figures 7-9) it was possible to deduct that biomass which was subjected to carbonization process or combustion during the forest fire, after pyrolysis produced more bio-char comparing to the raw biomass which was not affected by those processes. Also use of catalysts affected differently raw and burned biomass samples (Table 3)

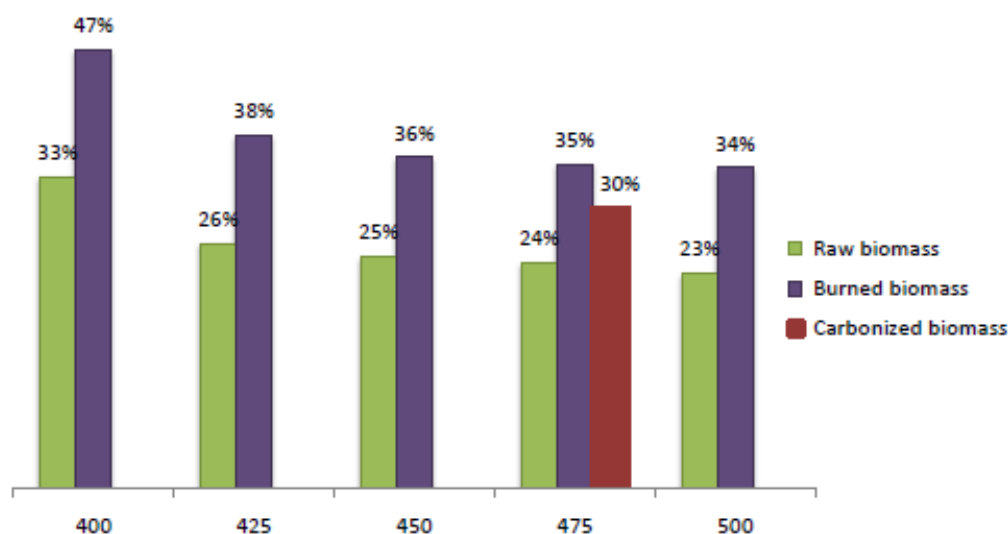


Figure 7 - Bio-char yield obtained for pyrolysis of raw, burned and carbonized at 250°C biomass

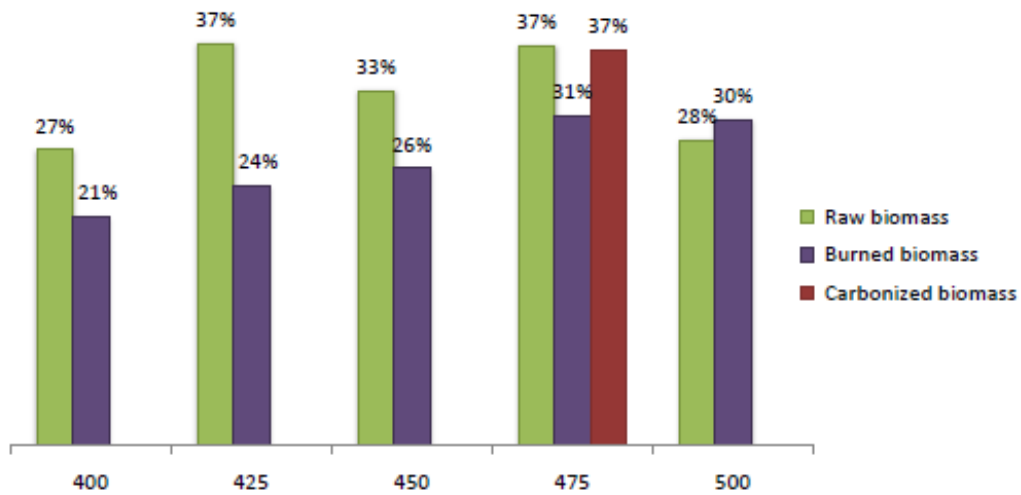


Figure 8 - Bio-oil yield obtained for pyrolysis of raw, burned and carbonized at 250°C biomass

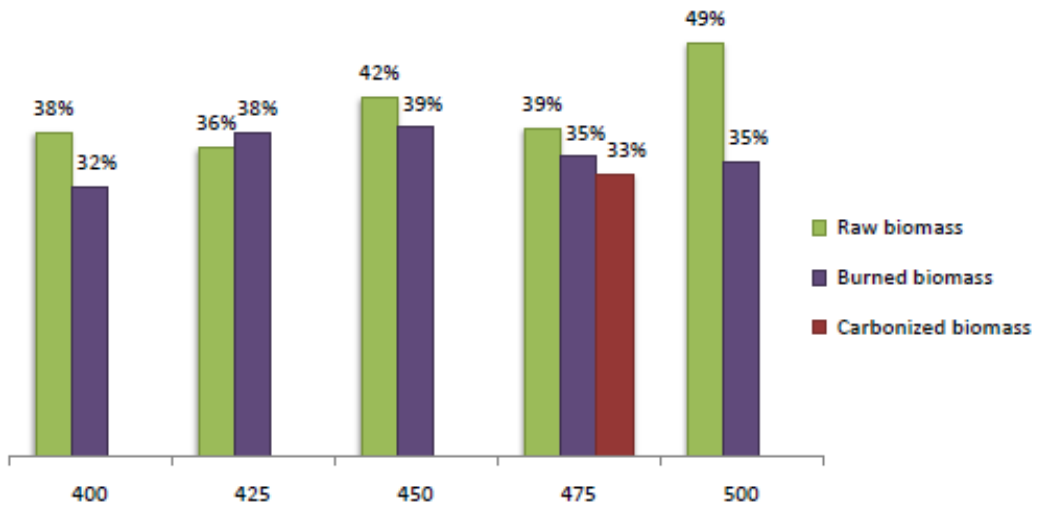


Figure 9 - Bio-gas yield obtained for pyrolysis of raw, burned and carbonized at 250°C biomass

Table 3 - Pyrolysis yields with catalysts for raw and burned biomass samples (↓ show decrease, ↑ increase in yield and = mean that yield was not affected by catalyst)

Catalyst	Bio-char yield difference [%]		Bio-oil yield difference [%]		Gas yield difference [%]	
	Raw biomass	Burned biomass	Raw biomass	Burned biomass	Raw biomass	Burned biomass
Y zeolite	↓ 3		↑ 5		↓ 2	
Limestone	↓ 1	↑ 3	↓ 2	↓ 2	↑ 3	=
CaCO ₃	↓ 6	↑ 1	=	↓ 3	↑ 6	↑ 2
Na ₂ CO ₃	=	↑ 1	↓ 12	↓ 8	↑ 12	↑ 7
Li ₂ CO ₃	=	↑ 1	↓ 7	↓ 11	↑ 7	↑ 9

3.2.2 RAMAN SPECTROSCOPY

Raman spectroscopy was used to characterize the bio-oils. Results showed that for raw biomass samples (Figure 10) two peaks in Raman intensity placed at the similar value of wave number could be observed. First around 1370 cm^{-1} and second bigger around 1600 cm^{-1} .

Regarding influence of pyrolysis temperature the lowest intensity value was obtained for 475°C, then 400°C, 450°C and the highest for 425 and 500°C. Raman Intensity results for burned biomass, as visible in Figure 11, was higher than for raw sample and also slightly bigger at 1600 cm^{-1} peak.

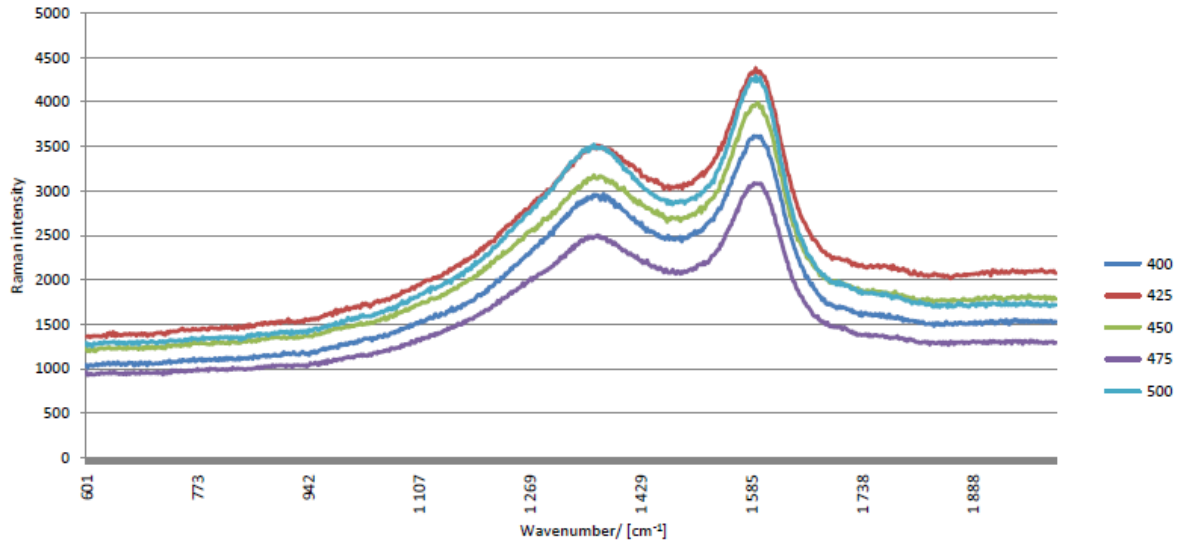


Figure 10 – Raman spectra for raw biomass samples from 400-500°C pyrolysis

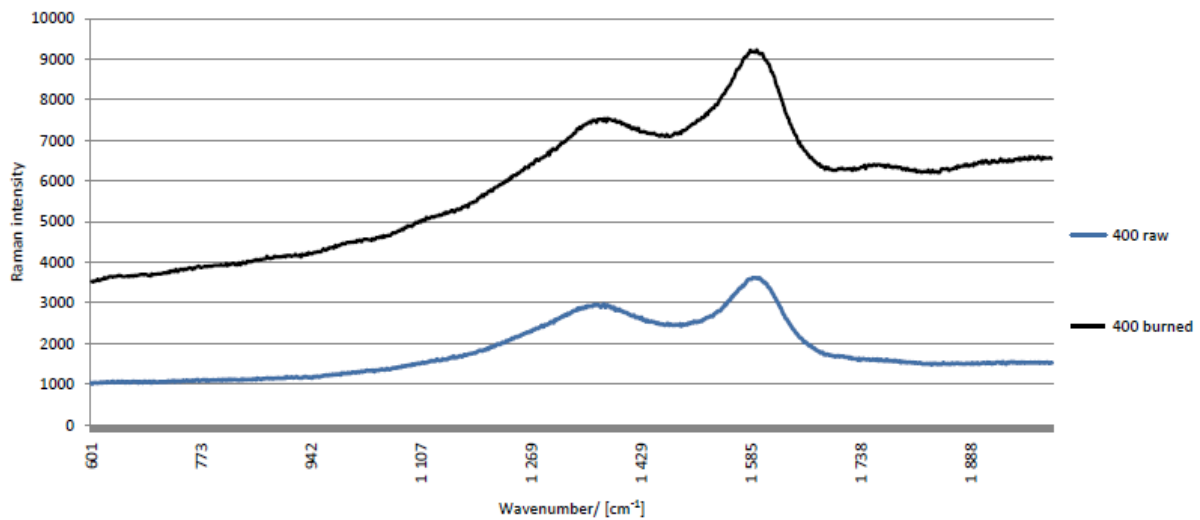


Figure 11 – Burned biomass Raman results for 400°C as compared to raw biomass 400°C sample

3.2.3 FTIR

Investigation of the bio-oil by FTIR with use of Table 4, showed that biggest deviations in composition observed on graphs was in case of raw biomass samples for lowest pyrolysis temperature 400°C (Figure 12), and for burned biomass for highest pyrolysis temperature of 500°C (Figure 14). For burned biomass bio-oil sample, the biggest deviation was observed for line representing 500°C in 3600-3000 cm⁻¹ range, so the O-H stretching and in range 1200 to 600 cm⁻¹.

Concerning the use of catalysts, the biggest influence on bio-oil composition in

case of raw biomass had zeolite Y which showed the biggest deviation among other catalysts, especially to C=O stretching and C-H bending (Figure 13). CaCO₃ and Li₂CO₃ had impact on O-H bending denoting aromatic compounds. When catalysts were used for burned biomass pyrolysis, as visible in Figure 14, limestone increased the peak around 3400 cm⁻¹, which denote O-H stretching, CaCO₃ produced small difference in the 1700 cm⁻¹ peak with C=O stretching and there was small shift for limestone in range of 800-600 cm⁻¹ with O-H bending denoting aromatic compounds.

Table 4 - Wavelengths and corresponding to them functional groups and classes of components in FTIR spectrum for bio-oil [7]

Wavelength [cm ⁻¹]	Functional group	Components
3500-3200	O-H stretching	Polymeric O-H, water impurities
3050-2800	C-H stretching	Alkanes
1750-1650	C=O stretching	Aldehydes, ketones, carboxylic acids, quinones, etc.
1645-1500	C=C stretching	Alkenes
1475-1350	C-H bending	Alkanes
1300-1150	C-O stretching	Primary, secondary and tertiary alcohols
1300-1150	O-H bending	Phenols, esters and ethers
1150-1000	C-H bending	Alkenes
900-675	O-H bending	Aromatic compounds

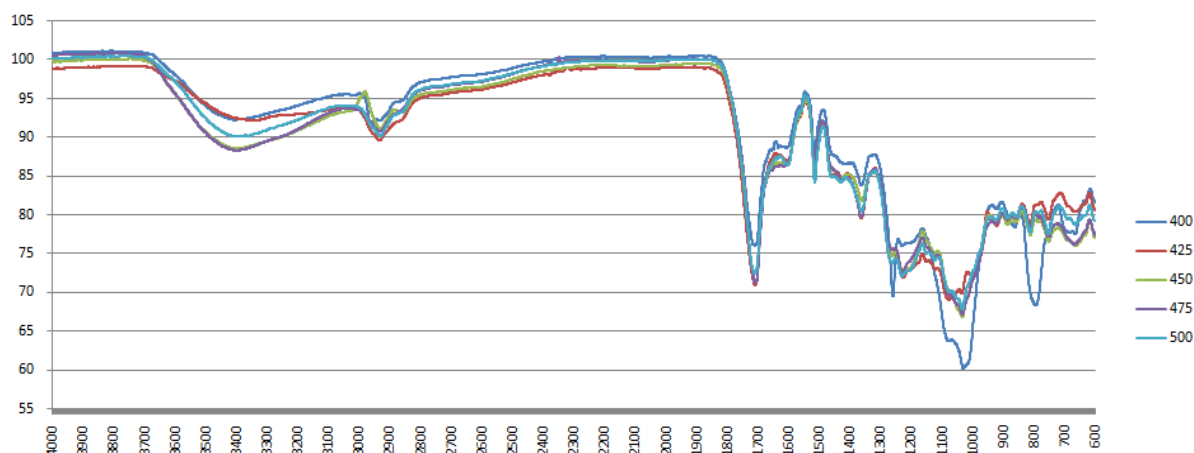


Figure 12 – FTIR results for raw biomass samples from 400-500°C pyrolysis

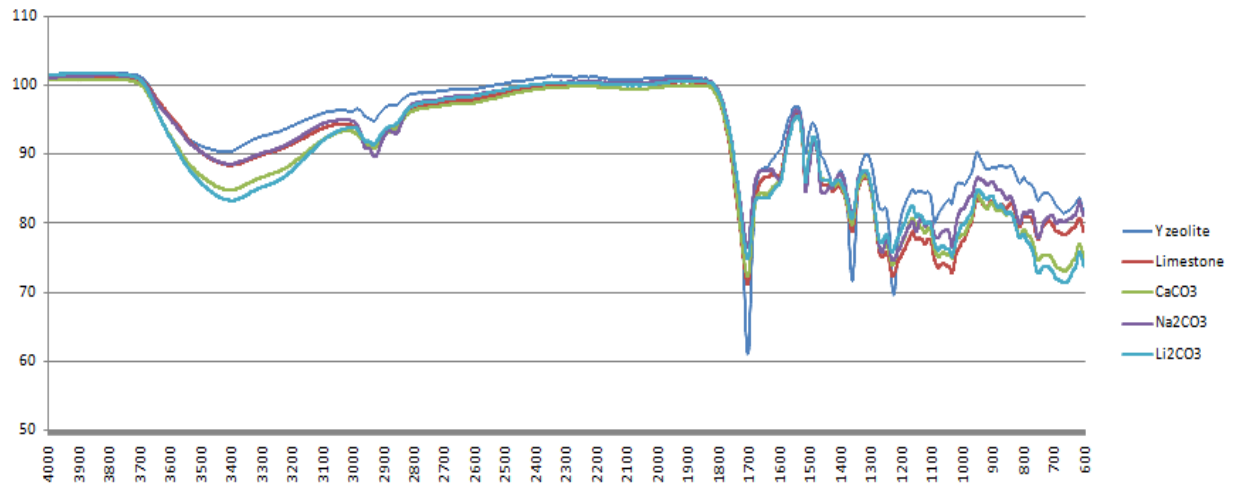


Figure 13 – FTIR results for raw biomass samples from 475°C pyrolysis with various catalysts

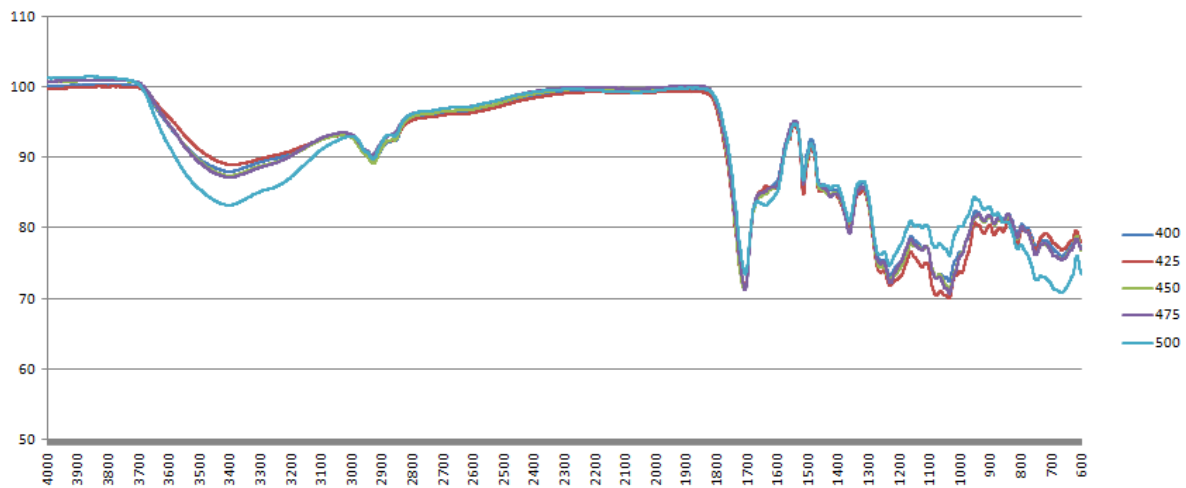


Figure 14 – FTIR results for burned biomass samples from 400-500°C pyrolysis

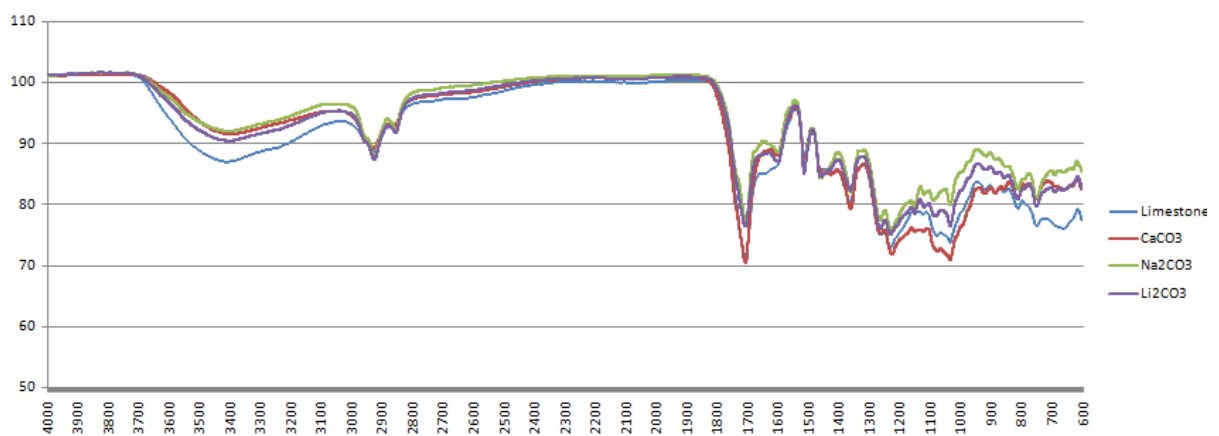


Figure 15 – FTIR results for burned biomass samples from 475°C pyrolysis with various catalysts

4 CONCLUSION

Results obtained during experiments and measurements performed in this research allowed for investigation of characteristics and composition of bio-char, bio-oil and bio-gas derived from *pinus pinaster* tree as well as comparison of differences between biomass affected during forest fire and those which were not subjected to direct fire.

Nineteen samples of biomasses were pyrolysed and characterized by FTIR and Raman spectroscopy.

Results showed that type of biomass feedstock, the fact if it was directly affected by fire, as well as pyrolysis trials temperature and use of catalysts have significant impact on the obtained yields, chemical composition and characteristics of the products.

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