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

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ABSTRACT

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

Pyrolysis trials were performed at temperatures ranging from 400 to 500^{o}C for15 min time. Next pyrolysis of sample mixed with catalysts at temperature 475^{o}C was made. Catalysts used were: $CaCO_3$, $Na_2CO_{3,}$ Li_2CO_3, limestoneand zeolite Y. Lastly, carbonization at temperatures between 250-300^{o}C was performed.

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

Results of pyrolysis at different temperatures indicated that amount of bio-char tended todecrease with temperature increase. Yields of bio-char, bio-oil and bio-gas showed that in most cases dominating pyrolysis product was 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 increase the bio-oil and decrease bio-gas yield.

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

RESUMO

Esta dissertação diz respeito à avaliação da biomassa restante após os incêndios florestais ocorridos em Portugal, para fins de produção de energia. Envolveu o estudo de restos pós-fogo de *pinus pinaster* por investigação e caracterização de bio-char e bio-óleo obtido da pirólise.

Foram realizados ensaios de pirólise em temperaturas variando entre os 400 e os 500^{o}C, durante um período de 15 min. A seguir, foi realizada uma pirólise da amostra misturada com catalisadores a uma temperatura de 475^{o}C. Os catalisadores utilizados foram: $CaCO_3$, Na_2CO_3, Li_2CO_3, calcário e zeólita Y. Por fim, foi realizada a carbonização a temperaturas entre 250 e 300^{o}C.

Os métodos utilizados para investigar a composição do material sólido e líquido obtidos foram: espectroscopia Raman e espectroscopia de infravermelhos por transformada de Fourier.

Os resultados da pirólise em diferentes temperaturas indicaram que, a quantidade de bio-char tendeu a diminuir com o aumento da temperatura. Os rendimentos de bio-char, bio-óleo e biogás, mostraram que, na maioria dos casos, o produto de pirólise dominante é o biogás. A comparação entre duas amostras afetadas e não afetadas pelo fogo diretorevelou que, quando as amostras foram submetidas ao fogo, produziram mais bio-char durante a pirólise, enquanto que, as que não foram afetadas pelo fogo, estavam produzindo mais bio-óleo. A pirólise com catalisadores mostrou que, os catalisadores promovem a gaseificação e diminuem a produção de bio-óleo, com exceção do zeólito Y, que aumenta ligeiramente o bio-óleo e diminui a produção de bio-gás.

Palavras-chave: Incêndios florestais, queima de biomassa, pirólise, bio óleo, FTIR

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ACRONYMS & ABBREVIATIONS

MBDOE	millions of barrels per day of oil equivalent
FTIR	Fourier-transform infrared spectroscopy
BA	Burned Area

CHAPTER I

1. INTRODUCTION

1.1. MOTIVATION

Biomass which remain after forest fires is a resource which require more attention, especially considering Iberian Peninsula and Portugal where fires are problem increasing each year. In Portuguese territory, between July and September during years 2003-2012 there was 31 forest fires larger than 5 000 ha (including 12 fires on area bigger than 10 000 ha) [1]. Some of those occur naturally due to high temperatures and lack of precipitation during summer season, however majority is human-induced as an act of vandalism. This events poses huge damage to environment and leave big amount of burned biomass which may be considered as waste. Therefore, evaluation should be made to establish if there is potential of this resource to be re-used again.

1.2 TOPIC OVERVIEW

1.2.1 NEED FOR GREEN ENERGY SOURCE

In the world we live today we require huge amount of energy, not only to maintain current level of development and but also provide opportunity for grow in the future [2]. As it can be seen from Fig 1. population as well as energy demand is constantly growing and this trend is predicted to maintain among the next years. Considering this information, we need to focus on transition to more sustainable energy production techniques, which should not only provide savings, better efficiency and incorporation of renewable resources but also introduction of new, flexible energy conversion methods and solutions [3].

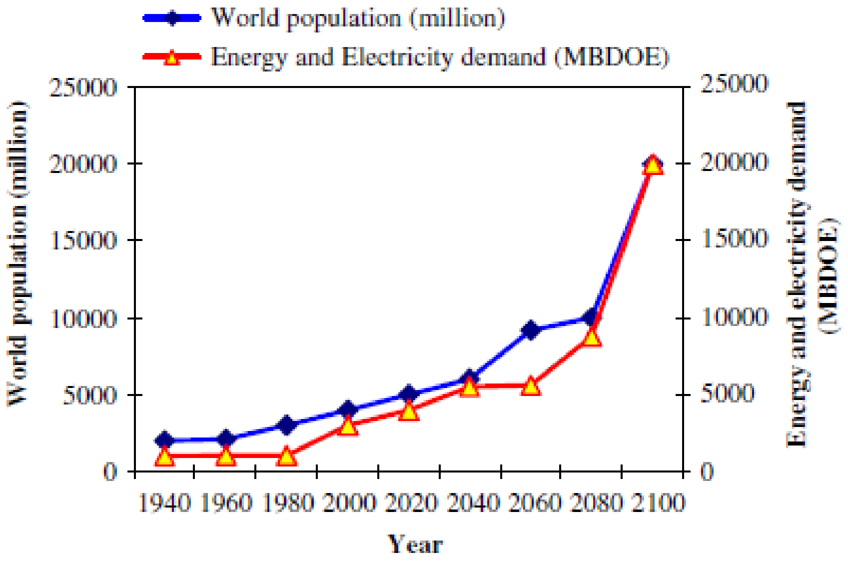

Figure 1 - Estimation of world population versus energy demand (in millions of barrels per day of oil equivalent - MBDOE). Adaptation of [4].

Taking into account environmental aspects, in particular reduction of emissions and declining non-renewable resources (such as coal, gas and petroleum) which use for energy production cause most damage to environmental, biomass is interesting and worth further investigation solution [5].

1.2.2 FOREST FIRES PROBLEM

According to European Forest Fire Information System, Portugal is the country most affected by fire incidences. ”*In the 1980–2013 period, Portugal was the country with the highest number of fires (…) and the second higher burnt area (BA), respectively, with 29% of the total number of fires and 22% of the total BA in Europe*.” [6].

Until 1970’s in Portugal forest fires was not considered as severe problem, situation changed when population lifestyle transitioned from agriculture to more industrial and lands which were previously used for productive farming became abandoned or converted into forest plantations. This lead further to ecological succession and conversion into woods with big amount of biomass accumulated on this areas making them susceptible to the occurrence of large fires. [1] From Fig.2 (b) which graphically show land cover in Portugal it is visible that forests and semi agricultural areas dominate in Portuguese territory.

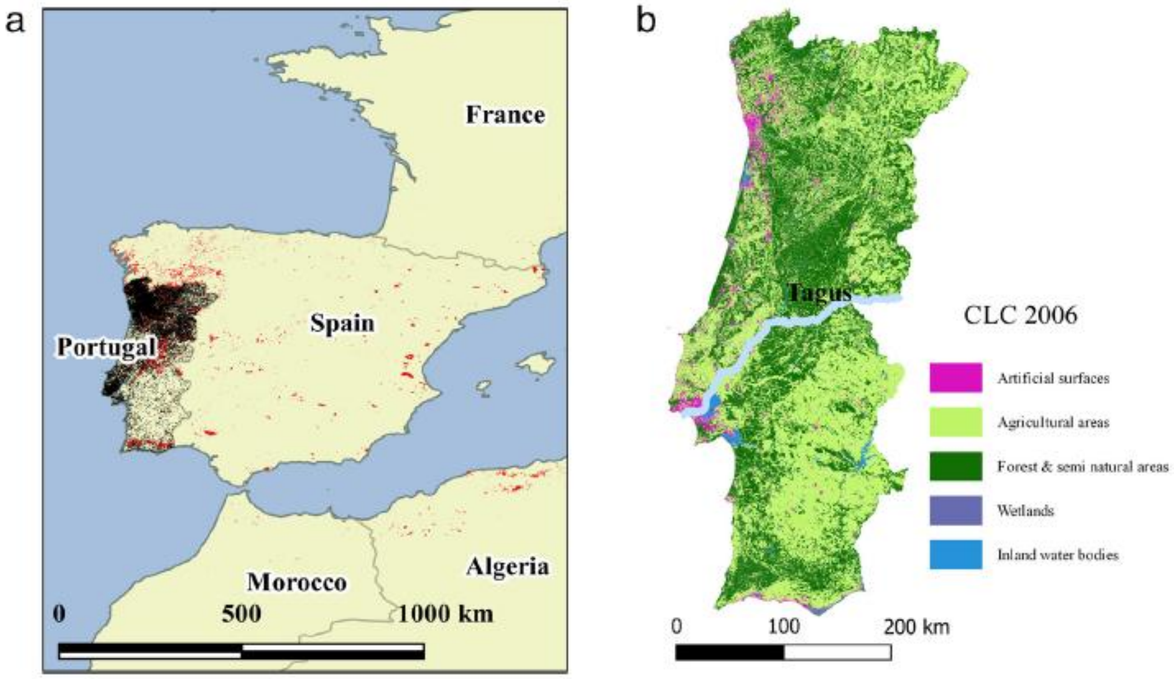

Figure 2 - (a) Iberian Peninsula with surrounding countries. Black dots represent spatial distribution of fire events between 2001–2013 and red polygons show burned areas in Europe within 2000–2013 period (b) Land cover in mainland Portugal in 2006. Adaptation of [6]

Main reasons standing behind forest fires, besides human-induced acts of vandalism are atmospheric conditions during summer season. The annual variability of the fires is related to Mediterranean type of climate. It is characterized by mild and wet part of the year which promote growth of vegetation and hot and dry part which lead to thermal and hydrological stress of vegetation [6]. Almost whole Portuguese territory, with exception of north-west region has a long hot and dry season which can last from three to five months [7].

As it can be seen on Fig. 2 (a) fires occurring in Portuguese territory are distributed irregularly in terms of the area burnt. Biggest fire events accumulation occur on lands marked on map (b) as forest and semi-agricultural areas[8]. Also north of the country reveals higher susceptibility for the fire incidents. Those differences may be related to topography, density of population and type of livestock, as those factors were found to be significant for both burnt area and ignition density [7].

Wildland fires problem is growing each year. Visible in Fig. 3 increase occurring since 1970's is result of mentioned Portuguese land transition and growing number of forest areas. Red line mark point from which large fires exceeding 30 000 ha start to appear in Portuguese territory.

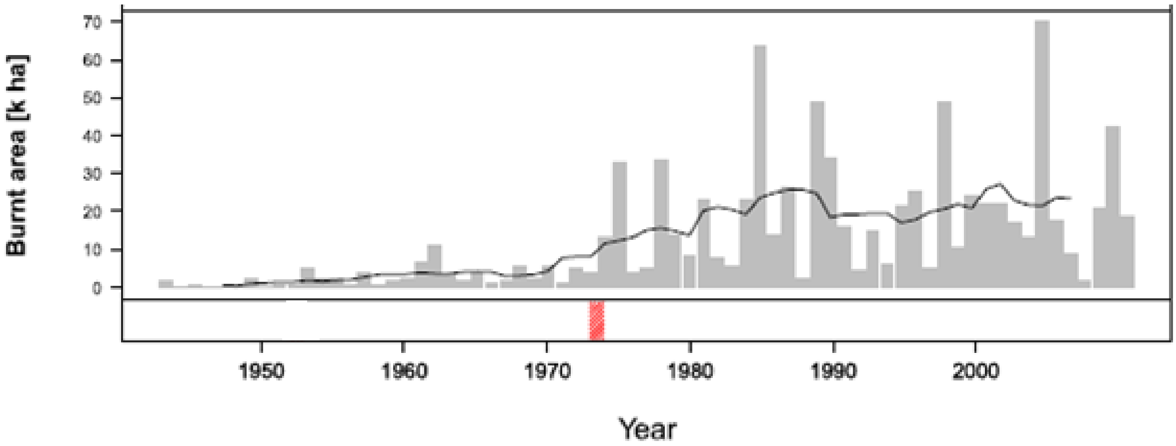

Figure 3 - Area burnt in Portuguese public forest, among years 1943-2011. Adaptation of [8].

According to future climate scenarios and burned area estimations for the next century, while taking into account changes in external factors, such as human activity or land use, by 2075 mean burnt areas in Portugal can be around two to three times larger than it is in the present. This will result in increasing amount of burned trees left after those incidents [9].

1.3 OBJECTIVES

Objective of the thesis is to investigate biomass remaining after forest fire to check it suitability for energy production. Methods used involve pyrolysis, carbonization and various types of spectroscopy for evaluation of the obtained products.

1.4 THESIS OUTLINE

Dissertation is divided in seven chapters which reveal the topic by providing theoretical background context, explaining methods and procedures of experimental part and discussing obtained results.

Chapter I introduce reader to objective and motivation of the work with special focus on the forest fires problem and need for green energy source.

Chapter II present biomass obtained from forest as useful energy source and addresses characteristics of biomass obtained after the fires.

Chapter III describes techniques used in experimental part of the work: pyrolysis, carbonization and in evaluation of the samples: Raman spectroscopy and Fourier-transform infrared spectroscopy.

Chapter IV covers general information about type of tree investigated and special characteristics of the samples provided for the research.

Chapter V addresses experimental procedures which were followed during pyrolysis, carbonization, Raman spectrometry and FTIR as well as the equipment used.

Chapter VI discuss results obtained and it is divided into sections corresponding to each test results and the section with comparison of results of different samples.

Chapter VII present final conclusion and recommendations for future work in the area.

CHAPTER II

2. FOREST BIOMASS AS ENERGY SOURCE

Gradual depletion and future expiration of fossil fuels incline the need for searching of new alternative energy sources. As biomass is one of the most abundant resource in the world and third after coal and oil larger energy production resource, it can be considered as an attractive substitution and effective way to reduce dependence on fossil fuels in energy sector. Moreover, through the growth of plants and trees it constantly replenishes itself which significantly reduce risk of supply deficiency.

2.1 BIOMASS STRUCTURE

Biomass is a form of solar energy accumulation, product of the photosynthesis, process as a result of which plants produce carbohydrates of carbon dioxide contained in the atmosphere and water in the presence of solar radiation.

The chemical composition of biomass consists of: carbon, hydrogen and oxygen. Dry matter obtained from plants is called lignocellulosic biomass (lignocellulose).

Lignocellulosic biomass consists of three basic components:

- cellulose - fibrous carbohydrates (forming the basic framework of the cell wall)
- hemicellulose (makes up about a quarter of the plant substance, it is made up of polysaccharides - complex sugars)
- lignin, which is a aromatic polymer (multiparticulates composed of regular or irregularly repeating atomic moieties of the same structure) and increasing the mechanical and chemical resistance of cellulose walls [10]

Cellulose chains are in form of clusters stabilized by hydrogen bonds. Those clusters, called microfibrils are embedded in hemicellulose and coated with lignin. They have diameters in the range of 10 to 20 nm and are packed so tightly that the enzymes or small water molecules cannot enter their complex structure.

Hemicellulose, as oppose to cellulose, is in form o branched polymer with random, unorganized structure and little strength towards hydrolysis.

Lignin is a hydrophobic, cross-linked polymer which interferes with carbohydrate hydrolysis process. As presented in Figure 4 it is composed of three phenolic components: coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol (indicated on Figure 4 with G, S and H letters respectively) and synthesized by their polymerization. Ratio of this components varies between cell wall layers and different wood tissues of the plants[11].

Content of each of the this polymer in the biomass depesnd on the plant origin, but it was established that lignin content increase with the age of plant. For pine tree which will be analyzed in this dissertation values of cellulose, hemicellulose and lignin are 45.6, 24 and 26.8% respectively [12].

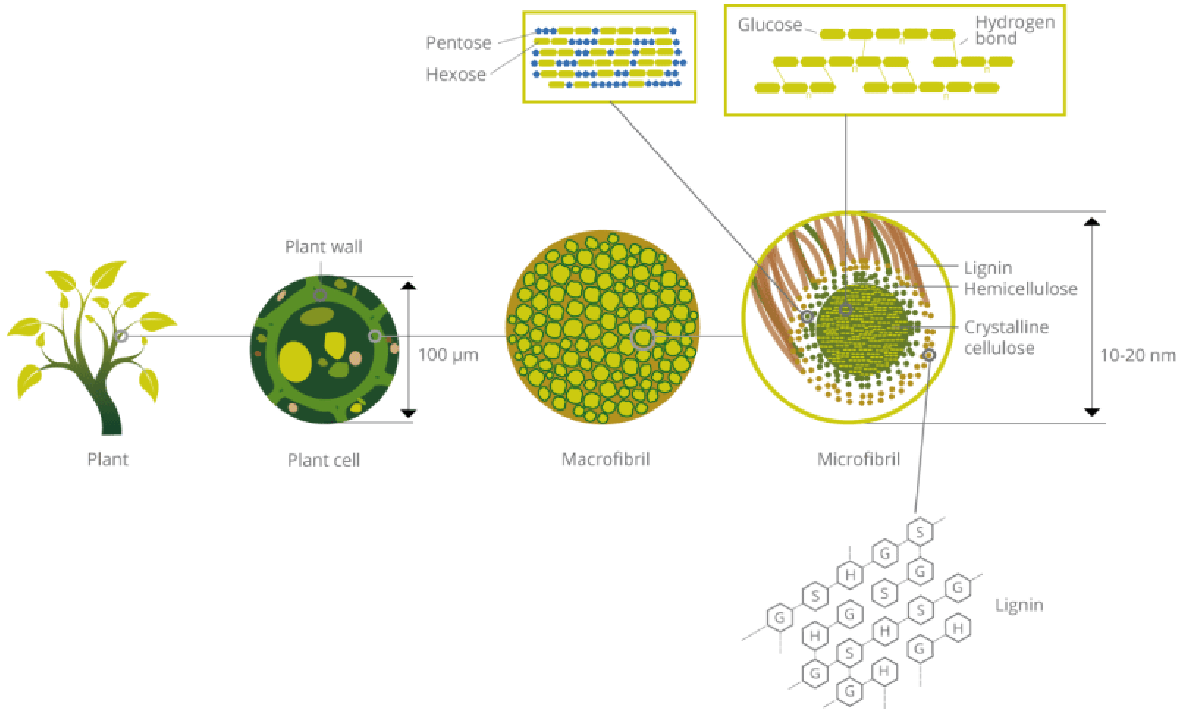

Figure 4 - Schme of lignocellulose structure. Hexagons indicate lignin subunits such as coniferyl alcohol (G), sinapyl alcohol (S) and p-coumaryl alcohol (H). Adaptation of [13].

Energy crops, waste biomass from agriculture and forestry as well as naturally occurring plants all can be classified into lignocellulosic material. First ones can be used to produce second generation biofuels while second after completing its life cycle can serve as material for production of methane by anaerobic digestion or be composted and transformed into fertilizer.

2.2 POST-FIRE BIOMASS

Wildfires drastically change structure of forest and reduce the biomass vegetation. Such events in short amount of time significantly transform landscape, produce disturbance in ecosystem and affect ecological and economical value of the forests. This problem is especially important when considering Iberian Penisula which is among the most fire-prone region in Europe. Therefore, it is crucial to investigate how trees respond to it and to what extent they are affected by the fire.

The ways in which forest biomass is affected by fire is determined strongly by its biological characteristics. Factors like: species of trees, their height, stage of growth as well as behavior, temperature and duration of fire determine the degree of damage done to plants after its occurrence [14]. Depending on the dominant type vegetation present in the forest, the degree of its degradation by fire will be different. Small trees along with bushes burn quicker and almost totally while high, bold trees may be affected only in their lower parts and only have the bark burned. Level of the biomass consumption by the fire is called fire serenity and it is one of the most important factor in determination of plants response to the wildfire events [15].

2.3. FOREST BIOMASS RESOURCES IN PORTUGAL

In Portugal as it is visible in Figure 5, forests are dominating type of land use and they contribute to more than 1/3 of total territory.

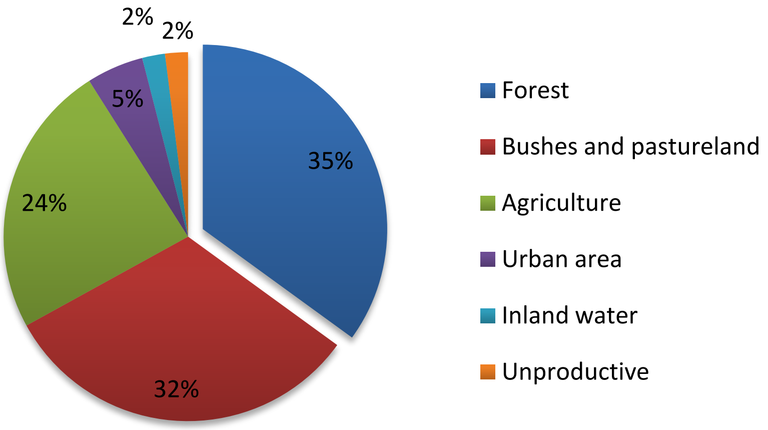

Figure 5 - Land use distribution in mainland Portugal. Adaptation of [16].

When focusing on tree species most prevailing species are: *Eucalyptus Globulus, Quercus Suber* and *Pinus Pinaster* (26, 23 and 23% respectively).Less occurring type of tree is *Quercus Rotundifolia* (around 11%).Broadleaf trees and other resinous trees contribute to around 9 and 8% [17].

Biomass quantities available in Portugal from forests and wood industry are listed in Table 1 As it can be seen biomass from burned areas contribute to around 18% of total available biomass.

Table 1 - Biomass from forestry in Portugal in 2013 [18]

Residues	Production [Mtonne/year]	Availability [Mtonne/year]	GWh/year
Brushwood (cultivated)	1	0,6	3167
Wood production	0,5	-	-
Branches and foliage of trees	1	1	5278
Biomass from burned areas	-	0,4	2111
Wood industry	-	0,2	1056
Total	**2,5**	**2,2**	**11611**

Considering above information, Portuguese forests represent high share in the land use and the wood form burned areas is significant source of biomass from forestry.

2.4. BIOMASS CONVERSION TECHNIQUES

Sustained development of biomass as an energy resource require understanding of environmental and technological concerns connected with it and evaluation of most effective conversion techniques [2].

Some of the currently used biomass conversion techniques include:

- Pyrolysis of biomass or solid wastes (products obtained: solid, liquid and gas)
- Gasification (gaseous products),
- Carbonization of wood biomass (obtained product: charcoal),
- Liquefaction of biomass (products in liquid form),
- Hydrolysis (sugars and ethanol as products),
- Anaerobic digestion (gaseous products),

Biomass fuels are more challenging to be used in energy production processes than conventional fossil fuels due to their properties, in particular: lower heating value, higher moisture content, minor constituents like sulfur, chlorine, nitrogen phosphorus and some ash-forming metals [19].

Those characteristics has to be taken into account when investigating combustion or pyrolysis of biomass. Another challenge related with simultaneous combustion of different types of biomass is interaction of fuel ashes.

CHAPTER III

3. EXPERIMENTAL

Following chapter provide theoretical information about experimental and investigation methods which were used during the research to process and analyze the sample material. Those include: pyrolysis, Raman spectroscopy and Fourier-transform infrared spectroscopy.

3.1 PYROLYSIS

Pyrolysis, among combustion, gasification and liquefaction is one of the main biomass conversion techniques to break down complex substances into simpler ones by use of heat. It differs from above processes since it does not involve addition of other reagent, such as oxygen or steam [20].Products obtained are bio-char, bio-oil and syngas in different amount depending on process used. The lower process temperature and longer residence time of vapor the higher percentage of char in final product. Longer residence time but higher temperature will result in increased conversion to gas. Lastly, short vapor residence time and moderate temperature will produce more liquid products [21]. We distinguish fast, intermediate and slow pyrolysis for which liquid, gas and solid share differ between each other. Estimated percentage can be seen in Table 2.

Table 2 - Product yields obtained for different types of pyrolysis of dry wood. Adaptation of [21]

Mode	Conditions	Liquid	Solid	Gas
Fast	~ 500 ^{o}C, short hot vapor residence time ~ 1 s	75%	12%	13%
Intermediate	~ 500 ^{o}C, vapor residence time ~ 10-30 s	50% in 2 phases (oil and aqueous)	35%	25%
Carbonisation (slow)	~ 400 ^{o}C, long vapor residence, hours to days	30%	30%	35%

Bio-char (also called charcoal) is solid mainly composed of carbon (63-91%) and oxygen (10-30%) [11]. It contains unconverted organic solids and carbonaceous residues produced during complete or partial decomposition of biomass components and the mineral fraction [22]. Due to its high carbon content can be used as low-grade fuel or to generate heat in process of active carbon preparation. It also finds application in agriculture where it improve fertility of soil and, because of its large surface area, for adsorption of pollutants in chemical processes [23].

Bio-oil is another pyrolysis product. It has form of dense, brown liquid and is composed of organic substances such as: sugars, amines, alcohols, esthers, ketones, phenols, ethers, furans, aromatic hydrocarbons and water obtained from moisture of biomass. Bio-oil due to its highly oxygenated and chemically unstable form need to be upgraded to reduce amount of oxygen. Its applications in industry include use as a fuel for boiler or, after processing, product to produce fuels and chemicals.

Bio-gas (also called pyrolytic gas or humid gas) is gas released during pyrolysis, consisting of carbon dioxide and monoxide, hydrogen gas, hydrocarbons such as methane, ethane and ethylene and other gases such as nitrogen oxides, sulphur oxides, ammonia or propane [22].

It need to be taken into consideration that type of biomass feedstock and pyrolysis parameters affect significantly products final composition and yield. Biomass with higher fraction of volatiles result in more bio-oil and these with higher fixed carbon in bigger amount of bio-char [23]. Also, when changing pyrolysis conditions, different chemical reactions are promoted [24]. For example, regarding decomposition of lignocellulosic materials, hemicellulose decomposes at 220-315^{o}C, cellulose at 315-400^{o}C and lignin at 400^{o}C [25]. Other parameters which has big influence on final pyrolysis products are: temperature, time, gas flow rate and particle size [11].

3.2 PYROLYSIS PRODUCTS CHARACTERIZATION TECHNIQUES

3.2.1 RAMAN SPECTROSCOPY

For characterization of bio-char samples Raman spectroscopy was used. This technique allows to observe rotational, vibrational and low-frequency modes of a system [26]. It finds application in chemistry for structural identification of the molecules and characterization of various carbonaceous materials. Experiment involves so called ‘Raman scattering’ with monochromatic light coming from laser with wavelength in range from ultraviolet, through visible to near-infrared depending on current application. The light interacts with photons, vibrations of the molecules or other excitations in system and result in shifting the energy of laser photons which when not absorbed by the probe, is scattered. Such shift gives us information about vibrational modes of the system.

Simplified scheme of setup for Raman experiment can be seen of Figure 6. It includes Raman spectrometer, measurement cell, computer and potentiostat.

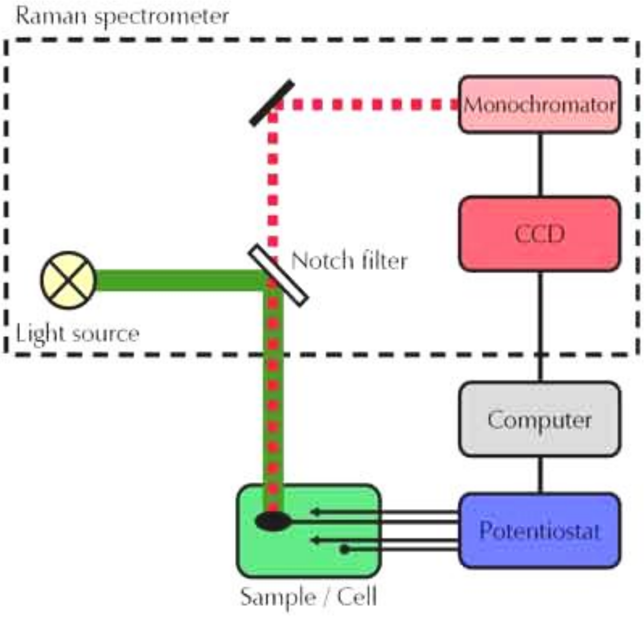

Figure 6 – Simple scheme of Raman experiment setup. Source [27].

Raman spectrum represent scattering resulting from different types of bonds present in the char. We distinguish two order spectral regions, which are essential in understanding structural features of carbonaceous materials. First in range of 800 – 1800 cm^{-1} and second from 2000 to 3300 cm^{-1}. First order spectra is used investigation for carbon materials such as char from pyrolysis and gasification of coal or biomass while second order spectra is mostly used for characterization of highly ordered carbon materials like graphite [28].

In graph of Raman spectra intensity of measured scattering is plotted versus Raman shift which is difference between incident light beam and measured frequency of scattered light. As the Raman spectra is independent on light source wavelength, Raman shift is given as change in wavenumber n (cm^{-1}) which is inversely proportional to wavelength [27].

3.2.2 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

Fourier-transform infrared spectroscopy (shortly FTIR) is technique was used to characterize the bio-oil samples by identification of their components and composition. It produces wide infrared spectra of emission or absorption. Example of such spectra can be seen in Figure 7.

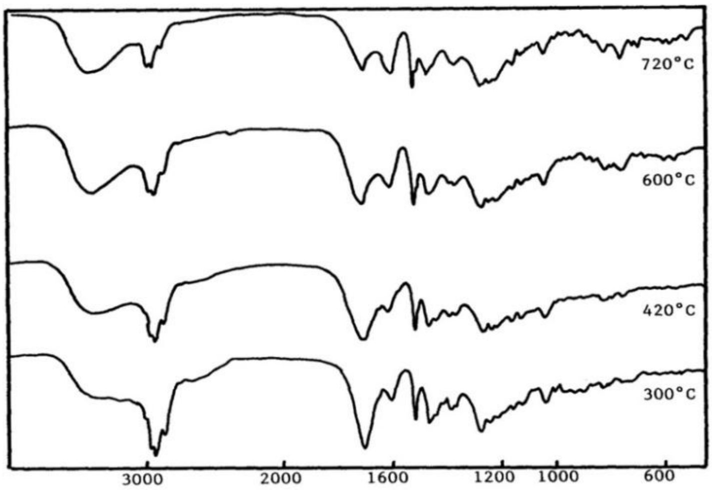

Figure 7 – Example of FTIR spectra for bio-oil from wood biomass pyrolysed at 300, 420, 600 and 720^{o}C. Adaptation of [29]

FTIR measurement involves few steps. In first we shine with a beam of light containing many frequencies at the sample and check how much of this been have been absorbed by it. Next, the beam is modified so it will contain different combination of frequencies and the process is repeated. Modification of the beam occurs with use of certain configuration of movable mirrors called Michelson Interferometer. Light shine at moving mirrors and due to occurred interference wavelengths are modified so that each of them have different spectrum. The changing of frequencies occurs many times and the obtained data is collected by computer which later work backward to deduce what was the absorption at each of the wavelength. The processing needed to convert data about light absorption at each wavelength use mathematical algorithm of Fourier transform, from which the name of techniques comes from.

For results analysis purposes it is important to know values of the obtained spectrum and the wavelengths with corresponding to them functional groups and components. Such information for bio-oil samples can be found in Table 3.

Table 3 - Wavelengths and corresponding to them functional groups and classes of components in FTIR spectrum for bio-oil. Adapted from [30]

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

CHAPTER IV

4. MATERIALS

Materials used in experiment were parts of Pine tree (*Pinus Pinaster*) from burned areas of Portuguese forests.

4.1 SAMPLE ORIGIN

As visible in Figure 8*pinus pinaster* trees are growing in region of Portugal, Spain, France, Italy, Morocco, Algeria and Tunes. In Iberian Peninsula there are distinguished two subspecies: Atlantic and Mediterranean. First grows in Northern Portugal and Galicia and second one in rest of Iberian Peninsula.

In Portugal *pinus pinaster* (also called *maritime pine* or *pinheiro bravo)*covers 976 000 ha which is around 30% of the total forest area. The largest accumulation occur in Central (57%) and Northern (37%) regions and in Lisbon and Tagus Valley (22%).

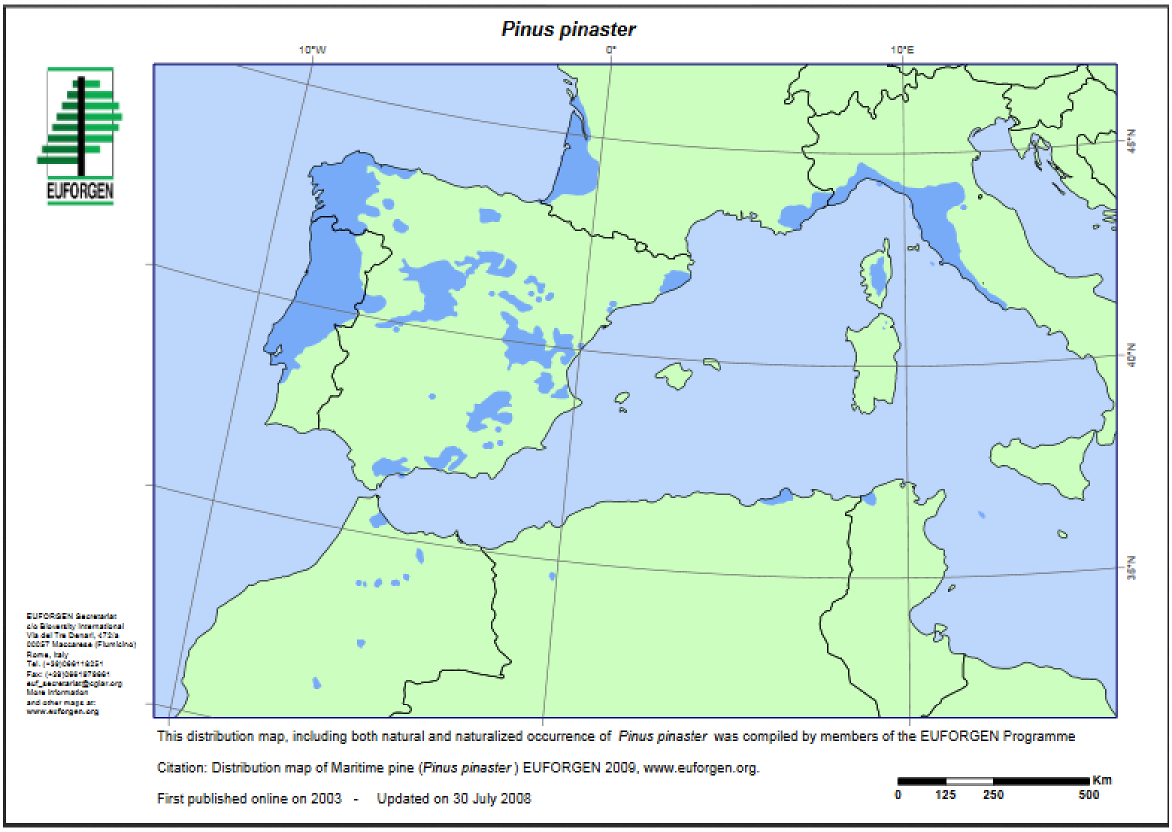

Figure 8 - Distribution map of Maritime pine (Pinus pinaster) EUFORGEN 2009, [www.euforgen.org]

Pinus pinaster presence in forest area among is of great importance, because it is one of the main resource and supply chain element in the wood-based industry. In Portugal and Galicia pine trees are considered as the crucial supply species for wood processing industry [31].

4.2 PREPARATION OF THE SAMPLE

Figure 9 shows main layers parts of the tree. As it can be seen on Figure 10 most samples obtained after forest fire were burn only in thin surface layer of cambium.

Figure 9 - layers of the tree
Source: westchestertreelife.com

Figure 10 - Samples provided for the research

Preparation procedure

1. Parts of the tree were cut to divide burned parts of the tree (called from now on ‘burned biomass’) from those not affected by fire (called ‘raw biomass’)

Figure 11 - Samples divided into burned (above) and those not affected by direct fire (below)

2. Then samples were blended to obtain the powder and later passed through a 710μ sieve.

Figure 12 - Sample ready to blend

Figure 13 - Obtained powder

CHAPTER V

5. EXPERIMENTAL PROCEDURES AND EQUIPMENT

5.1 PYROLYSIS

Pyrolysis trials were performed in one of laboratories belonging to Chemical department of the Instituto Superior Tecnico. Equipment used was cylindrical oven Eurotherm (Figure 14) and fixed bed vertical reactor (Figure 15) 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 collecting water and other humid substances which appeared during process and to gas chromatograph which recordings can be found in Appendix B.

Pyrolysis parameters:

- Trials time: 15 min
- Temperature: in range between 400 to 500^{o}C
- Sample size: >710μ
- Inter material: SiC – silicon carbide
- Separating material: glass wool
- Gas flow: 80.5 of N_2

Figure 14 - Fixed bed vertical reactor used for pyrolysis

Figure 15 - Reactor with inert material and raw biomass sample

Pyrolysis procedure:

1. Preheating oven to a temperature little lower than experimental temperature;
2. Addition of glass wool, on the bottom of reactor, inert material above it and covering everything with another layer of glass wool;
3. Weighting 10 g of sample (and 2 g of catalyst during second trials);
4. Placing sample in the reactor above glass wool layer;
5. Turning off the oven and nitrogen flow;
6. Placing prepared reactor inside the oven;
7. Turning on the oven and nitrogen flow and setting the experimental temperature;
8. Starting the trial when oven reaches desired temperature;
9. Turning off the oven and the nitrogen flow after 15 min;
10. Removing the reactor from the oven and leaving to cool down to room temperature;
11. Removing bio-char from the reactor;
12. Extraction of the bio-oil with use of acetone;
13. Removing inert and glass wool from reactor;

Obtained products (Figure 16) 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.

Figure 16 - Bio-char and bio-oil with acetone

5.2 CARBONIZATION

Raw biomass was subjected to carbonization process in 250, 275 and 300°C temperature. Resulted material can be seen on Figure 17. Later, one of carbonized biomass sample, 250°C was used for 15 min pyrolysis in 475°C. Samples of 275 and 300°C was not subjected to pyrolysis because of equipment problems which occurred during the experiment.

Figure 17 - Flasks with (from left): raw biomass, biomass carbonized at 250, 275 and 300°C

Carbonization parameters:

- Trials time: 1 h
- Temperature: in range between 250 to 300°C
- Inter material: SiC – silicon carbide
- Separating material: glass wool
- Gas: N_2

5.3 RAMAN SPECTROSCOPY

Raman spectroscopy was performed on the equipment belonging to one of the laboratories of Mathematics 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. Due to the insufficient availability of the equipment to perform further tests, only one sample of burned biomass were investigated.

5.4 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

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 which can be seen in Figure 18.

Procedure of the measurement was as follows:

1. Turning on the equipment and connected with it computer
2. Opening the program which show FTIR graphs
3. Placing drop of the sample on crystal
4. Starting the trial
5. Viewing the graph and saving the obtained data

Figure 18 - FTIR Spectrometer

CHAPTER VI

6. RESULTS

Chapter presents results from pyrolysis trials including 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 $CaCO_3$, Na_2CO_3, Li_2CO_3, limestone or zeolite Y for raw and burned biomass samples. Also the change in bio-char amount according to temperature increase is shown. Next the comparison between results for raw, burned and carbonized samples is made. Lastly, results from Raman and Fourier-transform infrared spectroscopy are presented with characterization of structures present in the samples.

For analysis purposes results were divided into sections corresponding to type of sample, obtained product and/or investigation method used. They include cumulative graphs from experiments and investigation measurements.

6.1 PYROLYSIS

6.1.1 RAW BIOMASS SAMPLE

6.1.1.1 BIO-CHAR YIELD CHANGE DUE TO INCREASING TEMPERATURE

Graph present change in amount of char corresponding to increase in temperature, during pyrolysis trials. It is clearly visible that the char amount decrease as the temperature increase. First decrease is quite significant, between 400 and 425°C char amount drop from 33 to 23%. Later from 425 to 500°C the decrease is much slower and only from 26 to 23%.

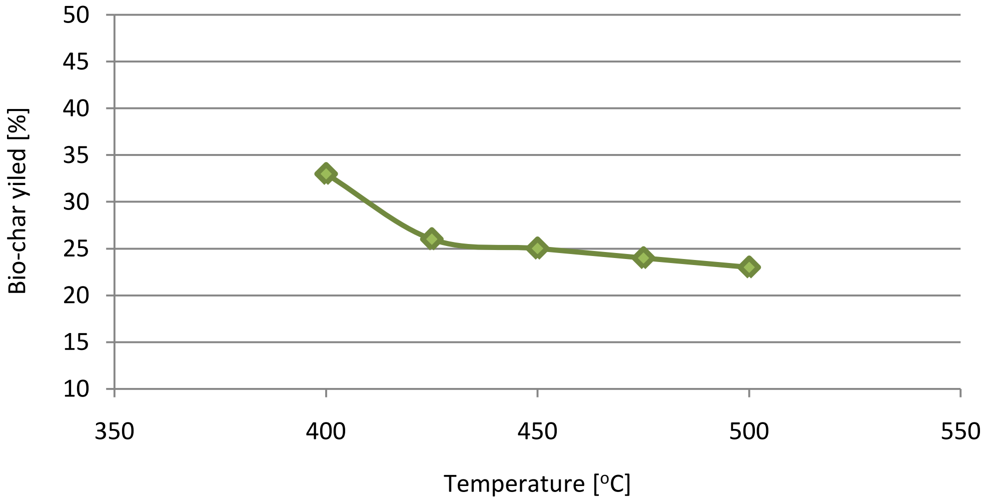

Figure 19 – Temperature influence on amount of char

This phenomenonoccurs in previous researches. Ayhan Demirbas in his work about effect of temperature on bio-char yield in pyrolysis of agricultural wastes says "*When the pyrolysis temperature is increased, the bio-char yield decreases*" [32].°

6.1.1.2 BIO-OIL, BIO-CHAR AND GAS YIELDS FOR DIFFERENT TEMPERATURES (WITHOUT AND WITH CATALYSTS)

First graph shows raw biomass pyrolysis yields for temperatures from 400 to 500°C with 25°C difference between each trial. First thing to notice is that bio-char amount decrease with increase of the temperature. Form 34% in 400°C it goes down to 23% for 500°C. Bio-oil and gas yield does not show any specific pattern with temperature changes. Concerning dominant type of pyrolysis product, it is gas which has biggest yield in almost all cases and only for 425°C it is little lower than bio-oil yield.

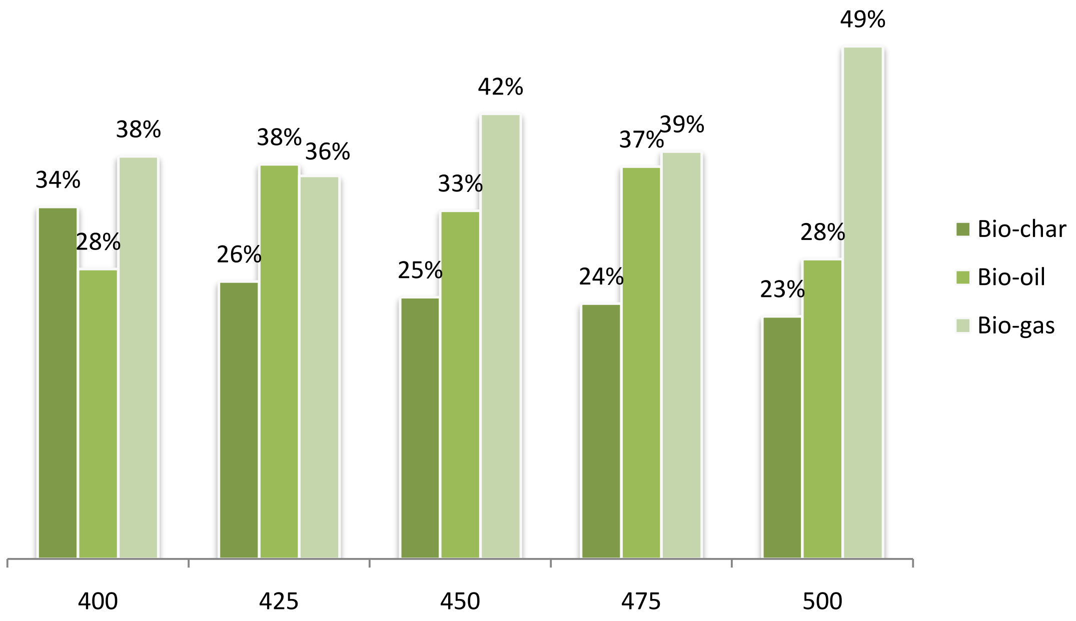

Figure 20 – Raw biomass bio-char, bio-oil and bio-gas pyrolysis yields

This result indicate that temperature used in pyrolysis trials has significant impact on amount of char obtained from biomass. With temperature increase more oil and gas is produced. Based on those results one can distinguish which product he is most interested in and adjust the temperature to obtain the biggest yield. For bio-char that would be lowest temperature of 400°C, for bio-oil around 425-475°C and for gas the highest temperature of 500°C. However, those conclusions apply only to 15 min pyrolysis trials and each change in pyrolysis parameters could produce slightly different result.

According to literature for slow pyrolysis, at temperatures from 300 to 800°C typical product yields are: bio-char 35%, bio-oil 30%, and bio-gas 35% [22]. From experiment results values closest to theoretical ones were those obtained at 400°C (char: 33%, bio-oil 28% and gas 38%).

Second graph show influence of adding different catalysts to the obtained yields. Temperature of those pyrolysis trials was 475°C so we for reference we can look at results from previous graph for this temperature (bio-char 24%, bio-oil: 37% and bio-gas 39%). It is visible that all catalysts except Y zeolite increased the gas yield (by 3 -12%). Y zeolite however, as the only one increased the bio-oil yield.

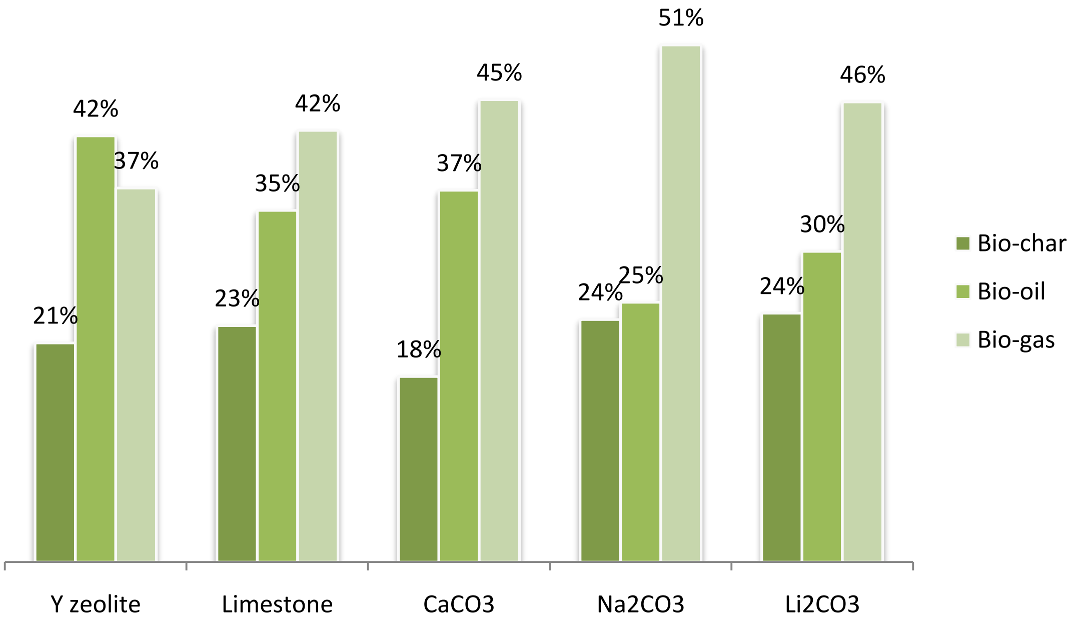

Figure 21 – Raw biomass pyrolysis yields of bio-char, bio-oil and bio-gas with addition of various catalysts

Concerning use of catalysts as addition to biomass during pyrolysis, Y zeolite showed the biggest production of bio-oil as pyrolysis product among all the catalysts. Use of $CaCO_3$ resulted in lowest bio-char yield and Na_2CO_3 produced highest gas yield when comparing to char and bio-oil produced during this trial. Limestone and Li_2CO_3 results were similar to those obtained for raw biomass at the same temperature without catalyst.

For raw biomass used in given pyrolysis conditions Y zeolite appeared to be the best catalysts to obtain highest amount of bio-oil and also quite good percentage of bio-char. Considering yield of bio-char, highest was observed with Na_2CO_3 and Li_2CO_3, however those ones presented much lower bio-oil yield than mentioned before Y zeolite.

As stated in the work of by Aysu and Küçük [33]: *"The usage of catalyst could make significant changes on the properties and yields of pyrolysis products. Generally, using catalyst has been increased the liquid yields while in some studies, it had negative effect and decreased the liquid product yields (…) Similar results were obtained for bio-char and gaseous product yields which were either increased or decreased by using catalysts"*.

6.1.2 BURNED BIOMASS SAMPLE

6.1.2.1 BIO-CHAR YIELD CHANGE DUE TO INCREASING TEMPERATURE

Similar to previous, raw biomass case, char amount from burned biomass is decreasing with the temperature increase. The quickest drop is between 400 and 425°C where amount of obtained decrease from 47 to 38%. Later from 425 to 500°C decrease is slower and occur from 38 to 34g.

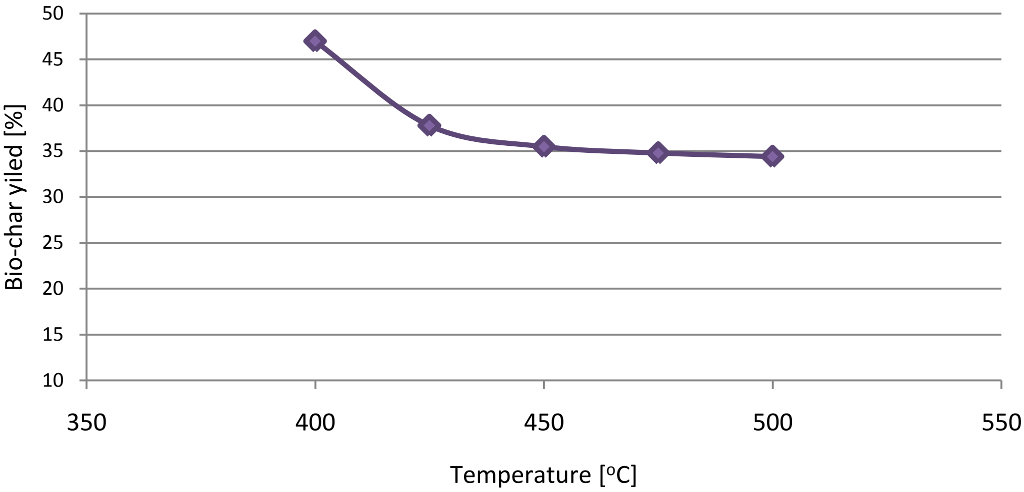

Figure 22 – Temperature influence on amount of char

The bio-char decrease with increase of temperature followed the trend observed for raw biomass and found in literature [32]. This indicates that, regardless of fact if biomass was subjected to direct fire before pyrolysis or not, increase of temperature result in decrease of char amount.

According to Al-Wabel et al. [25] in their work about temperature induced changes in char composition: "*Decline in yield content is mainly due to the destruction of some compounds such as cellulose and hemicellulose as well as combustion of organic materials with increased pyrolysis temperature"*

6.1.2.2 BIO-OIL, BIO-CHAR AND GAS YIELDS FOR DIFFERENT TEMPERATURES (WITHOUT AND WITH CATALYSTS)

As it visible on first graph, showing burned biomass pyrolysis yields for temperatures 400, 425, 450, 475 and 500°C, biggest bio-char yield was obtained for 400°C and it is 47%. With increase of temperature char amount was decreasing. Bio-oil yield was increasing simultaneously with temperature, reaching highest level at 475°C. Gas yield remain on similar level through the trials (between 35-39%) being slightly lower at 400°C (32%).

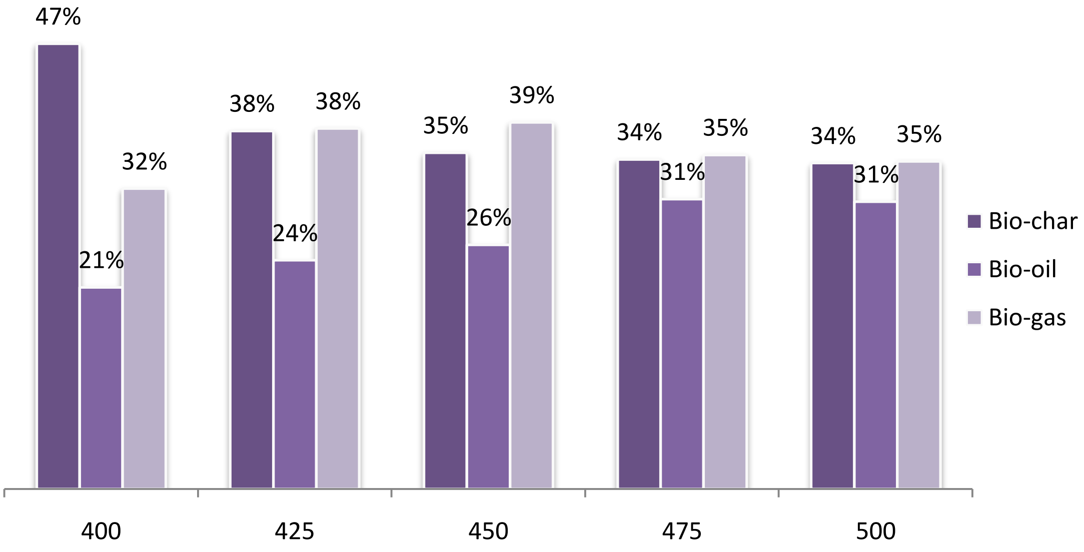

Figure 23 – Burned biomass bio-char, bio-oil and bio-gas pyrolysis yields

The maximum conversion of biomass to bio-char was obtained for lowest pyrolysis temperature of 400^{o}C. Result was similar to raw biomass sample and trend found in literature for pine wood pyrolysis where it is indicated that the lower the trial temperature the higher char yield obtained[29].

Second graph present results from pyrolysis of burned biomass with addition of catalysts. In this case Y zeolite was not used due to insufficient amount of sample to perform the test. Considering the rest of catalysts, as visible on graph, the bio-char amount was similar in each case and also correspond to the value without catalyst at the same temperature. Bio-oil yield was the highest for limestone and lowest for Li_2CO_3. Dominance of gas yield among other products can be observed for Na_2CO_3 and Li_2CO_3.

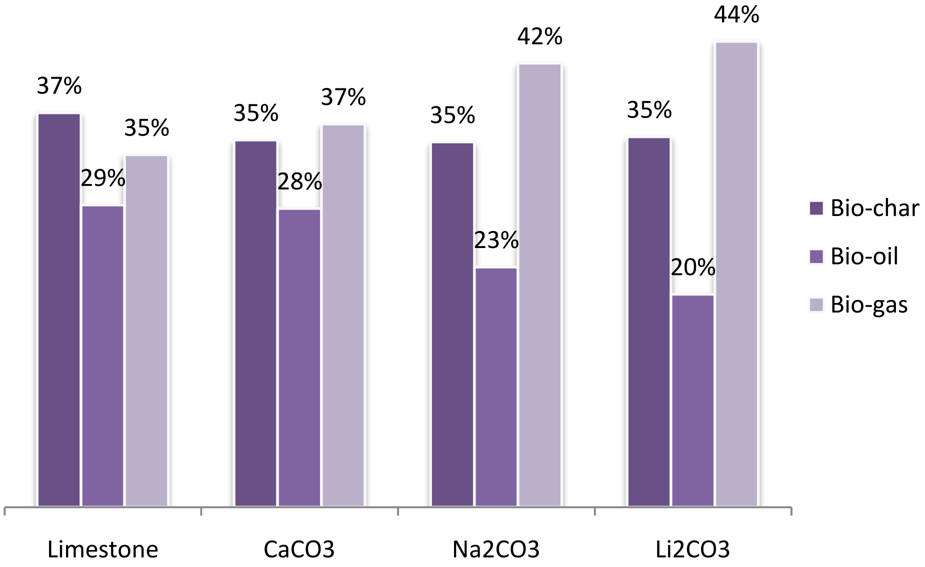

Figure 24 – Burned biomass pyrolysis yields of bio-char, bio-oil and bio-gas with addition of various catalysts

Concerning use of catalysts in case of burned biomass, the most efficient catalyst to obtain biggest amount bio-oil and bio-char yield was limestone. Carbonate-based catalysts showed lower results of bio-oil and bio-char. Limestone is composed of minerals which are different crystal forms of $CaCO_3$ which explain why results of those two are similar. However, as visible on graph this different crystal form of limestone has positive effect on bio-char and bio-oil yield.

6.1.3 CARBONIZED BIOMASS

Pyrolysis yield for raw biomass carbonized at 250°C was equal 30% for bio-char, 37% for bio-oil and 33% for bio-gas. As mentioned in Chapter 5, section 5.2 describing experimental procedures and equipment, 275 and 300°C samples were not subjected to pyrolysis due to laboratory equipment problems. Obtained result in included in next section for comparison with raw and burned samples.

6.1.4 COMPARISON BETWEEN RAW, BURNED AND CARBONIZED BIOMASS SAMPLES

6.1.4.1 BIO-CHAR YIELD CHANGE

The rate of change between raw and burned samples is parallel, however, as it can be seen in Figure 25 overall char weight was bigger in case of burned biomass than the raw one. This indicate that for the same amount of biomass sample, the one which was affected by direct fire, when subjected to heat treatment produced more solid product. This may be due to the fact that burned part is cambium of the tree and it has larger lignin content than wood part.

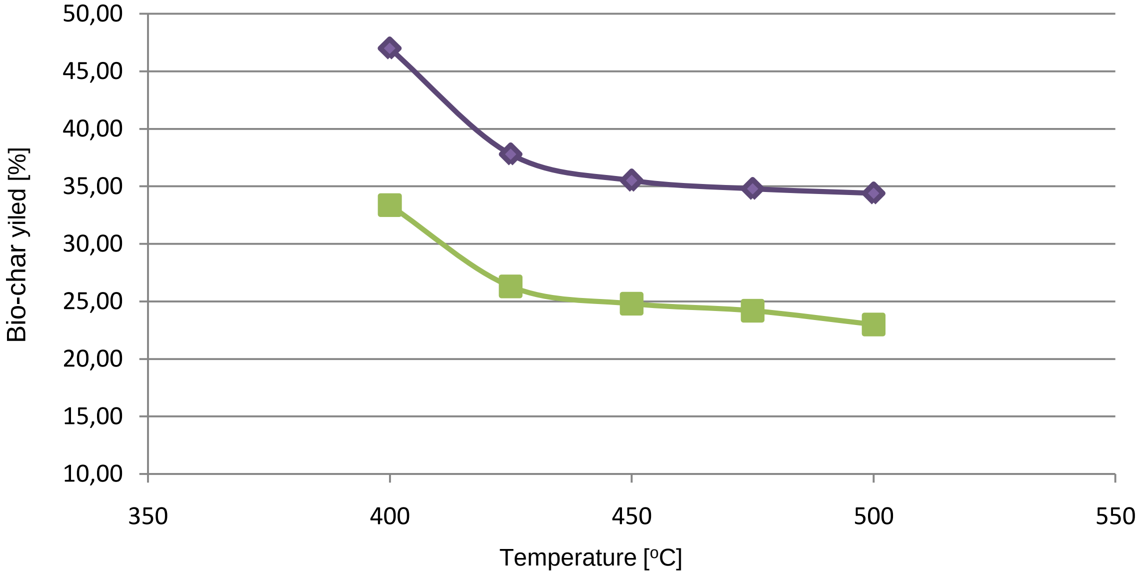

Figure 25 - Comparison of bio-char amount after pyrolysis (400-500°C) for raw and burned biomass samples

6.1.4.2 BIO-CHAR YIELD

As it can be seen on Figure 26 char amount both raw and burned sample bio-char was decreasing with the temperature increase. Carbonized sample was compared with 475°C results as it was the temperature used for its pyrolysis. Bio-char obtained from carbonized sample was in amount bigger than for raw (by 7%) and lower than for burned (by 5%) at the same temperature.

Observed phenomena indicate that biomass which was subjected to heat (by combustion during forest fire) before pyrolysis, produce more bio-char comparing to the one which was not affected by heat.

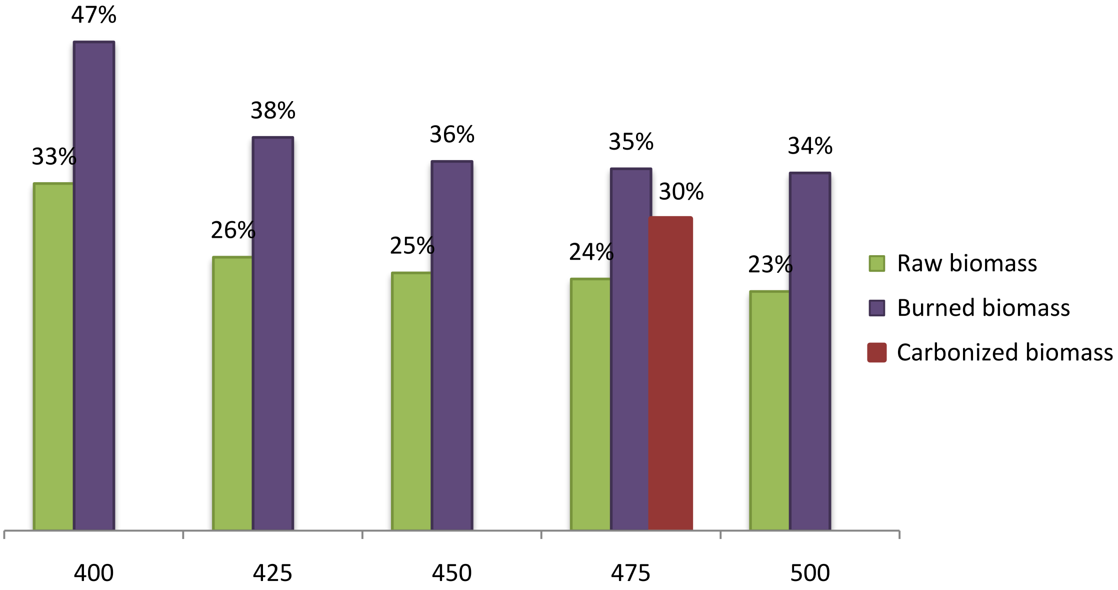

Figure 26 - Bio-char yield obtained for pyrolysis of raw, burned and carbonized at 250°C biomass

6.1.4.3 BIO-OIL YIELD

On Figure 27 bio-oil amount for different samples is presented. As in previous case carbonized sample was compared with raw and burned at 475°C. Bio-oil yield was higher for raw biomass with exception for 500°C where it was lower by 2% than for burned biomass. Carbonized sample produced the same amount of bio-oil as raw biomass sample and this result was higher (by 6%) that in case of burned biomass.

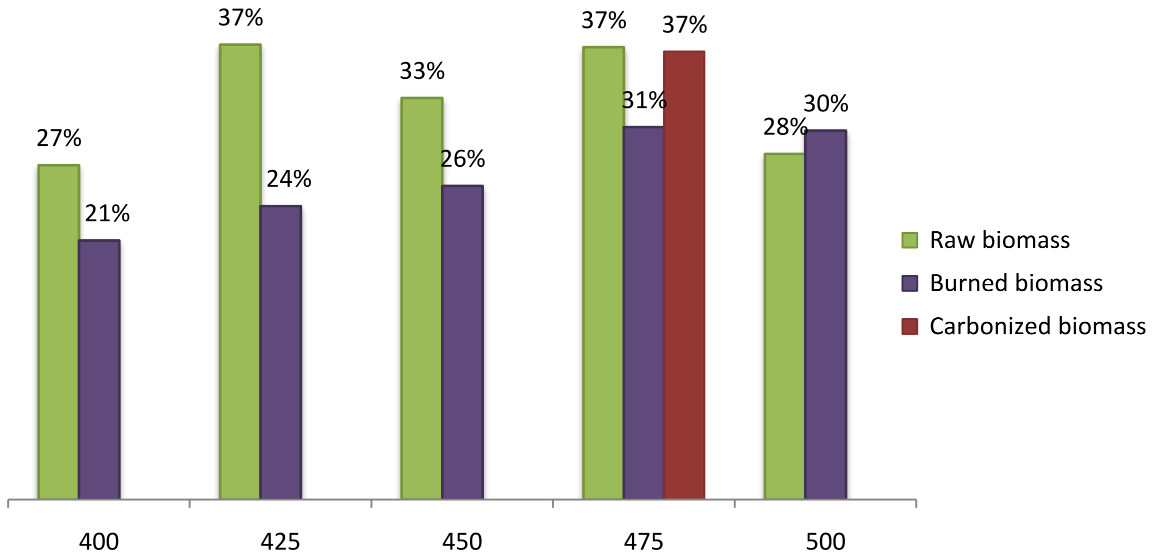

Figure 27 - Bio-oil yield obtained for pyrolysis of raw, burned and carbonized at 250°C biomass

6.1.4.4 BIO-GAS YIELD

Lastly, the bio-gas yield is compared onFigure 28. Here it can be seen that pyrolysis of raw biomass produced more gas than burned or carbonized sample and the biggest amount (49%) was obtained for highest trial temperature of 500°C.

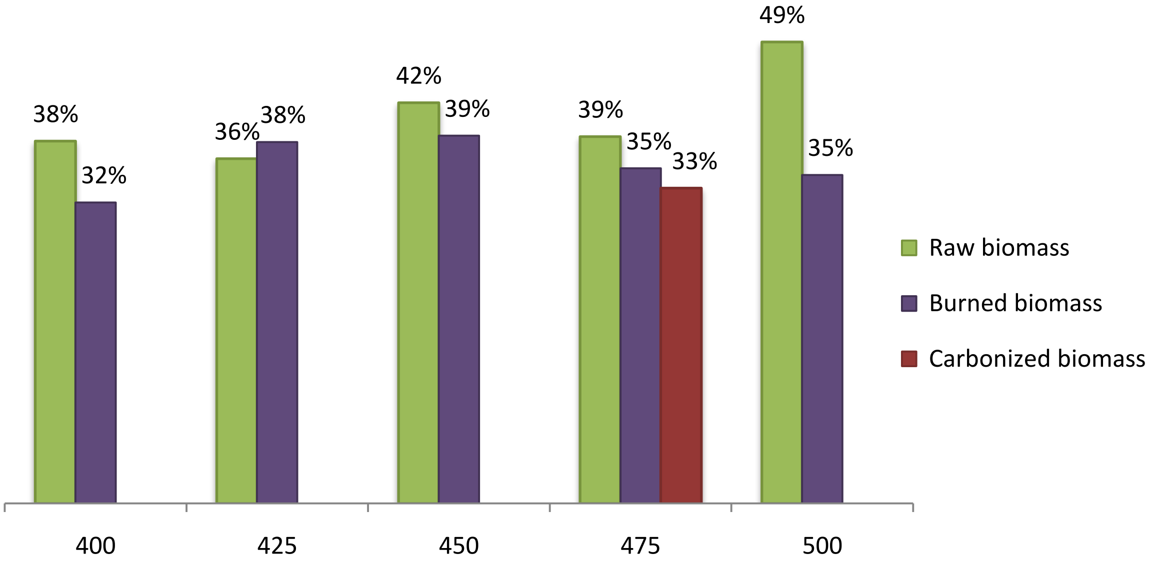

Figure 28 - Bio-gas yield obtained for pyrolysis of raw, burned and carbonized at 250°C biomass

6.1.4.5 CATALYSTS EFFECT ON PYROLYSIS YIELDS

Catalyst effect on obtained pyrolysis yields as comparing to samples from 475°C pyrolysis trial without catalyst are summarized in Table4 it is visible that most catalysts increased gas yield, and in case of burned biomass also char yield. It is interesting to notice that also char amount was bigger for burned biomass than for raw biomass in pyrolysis where no catalyst was used (Figure25). Considering bio-oil, zeolite Y increased the yield, however we only have the result for raw biomass.

Table 4 - Pyrolysis yields with catalysts for raw and burned biomass samples (↓ show decrease, ↑ increase in yield and = mean that yield was not affected by catalyst)

	Bio-char yield difference [%]		Bio-oil yield difference [%]		Gas yield difference [%]	
Catalyst	**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_2CO_3	=	↑ 1	↓ 12	↓ 8	↑ 12	↑ 7
Li_2CO_3	=	↑ 1	↓ 7	↓ 11	↑ 7	↑ 9

6.2 RAMAN SPECTROSCOPY

6.2.1 RAW BIOMASS BIO-CHAR

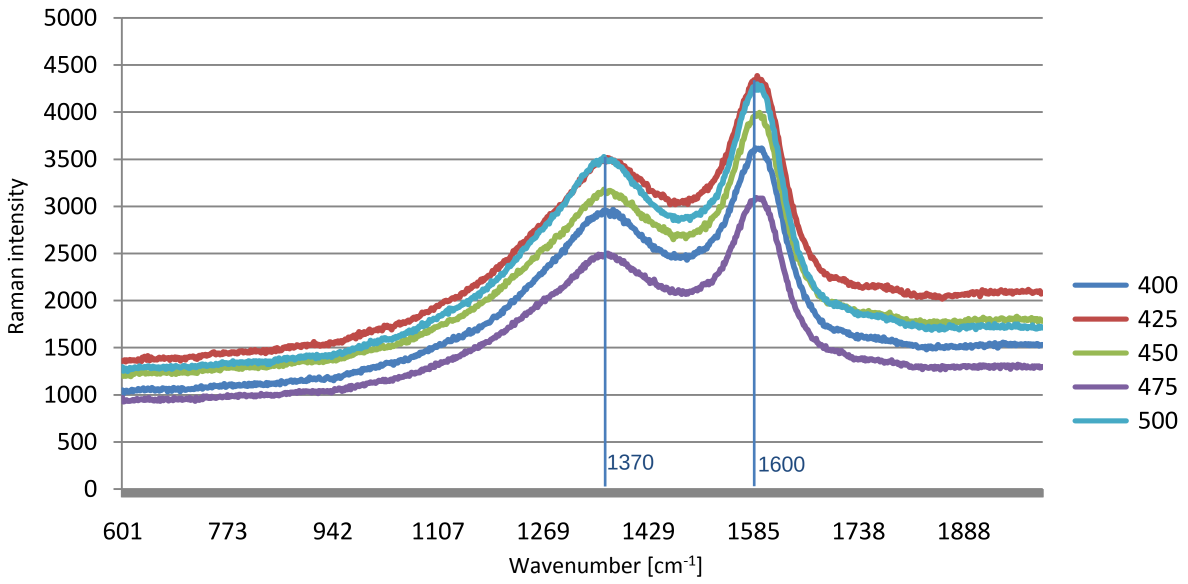

Figure 29 – Raman spectra for raw biomass samples from 400-500°C pyrolysis

Above graph presents spectroscopy results for raw biomass. Two main peaks in Raman intensity can be observed. First at around 1370 cm^{-1} and second bigger around 1600 cm^{-1}. Concerning influence of pyrolysis temperature, the lowest intensity value was obtained for 475°C, then higher values for 400°C, 450°C and the highest for 425 and 500°C which were almost overlapping at the peaks. According to literature such graph indicate that we are dealing with non-graphite material with aromatic carbon which has highly disordered carbon solids.

6.2.2 RAW AND BURNED BIOMASS BIO-CHAR COMPARISON

Considering burned biomass samples, only the one from 400°C pyrolysis was evaluated by Raman spectroscopy due to insufficient availability of the equipment to perform more tests. Due to this fact, obtained result is compared with result of raw biomass at the same temperature (400°C).

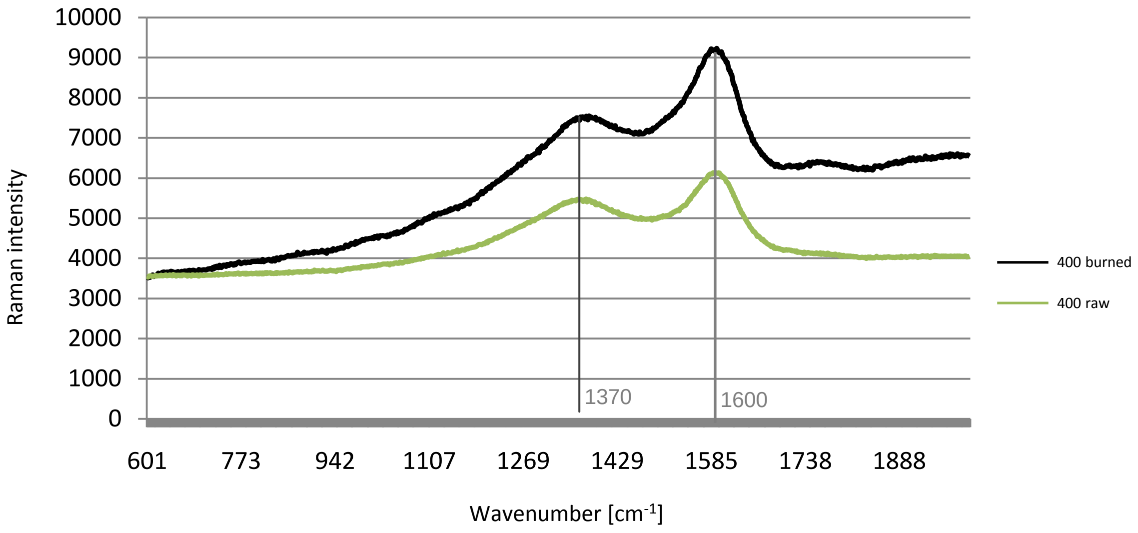

Figure 30 – Burned biomass Raman results for 400°C as compared to raw biomass 400°C sample

It can be seen on graph that values for burned biomass are higher than for raw sample. It is interesting to notice that situation is similar to graph of char amount in which also burned biomass was dominating over raw biomass. This indicate that there is more disordered solids in burned biomass sample than in raw one.

6.3 FOURIER-TRANSFORM INFRARED SPECTROSCOPY

6.3.1 RAW BIOMASS BIO-OIL

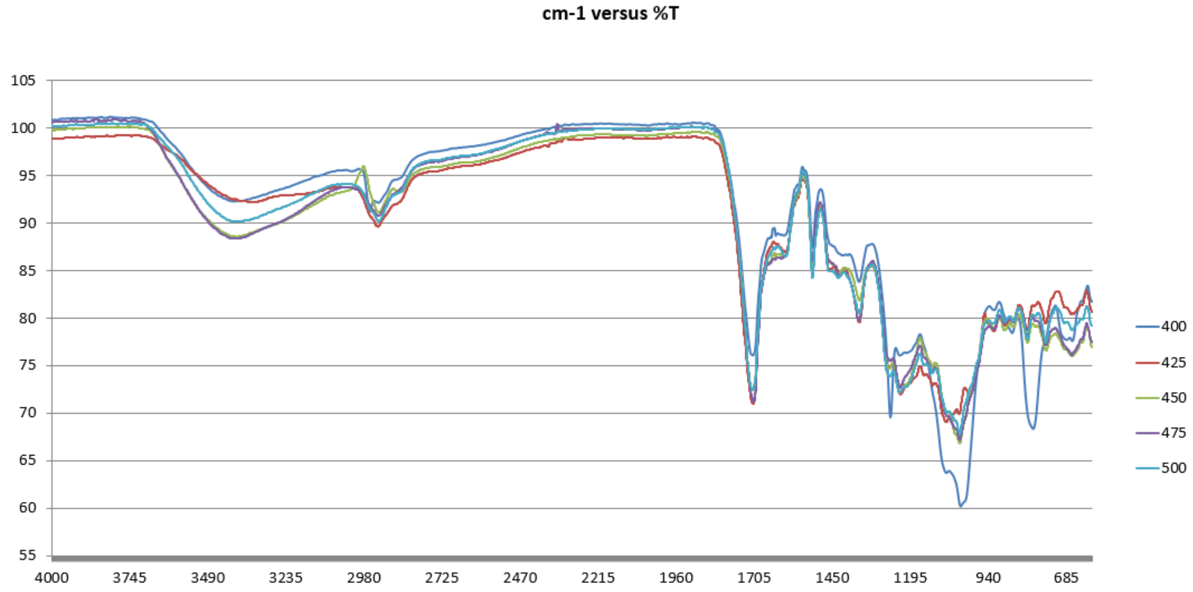

Figure31 – FTIR results for raw biomass samples from 400-500°C pyrolysis

Values on the graph present FTIR results for bio-oil samples from pyrolysis of raw biomass in temperatures from 400 to 500. Lines very similar for almost all temperatures, the only exception being 400 degrees where we can observe some differences, especially in range of 1150 to approximately 700. Using data from Table 3, we can identify that places of biggest difference for 400°C corresponds to C-H bending (1150-1000 cm^{-1}wavelength) so the alkanes and O-H bending (900-675 cm^{-1}) which represent aromatic compounds.

6.3.2 RAW BIOMASS + CATALYSTS BIO-OIL

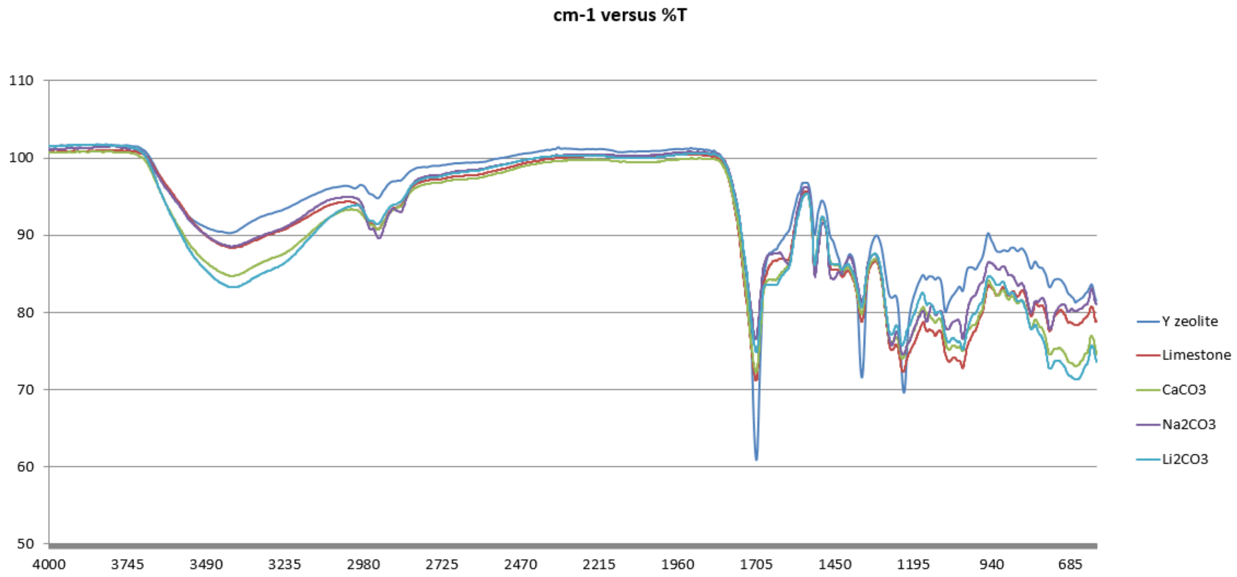

Figure 32– FTIR results for raw biomass samples from 475°C pyrolysis with various catalysts

In this graph we can see how use of catalysts added to biomass samples during pyrolysis affect composition of the bio-oil. It can be seen that Y zeolite show biggest deviation among other catalysts. This situation is mostly visible for 1700 cm^{-1}wavelength, which from Table 3 we know that it corresponds to C=O stretching which can be aldehydes, ketones, carboxylic acids etc. Similarly, for 1350 cm^{-1}, the C-H bending representing alkanes and in range 1200 to 600 cm^{-1}. We can also observe difference for lines of $CaCO_3$ and Li_2CO_3 from 800 to 600 cm^{-1} in O-H bending denoting aromatic compounds.

6.3.3 BURNED BIOMASS BIO-OIL

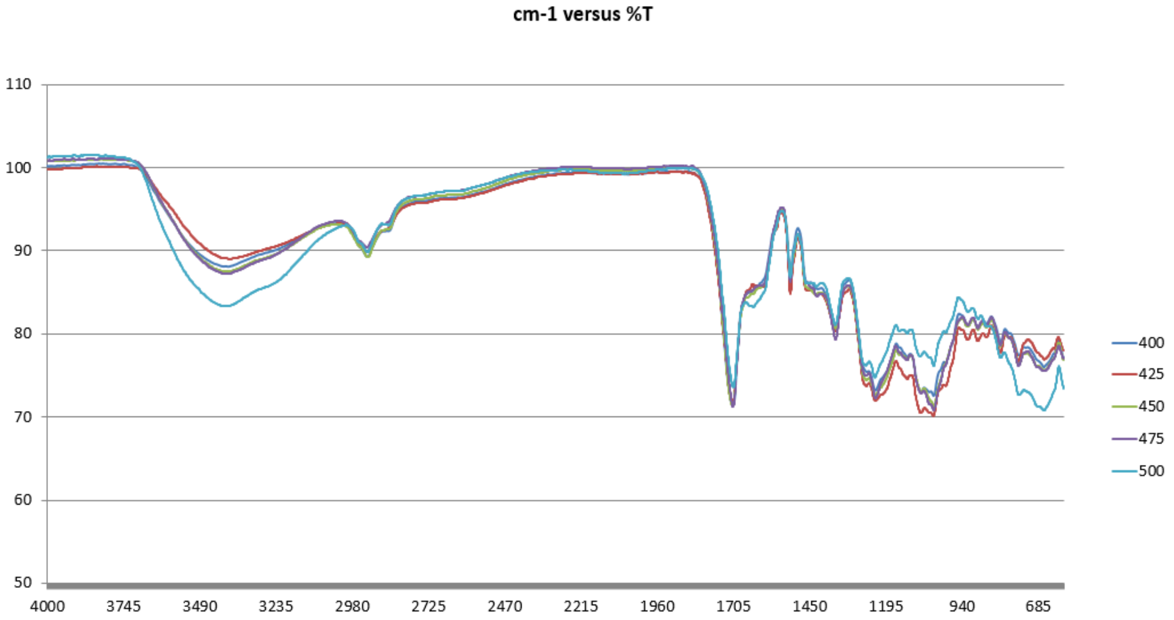

Figure 33 – FTIR results for burned biomass samples from 400-500°C pyrolysis

Values on this graph present results for samples from pyrolysis of burned biomass in temperatures from 400 to 500. Here the biggest deviation observed is for line representing 500°C. This happens in 3600-3000 cm^{-1} range which may be due to water impurities (3500-3200 cm^{-1} denotes O-H stretching) and in range 1200 to 600 cm^{-1}.

6.3.4 BURNED BIOMASS + CATALYSTS BIO-OIL

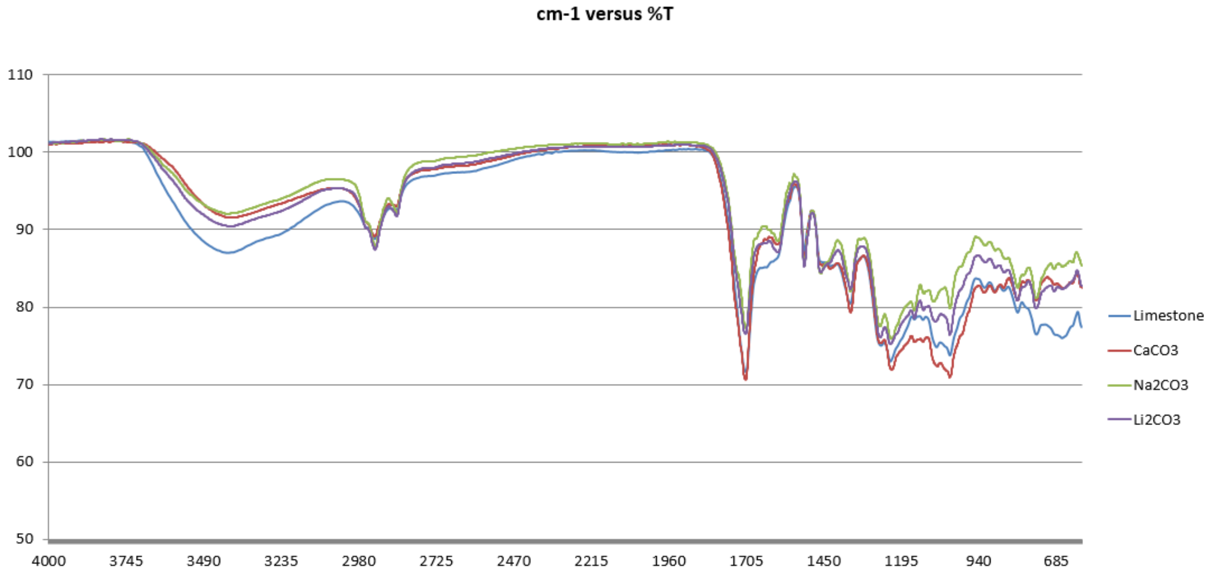

Figure 34 – FTIR results for raw biomass samples from 475°C pyrolysis with various catalysts

This graph shows effect of different catalysts use as addition to biomass sample during pyrolysis. We can see Limestone increase the peak around 3400 cm^{-1}, which denotes O-H stretching. $CaCO_3$ produce small difference in the 1700 cm^{-1} peak so the C=O stretching and there is small shift for limestone in range of 800-600 cm^{-1} so the O-H bending denoting aromatic compounds.

6.3.5 FTIR OBSERVATIONS

In all FTIR spectra results high peak at around 3400 cm^{-1} could be observed. This indicate presence of O-H stretching so the strong hydrogen bonding in the samples. The peak intensity however, was decreasing with temperature increases it can be seen on graphs representing raw and burned biomass samples pyrolysed in 400-500^{o}C. Reason of this phenomena can be ignition loss of OH at the elevated temperature.

The absorption peaks at around 2900, 1700 cm^{-1} were also visible on the graphs. The first one indicates C-H stretching and alkynes components. Second one, around 1700cm_{-1} which have higher intensity in case of raw biomass than burned sample, denotes C=O stretching and components such as aldehydes, ketones or carboxylic acids.

Smaller peaks appeared also from 600 to 1600 cm cm^{-1} which suggest existence of cellulosic and ligneous constituents. According to [25] vibrations between1500–1640 cm^{-1} are responsible for lignin presence in the sample.

CHAPTER VII

7. CONCLUSIONS

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 were subjected to direct fire.

The pyrolysis results indicated that in case of raw biomass, bio-char amount was decreasing with the temperature increase and more oil and gas was produced. 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 Li_2CO_3 and Na_2CO_3. Highest bio-oil yield was obtained with Y zeolite and bio-gas when Na_2CO_3 was used.

For burned biomass biggest char yield was obtained for the smallest pyrolysis temperature, 400^oC. and its amount was decreasing with temperature increase. This indicate that regardless of fact if biomass was subjected to direct fire before pyrolysis or not, increase of temperature result in decrease of char amount. Bio-oil yield was increasing simultaneously with temperature and gas yield except for 400^oC' Bio-gas yield remained on similar level with only few percent variation through the trials. 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 Li_2CO_3. Carbonate-based catalysts showed lower results of bio-oil and bio-char and dominance of gas yield among other products was observed for Na_2CO_3 and Li_2CO_3.

Carbonized biomass data due to insufficient amount for independent analysis were included in raw and burned biomass pyrolysis comparison section to serve as an additional reference point.

From comparison analysis it could be concluded that biomass which was subjected to combustion during forest fire, after pyrolysis produced more bio-char comparing to the raw biomass which was not affected by those processes. This was due to the fact that burned part was cambium of the tree and it has larger lignin content than wood part. Also use of catalysts affected differently raw and burned biomass samples.

Raman results showed that for raw biomass samples two peaks in Raman intensity placed at the similar value of wavenumber could observed. First around 1370 cm^{-1} and second bigger around 1600 cm^{-1}. Concerning influence of pyrolysis temperature, the lowest intensity value was obtained for 475^oC, then 400^oC, 450^oC and the highest for 425 and 500^oC. Raman Intensity results for burned biomass was higher than for raw sample and also slightly bigger at $1600cm^{-1}$ peak.

FTIR investigation of the bio-oil showed that biggest deviations in composition observed on graphs was in case of raw biomass samples for lowest pyrolysis temperature, 400^oC and for burned biomass for highest pyrolysis temperature of 500^oC. For burned biomass bio-oil sample, the biggest deviation was observed for line representing 500^{o}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 toC=O stretching and C-H bending.$CaCO_3$ and Li_2CO_3 had impact on O-H bending denoting aromatic compounds. When catalysts were used for burned biomass pyrolysis, limestone increased the peak around 3400 cm^{-1}, which denote O-H stretching, $CaCO_3$ 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.

The 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 bio-char, bio-oil and gas yields, chemical composition and characteristics of the products.

7.1 RECOMMENDED FUTURE WORK

Pyrolysis of biomass has a potential for production of environmental friendly fuels and chemicals. However, there is still work to do towards better understanding and optimization of process conditions to achieve desired product yields.

Regarding this particular research, more attention could be put on spectroscopy results. Specialist opinion would provide better description of obtained results and more in-depth analysis of chemical characteristic of the products.

In the field of biomass pyrolysis, further work should focus on investigation of impact of different catalysts, trial time and temperature on final products as well as the evaluation with more measurement tools, such as thermogravimetry or mass spectroscopy which would allow for more precise description of products composition.

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Appendix A

Table 5 show bio-oil, bio-char and gasification yields obtained during pyrolysis trials for raw biomass for temperatures from 400 to 500^{o}C with or without catalyst.

Table 5 - Raw biomass char, bio-oil and gas yield results

Sample no.	Mass [g]	Temp. [^{o}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_2CO_3	2	24	25	51
10	10	475	15	Li_2CO_3	2	24	30	46

Table 6 show bio-oil, bio-char and gasification yields obtained during pyrolysis trials for burned biomass for temperatures from 400 to 500^{o}C with or without catalyst.

Table 6 Burned biomass with catalysts char, bio-oil and gas results

Sample no.	Mass [g]	Temp. [^{o}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	-	-	35	26	39
4	10	475	15	-	-	34	31	35
5	10	500	15	-	-	34	31	35
6	10	475	15	Limestone	2	37	29	35
7	10	475	15	$CaCO_3$	2	35	28	37
8	10	475	15	Na_2CO_3	2	35	23	42
9	10	475	15	Li_2CO_3	2	35	20	44

Appendix B

Table 7presents gas chromatography results for pyrolysis trials of raw biomass for temperatures 425, 450 475 and to 500^{o}C.

Table 7 - Gas chromatography pyrolysis results for raw biomass in temperature range 425-500^{o}C

Temp [^{o}C]	pkno	time	area	mk	conc
425	1	0.978	292429	V	45.686
	2	1.153	106853	V	16.6935
	3	1.798	74403	SV	11.6239
	4	2.917	4987	T	0.7792
	5	3.533	2386	TV	0.3728
	6	4.05	3191	TV	0.4985
	7	4.382	16451	V	2.5702
	8	4.675	9911	V	1.5484
	9	5.048	6783	V	1.0598
	10	5.693	4991	V	0.7798
	11	6.267	2705	V	0.4225
	12	7.115	1189	V	0.1857
	13	11.672	44675		6.9795
	14	13.98	1907		0.298
	15	14.715	2099	V	0.328
	16	16.328	3494	V	0.5459
	17	16.995	1040	V	0.1625
	18	18.947	23329		3.6446
	19	21.033	12772	V	1.9954
	20	23.267	4541	V	0.7094
	21	24.547	19949	V	3.1166
450	1	0.9831	1443242		34.8495
	2	1.163	445161	SV	10.7492
	3	1.515	5421	T	0.1309
	4	1.827	20975	SV	6.7846
	5	2.55	557	T	0.0135
	6	2.675	169723	TV	4.0983
	7	3.59	47705	TV	1.1519
	8	4.122	47814	TV	1.1546
	9	4.453	31482	TV	0.7602
	10	4.752	68312	TV	1.6495
	11	5.122	22089	TV	0.5334
	12	5.773	22913	TV	0.5533
	13	6.34	27922	TV	0.6742
	14	7.15	194257		4.6907
	15	8.59	54686	V	1.3205

Table 7 - Gas chromatography pyrolysis results for raw biomass in temperature range 425-500^{o}C (cont.)

475	1	0.99	995490		42.1173
	2	1.168	305126	SV	12.9093
	3	1.51	4807	T	0.2034
	4	1.823	192055	V	8.1255
	5	2.477	13095	V	0.554
	6	2.66	172095	V	7.281
	7	3.56	44129	V	1.867
	8	4.087	38148	V	1.614
	9	4.423	11438	V	0.4839
	10	4.71	52758	V	2.2321
	11	5.075	23091	V	0.9769
	12	5.722	24430	V	1.0336
	13	6.283	29287	V	1.2391
	14	7.073	142450	V	6.0268
	15	7.883	57599	V	2.4369
	16	9.098	41001	V	1.7347
	17	9.497	91258	V	3.8609
	18	11.552	16368	V	0.6925
	19	12.483	21481	V	0.9088
	20	13.9	18614	V	0.7875
	21	14.588	3913	V	0.1655
	22	16.333	30288		1.2814
	23	21.058	34695	V	1.4679
500	1	0.995	1145253		13.9472
	2	1.175	426490	SV	5.1939
	3	1.523	6070	T	0.0739
	4	1.838	236289	SV	2.8776
	5	2.748	134866	TV	1.6424
	6	3.608	35544	TV	0.4329
	7	4.128	48426	TV	0.5897
	8	4.553	20874	TV	0.2542
	9	4.753	63257	TV	0.7704
	10	5.122	20753	TV	0.2527
	11	5.768	22117	TV	0.2693
	12	6.323	26156	TV	0.3185
	13	7.162	91538	T	1.1148
	14	16.323	1136	T	0.0138

Table 8 presents gas chromatography results for pyrolysis trials of raw biomass for temperature 475°C and with different catalysts.

Table 8 - Gas chromatography pyrolysis results for raw biomass for temperature 475°C and with different catalysts

Catalyst	pkno	time	area	mk	conc
Marble waste	1	0.992	1013925		34.3608
	2	1.172	384852	SV	13.0422
	3	1.517	5239	T	0.1776
	4	1.837	265223	V	8.9881
	5	2.425	568		0.0192
	6	2.547	270707	V	9.174
	7	3.367	20429	V	0.6923
	8	3.603	24665	V	0.8359
	9	4.127	44369	V	1.5036
	10	4.458	8607	V	0.2917
	11	4.75	67397	V	2.284
	12	5.13	31640	V	1.0722
	13	5.78	81365	V	2.7574
	14	6.308	71767	V	2.4321
	15	7.-78	242224	V	8.2087
	16	8.823	51100	V	1.7317
	17	9.602	44920	V	1.5223
	18	11.708	3411	V	0.1156
	19	12.518	7511		0.2545
	20	14.075	44003		1.4912
	21	14.65	52807	V	1.7896
	22	16.375	20833	V	0.706
	23	17.023	8337	V	0.2825
	24	21.17	34875	V	1.1819
	25	23.32	150047		5.0849
Limestone	1	1.007	1981591		43.5974
	2	1.19	682309	SV	15.0116
	3	1.537	5368	T	0.1181
	4	1.855	445457	V	9.8006
	5	2.602	293842		6.4649
	6	3.628	53117	V	1.1686
	7	4.153	78279	V	1.7222
	8	4.465	5473	V	0.1204
	9	4.78	109239	V	2.4034
	10	5.155	32210	V	0.7086
	11	5.813	40735	V	0.8962
	12	6.343	44259	V	0.9738
	13	7.102	281229	V	6.1874

Table 8 - Gas chromatography pyrolysis results for raw biomass for temperature 475°C and with different catalyst (cont.)

	14	8.805	61157	V	1.3455
	15	9.672	53201	V	1.1705
	16	11.278	3248	V	0.0715
	17	11.78	7199	V	0.1584
	18	12.583	12370	V	0.2722
	19	14.077	95911		2.1102
	20	14.782	58544	V	1.288
	21	16.515	24767	V	0.5449
	22	17.21	7703	V	0.1695
	23	21.315	17680		0.389
	24	23.517	150316		3.3071
Y zeolite	1	1..005	1982335		41.6045
	2	1.182	762198	SV	15.9967
	3	1.537	5841	T	0.1226
	4	1.86	649153	SV	13.6242
	5	2.605	300942	T	6.3161
	6	3.658	63349	TV	1.3295
	7	4.18	86012	TV	1.8052
	8	4.808	126875	TV	2.6628
	9	5.183	41342	TV	0.8677
	10	5.852	61631	TV	1.2935
	11	6.367	39782	TV	0.8349
	12	7.103	369068	TV	7.7459
	13	9.032	25997	T	0.5456
	14	9.742	27834	TV	0.5842
	15	11.395	704	TV	0.0148
	16	11.883	12216	TV	0.2564
	17	12.615	6357	TV	0.1334
	18	14.153	18328	T	0.3847
	19	14.9	1812	TV	0.038
	20	15.363	30255	TV	0.635
	21	16.6	41109	TV	0.8628
	22	17.332	21380	TV	0.4487
	23	18.173	43671	TV	0.9166
	24	19.985	13277	TV	0.2787
	25	21.367	30882	TV	0.6481
	26	22.423	2364	TV	0.0496
Na_2CO_3	1	0.983	1583090		38.5482
	2	1.17	730660	SV	17.7915
	3	1.51	2663	T	0.0648

Table 8 - Gas chromatography pyrolysis results for raw biomass for temperature 475°C and with different catalyst (cont.)

	4	1.827	545470	SV	13.2822
	5	2.542	232619	TV	5.6643
	6	3.408	8957	TV	0.2181
	7	3.592	28674	TV	0.6982
	8	4.108	66717	TV	1.6246
	9	4.442	1839	T	0.0448
	10	4.698	157043	V	3.824
	11	5.1	34363	V	0.8367
	12	5.757	89808	V	2.1868
	13	6.288	69530	V	1.693
	14	7.067	199099	V	4.848
	15	8.808	35521	V	0.8649
	16	9.592	41449	V	1.0093
	17	11.692	12702	V	0.3093
	18	12.503	12040		0.2932
	19	13.955	144200	V	3.5113
	20	14.675	52279	V	1.273
	21	16.4	27248	V	0.6635
	22	17.09	30813	V	0.7503
Li_2CO_3	1	1	2198566		40.4084
	2	1.18	1067221	SV	19.6149
	3	1.533	4597	T	0.0845
	4	1.853	761434	SV	13.9947
	5	2.585	288853	T	5.3089
	6	3.648	46539	TV	0.8554
	7	4.173	89318	TV	1.6416
	8	4.508	3215	T	0.0591
	9	4.787	202757	V	3.7266
	10	5.178	47371	V	0.8707
	11	5.843	59866	V	1.1003
	12	6.382	47171	V	0.867
	13	7.16	199592	V	3.6684
	14	9.032	30136	V	0.5539
	15	9.745	54324	V	0.9984
	16	11.867	14015	V	0.2576
	17	12.658	14281		0.2625
	18	13.25	33294	V	0.6119
	19	14.147	148160	V	2.7231
	20	14.875	64698	V	1.1891
	21	16.583	36779	V	0.676
	22	17.278	28687	V	0.5272

Table 9presents gas chromatography results for pyrolysis trials of burned biomass for different temperatures ranging from 400 to 500^{o}C.

Table 9 - Gas chromatography pyrolysis results for burned biomass in temperature range 425-500^{o}C

Temp (^{o}C)	pkno	time	area	mk	conc
425	1	0.985	711444		29.1572
	2	1.152	296454	SV	12.1572
	3	1.513	10555	T	0.4396
	4	1.828	213947	SV	8.7682
	5	2.607	242253	V	9.9283
	6	3.585	48184	V	1.9747
	7	4.115	45172	V	1.8513
	8	4.747	75877	V	3.1097
	9	5.108	16930	V	0.6939
	10	5.762	18010	V	0.7381
	11	6.322	28384	V	1.1633
	12	7.097	365650	SV	14.9855
	13	9.033	17040	T	0.6984
	14	9.59	17232	TV	0.7062
	15	11.668	1835	T	0.0752
	16	12.582	3493	T	0.1431
	17	14.008	10458	T	0.4286
	18	14.803	68988	T	2.8274
	19	16.342	31118	TV	1.2753
	20	16.973	26836	TV	1.0998
	21	21.17	49235	TV	2.0178
	22	22.348	4073	TV	0.1669
	23	23.658	136862		5.609
475	1	0.807	4095	V	0.1212
	2	0.987	1270138	V	37.595
	3	1.157	486067	SV	14.3871
	4	1.518	10406	T	0.308
	5	1.835	347983	V	10.3
	6	2.6	300245	V	8.887
	7	3.605	54050	V	1.5998
	8	4.132	65951	V	1.9521
	9	4.465	22739	V	0.6731
	10	4.762	99148	V	2.9347
	11	5.13	29398	V	0.8702
	12	5.785	32890	V	0.9735
	13	6.338	32809	V	0.9711
	14	7.108	375614	SV	11.1178

Table 9 Gas chromatography pyrolysis results for burned biomass in temperature range 425-500^{o}C (cont.)

	15	9.092	17927	T	0.5306
	16	9.643	24890	TV	0.7367
	17	11.725	3542	TV	0.1048
	18	12.592	7161	T	0.212
	19	14.037	16905	T	0.5004
	20	14.915	59192	T	1.752
	21	16.423	38073	TV	1.1269
	22	17.055	49223	TV	1.4569
	23	19.745	3260	TV	0.0965
	24	20.167	4000	TV	0.1184
	25	21.208	22779	TV	0.6742
500	1	0.98	2130844		45.8004
	2	1.152	648271	SV	13.9339
	3	1.507	9084	T	0.1952
	4	1.822	431479	V	9.2742
	5	2.573	253248	V	5.4433
	6	3.567	51230	V	1.1011
	7	4.083	71007	V	1.5262
	8	4.41	12564	V	0.2701
	9	4.698	105005	V	2.257
	10	5.065	29843	V	0.6414
	11	5.715	39554	V	0.8502
	12	6.247	63037	V	1.3549
	13	7.002	371298	SV	7.9807
	14	8.832	19700	T	0.4234
	15	9.52	21673	TV	0.4658
	16	11.6	3621	TV	0.0778
	17	12.432	6046	T	0.1299
	18	13.922	55908		1.2017
	19	14.58	72566	V	1.5597
	20	16.25	33829	V	0.7271
	21	16.915	18290	V	0.3931
	22	20.983	18131		0.3897
	23	23.335	176226	S	3.7878
	24	27.195	7420	T	0.1595
	25	27.582	2591		0.0557

Table 10 presents gas chromatography results for pyrolysis trials of burned biomass for temperature 475°C and with different catalysts.

Table 10 -Gas chromatography pyrolysis results for burned biomass for temperature 475°C and with different catalysts

Catalyst	pkno	time	area	mk	conc
marble	1	0.998	1086081		36.7616
	2	1.177	382795	SV	12.9568
	3	1.527	7292	T	0.2468
	4	1.848	266955	V	9.0359
	5	2.558	273078	V	9.2431
	6	3.417	14858	V	0.5029
	7	3.63	25208	V	0.8532
	8	4.155	45498	V	1.54
	9	4.492	14989	V	0.5073
	10	4.787	70790	V	2.3961
	11	5.157	17834	V	0.6036
	12	5.825	49627	V	1.6798
	13	6.35	62853	V	2.1275
	14	7.103	318130	SV	10.7681
	15	9.007	19102	T	0.6466
	16	9.7	17216	TV	0.5827
	17	11.798	1954	T	0.0661
	18	12.58	5043	T	0.1707
	19	14.348	25202	T	0.853
	20	14.783	58798	TV	1.9902
	21	16.502	24611	TV	0.833
	22	17.183	13109	TV	0.4437
	23	18.85	646	TV	0.0219
	24	21.282	12196		0.4128
	25	23.667	140525		4.7565
limestone	1	1.005	972219		31.8013
	2	1.182	373452	SV	12.2156
	3	1.532	9666	T	0.3162
	4	1.858	266044	V	8.7023
	5	2.58	271304	V	8.8744
	6	3.642	42685	V	1.3962
	7	4.168	48588	V	1.5893
	8	4.505	14405	V	0.4712
	9	4.8	73818	V	2.4146
	10	5.172	21254	V	0.6952
	11	5.838	25057	V	0.8196
	12	6.36	47113	V	1.5411

Table 10 - Gas chromatography pyrolysis results for burned biomass for temperature 475^{o}C and with different catalyst (cont.)

	13	7.103	445854	SV	14.5839
	14	9.032	16964	T	0.5549
	15	9.715	15783	TV	0.5163
	16	11.832	2056	T	0.0673
	17	12.598	6629	T	0.2168
	18	14.115	12718	T	0.416
	19	14.85	72846	TV	2.3828
	20	16.55	33411	TV	1.0929
	21	17.245	37276	TV	1.2193
	22	19.365	10572	TV	0.3458
	23	21.348	19068	TV	0.6237
	24	22.482	1739	TV	0.0569
	25	23.748	203329	V	6.6509
	26	27.673	13320	V	0.4357
Na_2CO_3	1	0.997	1011495		32.0951
	2	1.183	447564	SV	14.2014
	3	1.528	2097	T	0.0665
	4	1.847	339404	V	10.7694
	5	2.605	226612	V	7.1905
	6	3.628	32016	V	1.0159
	7	4.147	53498	V	1.6975
	8	4.478	13169	V	0.4178
	9	4.748	106360	V	3.3748
	10	5.143	28188	V	0.8944
	11	5.795	82679	V	2.6234
	12	6.333	68538	V	2.1747
	13	7.117	212284	V	6.7359
	14	9.195	19260	V	0.6111
	15	9.648	61976	V	1.9665
	16	11.738	16934	V	0.5373
	17	12.6	7481	V	0.2374
	18	14.257	44695	V	1.4182
	19	14.772	78482	V	2.4903
	20	16.457	40964	V	1.2998
	21	17.15	52789	V	1.675
	22	18.677	6593	V	0.2092
	23	19.152	29162	V	0.9253
	24	21.247	43170	V	1.3698
	25	22.477	8427	V	0.2674
	26	23.877	117721	V	3.7353

Table 10 - Gas chromatography pyrolysis results for burned biomass for temperature 475°C and with different catalyst (cont.)

Li_2CO_3	1	0.673	1832	V	0.0631
	2	1	1069005	V	26.823
	3	1.187	440666	SV	15.1792
	4	1.535	4535	T	0.1562
	5	1.855	360125	SV	12.4049
	6	2.692	208951	T	7.1976
	7	3.645	31680	TV	1.0913
	8	4.173	43013	TV	1.4816
	9	4.505	5056	T	0.1742
	10	4.797	96652	V	3.3293
	11	5.18	27139	V	0.9348
	12	5.843	29992	V	1.0331
	13	6.388	35380	V	1.2187
	14	7.177	209226	SV	7.207
	15	9.323	731	T	0.0252
	16	9.75	49695	V	1.7118
	17	11.857	9585	V	0.3302
	18	12.692	4447	V	0.1532
	19	14.142	121693		4.1918
	20	14.828	78938	V	2.7191
	21	16.572	35922	V	1.2374
	22	17.253	35090	V	1.2087
	23	19.102	1577	V	0.0543
	24	19.507	2159	V	0.0744