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**Faculty of Tropical AgriSciences**



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**Energy assessment of pyrolysis products made of  
different biomass feedstocks**

MASTER'S THESIS

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## **Declaration**

I, Karolína Jičínská, hereby declare that this Thesis entitled “Energy assessment of pyrolysis products made of different biomass feedstocks” is my own work and all the sources have been quoted and acknowledged by means of complete references.

In Prague,

.....

Karolína Jičínská

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## **Abstract**

The rapid depletion of fossil fuels reserves and their negative environmental impact lead to use of alternative fuels, where one of renewable and clean energy source is biomass. Biomass has a big potential as it contains carbon and can be processed by thermochemical and biochemical processes into a material with a higher calorific value. One of the thermochemical processes is pyrolysis, which is the process where temperature heats an input material without access of oxygen in order to get three kinds of products such as biooil, biochar and pyrolysis gas. The pyrolysis processes can be divided into several types according to process parameters. Description and summarization of the main pyrolysis reactors, their parameters, technologies as well as products are presented in the literature review of the Master's Thesis.

Interesting input materials (residual biomass) like bamboo chips, coffee ground, medicine residue, mushroom dreg and tea leaves obtained from China were studied in the practical part of this Thesis. These experimental materials were processed in a bench scale pyrolyser under the conditions of slow pyrolysis with temperature 450 °C. The main physical and chemical properties as moisture content, calorific value, content of carbon, hydrogen and nitrogen as well as ash content were determined. The quality and suitability of the materials for energy utilization, primarily raw feedstock materials vs produced biochars, were evaluated by confrontation with the current EN and ISO technical standards for solid biofuels, and discussion with the findings of other authors. Results showed that materials after pyrolysis process had lower moisture content, higher calorific value, higher nitrogen and ash content as well as the majority of samples had higher carbon content comparing to the raw materials. As the best material for fuel production was found bamboo chips, followed by coffee ground.

**Key words:** biochar, biofuels properties, biooil, China, pyrolysis technologies, residual biomass, thermochemical process

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## List of the abbreviations used in the thesis

a.r.	As received
d.b.	Dry basis
CHN	Carbon, hydrogen and nitrogen
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
CULS	Czech University of Life Sciences Prague
etc	Et cetera
FTA	Faculty of Tropical AgriSciences
FE	Faculty of Engineering
GCV	Gross calorific value
GHG	Greenhouse gas
H <sub>2</sub>	Hydrogen
CH <sub>4</sub>	Methane
i.e.	For example ( <i>exemplī grātia</i> )
MC	Moisture content
N <sub>2</sub>	Nitrogen
NO <sub>x</sub>	Nitrogen oxides
NCV	Net calorific value
O <sub>2</sub>	Oxygen
RIAE	Research Institute of Agricultural Engineering in Prague

# 1. Introduction

Energy is one of the basic needs in our everyday life and plays an important role in different sectors such as transport, manufacture and many others. It is also important for the development of any country (Silitonga et al. 2011; Tripathi et al. 2016). Fossil fuels are the main source of energy all over the world. The current demand for fossil fuels (crude oil) is about 94 million barrels per day and this consumption continues to grow with an increasing number of the inhabitants. The direct burning of fossil fuels releases huge amounts of carbon dioxide (CO<sub>2</sub>), nitrogen oxides (NO<sub>x</sub>) and other substances into the air (Chen et al. 2015). Environmental pollution and rapid depletion of fossil fuel sources lead to the necessity to search for and use of renewable resources (Anex et al. 2010). Renewable energy sources include solar, wind, water, tidal, geothermal and biomass energy which can contribute to a reduction of greenhouse gases (Mohammed et al. 2015).

Biomass is one of the largest and the most sustainable sources of energy in the world (Zhang et al. 2010). The great potential of biomass is that it contains carbon as the only available renewable resource. Therefore, it can be converted into liquid fuel (Mohammed et al. 2015), which is highly desirable due to its wide range of uses. The conversion of biomass can be achieved primarily by thermochemical or biochemical processes. One of the thermochemical processes is pyrolysis that is a process that can produce three main products such as solid, liquid and gaseous products (Patel et al. 2016). Pyrolysis is a promising technology for converting biomass into energy, for the production of chemicals and, above all for the fuels (Johansson et al. 2016).

Treatment of different residual biomass materials originated from China by pyrolysis process and mainly evaluation of energy properties of produced biofuels in comparison with the properties on input materials is the research focus of the present Thesis.

## 2. Literature review

### 2.1. Basics of pyrolysis

Pyrolysis belongs to the group of thermal and reductive processes. It is technology where the temperature affects material. The temperature is higher than range of chemical stability of a particular material and at the same time, this process is without medium containing oxygen. The temperature range can be up to 2 000 °C. It is a thermochemical process in which a raw material is decomposed into low-molecular substances and a solid residue (Šejvl 2013). Pyrolysis consists of three processes, namely drying, carbonization and gas production (Tripathi et al. 2016). This process produces material with higher energy value than input material. Pyrolysis is an evolving technology that can produce a range of products that can be used for renewable energy and other applications. It produces always three main products but its products ration is influenced by many parameters such as type of input material and its particle size, temperature and heating rate, reaction atmosphere and vapor residence time (Akhtar and Amin 2012; Park et al. 2012; Liu and Han 2015). The aim of pyrolysis is the maximum yield of the liquid products, i.e. biooil, the secondary products are solid and gaseous products (Zámostný and Kurc 2011). Also, biochar can be valuable product and it can improve profitability of pyrolysis. Pyrolysis is very promising technology, because it can transform biomass into renewable biofuels. One of the advantages of pyrolysis is that it can be carried out at lower temperatures than gasification (> 700 °C) or combustion (> 900 °C) (Demirbas 2004; Roy and Dias 2017).

The process of pyrolysis is energy-intensive. This process can process different kinds of materials and this is the great potential/benefit (Prokeš 2011). According to Xu et al. (2011) the thermal efficiency (PTE) of the pyrolysis process can be calculated using the following equation:

$$\text{PTE} = \frac{\text{GCV (biooil + biochar + biogas)}}{\text{GCV input material} + \text{E pyrolysis}} \times 100 \text{ [\%]}$$

where:

GCV - gross calorific value of pyrolysis products: biooil, biochar and biogas or input material [MJ/kg]

E pyrolysis - external heat and electricity requirement for this process

Pyrolysis can be divided according to several criteria and into several different groups According to Molek (2015) the pyrolysis process can be divided into several temperature ranges:

- low temperature (temperature to 500 °C),
- medium temperature (in range 500 - 800 °C),
- high temperature (temperature is higher than 800 °C).

Tripathi et al. (2016) divide pyrolysis processes into:

- slow pyrolysis,
- fast pyrolysis,
- flash pyrolysis,
- vacuum pyrolysis,
- intermediate pyrolysis,
- hydrolysis.

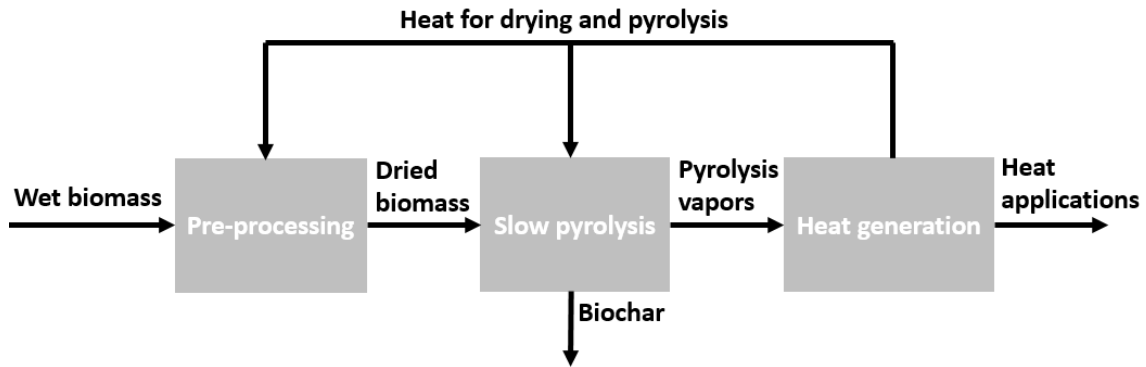
The most commonly used processes are the slow and fast pyrolysis (Roy and Dias 2017).

### **2.1.1. Slow pyrolysis (carbonization)**

During slow pyrolysis or carbonization the temperature range is between 400 - 600 °C and pressure 0.001 MPa to 0.1 MPa (Molek 2015). Slow pyrolysis is used to produce biochar for the production of the heat and electricity or can be used directly as a fuel or as a soil amendment (Madsen 2015; Weber and Quicker 2018). This process is characterized by a slow heating rate and long residence times. The residence time of the steam is between 10 and 30 seconds (Bridgwater 2012) and the rate of heating is 0.1 - 1

°C per second for a period ranging between 5 and 30 minutes (Demirbas and Arin 2002).

Slow pyrolysis processes have four major steps: pre-treatment, pyrolysis, solids removal and heat generation. It is shown in the Figure 1.



**Figure 1: Slow pyrolysis process**

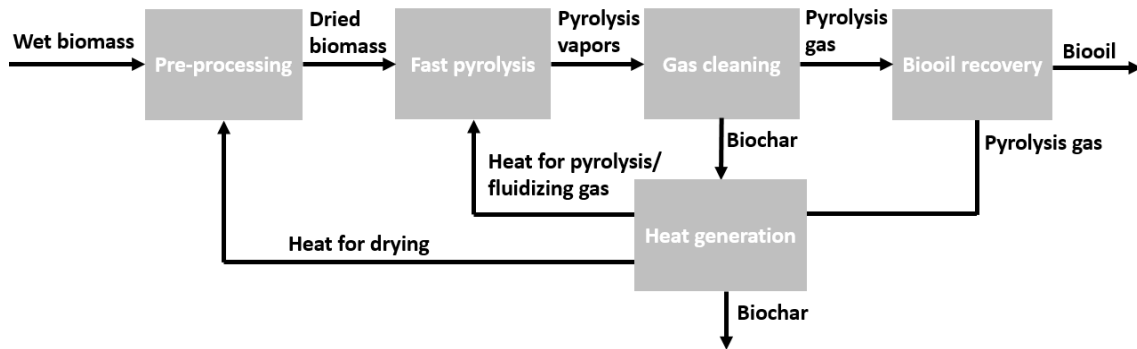
Source: Modified based on Duku et al. 2011

### **2.1.2. Fast pyrolysis (liquefaction)**

Fast pyrolysis is a slightly endothermic process (Braimakis et al. 2014). During the fast pyrolysis is the temperature range higher than during the slow pyrolysis, and varies from 850 °C up to 1250 °C (Yang et al. 2016; Tripathi et al. 2016). The pressure is 0.1 MPa (Molek 2015). The heating speed of the feedstock is extremely high and ranges from 10 - 200 °C in a very short time 1 to 10 seconds (Tripathi et al. 2016). In order to achieve such rapid heat transfer, it is important to feed the input material into small particles (Choi et al. 2012). If the particle size of a material is bigger the heat transfer rate decreases and this affects yields, i.e. yield of biochar is increasing and the yield of biooil and syngas is decreasing (Roy and Dias 2017). This process has a short residence time of about 1 second (Bridgwater 2012). It is used for maximum production of liquid products (Molek 2015). Under favorable fast pyrolysis conditions, the yield of pyrolysis oil can be up to 80 % by weight of the feed material, while the yields of the solid residue and the pyrolysis gas are about 12 % by weight (Bridgwater 2012). Most

often fluidized bed reactor is used for fast pyrolysis because this reactor produces a high yield of the liquid product (Henkel et al. 2016).

Steps of fast pyrolysis process are shown in the Figure 2.



**Figure 2: Fast pyrolysis process**

Source: Modified based on Duku et al. 2011

### 2.1.3. Flash pyrolysis

Flash pyrolysis is considered to be better and is modified form of fast pyrolysis. The temperature range is 900 to 1 200 °C with very short residence time, which is 0.1 - 1 second. Rapid heating combined with high temperature and low residence time of vapors leads to high yield of liquid product, but also reduces the yield of the solid product (Tripathi et al. 2016).

### 2.1.4. Vacuum pyrolysis

Vacuum pyrolysis is the thermal degradation of a biomass. This process is with low pressure and absence of oxygen. The pressure range during this type of pyrolysis is typically 0.05 to 0.20 MPa and the temperature is maintained between 450 and 600 °C (Carrier et al. 2011). The rate of heating of the material in vacuum pyrolysis is comparable to slow pyrolysis, i.e. 0.1 - 1 °C per second (Demirbas and Arin 2002). The short residence time of the vapor of organic matter generated during the primary pyrolysis process ensures a high yield of the liquid product. The vacuum pyrolysis is

costly due to the high vacuum, but the advantage is that even larger particles of input material can be used (Tripathi et al. 2016).

#### **2.1.5. Intermediate pyrolysis**

This type of pyrolysis is generally used for the equilibrium yield of liquid and solid products. Slow pyrolysis produces a higher yield of solid product rather than liquid one, while fast pyrolysis works opposite way. The operating conditions for medium-temperature pyrolysis are in the range between slow and fast pyrolysis, i.e. between 500 - 650 °C. The pressure during the process is 0.1 MPa. Temperatures of medium-temperature pyrolysis prevent the formation of high-molecular tars. This process produces high quality biooil and dry flue gas which are suitable for use in agriculture or for energy production. Heating speed of material is in the range of 0.1 and 10 °C per minute with a residence time of between 300 - 1 000 seconds. The advantage of this process is that unlike fast pyrolysis liquid products do not contain high amount of reactive tar and can be used directly in boilers and engines (Mahmood et al. 2013; Tripathi et al. 2016).

#### **2.1.6. Hydrolysis**

Hydrolysis is a relatively new technology for converting biomass to high quality biooil. This process could be considered as a process of fast pyrolysis only with the difference of high pressure, which is required for higher yield of solid product. During this process the pressure is higher than atmospheric pressure in the range of 5 - 20 MPa. The heating rate, residence time and temperature are almost the same as for the fast pyrolysis (Tripathi et al. 2016). Hydrolysis is often used with a catalyst to remove oxygen, water and other undesirable substances from a liquid product (Marker et al. 2012).

Table 1 summarizes the conditions of certain pyrolysis processes according to Tripathi et al. (2016), Roy and Dias (2017) and Molek (2015).



**Table 1: Conditions of pyrolysis processes**

<b>Pyrolysis</b>	<b>Slow</b>	<b>Fast</b>	<b>Flash</b>	<b>Intermediate</b>	<b>Vacuum</b>	<b>Hydro</b>
Temperature [°C]	400 - 600	850 - 1 250	900 - 1 200	500 - 650	300 - 600	350 - 600
Heating rate [°C/s]	0.1 - 1	10 - 200	> 1 000	1 - 10	0.1 - 1	10 - 300
Residence time [s]	300 - 550	0.5 - 10	< 1	0.5 - 20	0.001 - 1	> 15
Pressure [MPa]	0.1	0.1	0.1	0.1	0.01 - 0.02	5 - 20
Particle size [mm]	5 - 50	< 1	< 0.5	1 - 5	-	-
Biooil yield [%]	25 - 50	60 - 75	60 - 75	35 - 50	-	-
Biochar yield [%]	25 - 35	10 - 25	10 - 25	25 - 40	-	-
Biogas yield [%]	20 - 50	10 - 30	10 - 30	20 - 30	-	-

## **2.2. Pyrolysis reactors**

According Roy and Dias (2017) typically the pyrolyser consists of a reactor, a cyclone and a condenser.

Biomass is inserted into the reactor and converted into different products due to various thermochemical reactions. For separation of solid products from liquid and gases is used cyclone. When solid products are separated, the gaseous products are quickly inserted into the condenser and then biooil is separate from the other gases. Non-condensable gases are generally recycled to the pyrolyser for fluidization and heating. Catalysts can improve the quality and conversion efficiency of pyrolysis

products or it is used for upgrading of products. Screw feeder can be used in pyrolyser for better handling with biomass which is difficult to feed into the reactor (Veses et al. 2014; Roy and Dias 2017).

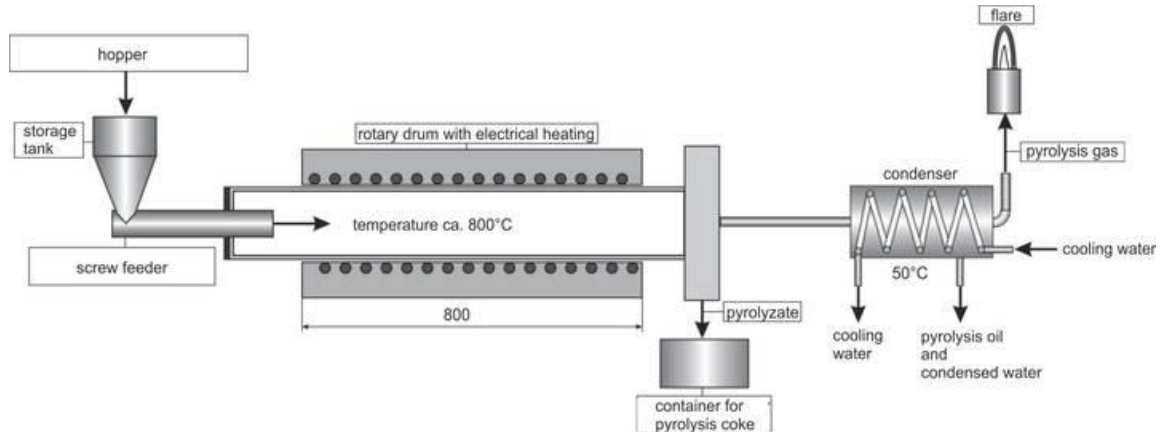
### 2.2.1. Slow pyrolysis reactors

The most common reactors are rotary kilns and screw/auger.

#### Rotary kiln reactor

The rotary kiln is mainly used in industry, especially in cement industry. These reactors have the same advantages like other reactors for biomass processing. The big advantage of the reactor is that it can use solid biomass of several shapes and sizes and also it can be used in continuous mode (Silvestre et al. 2018).

The diagram of rotary kiln reactor is shown in the Figure 3.



**Figure 3: Diagram of rotary kiln reactor**

Source: Poyraz 2019

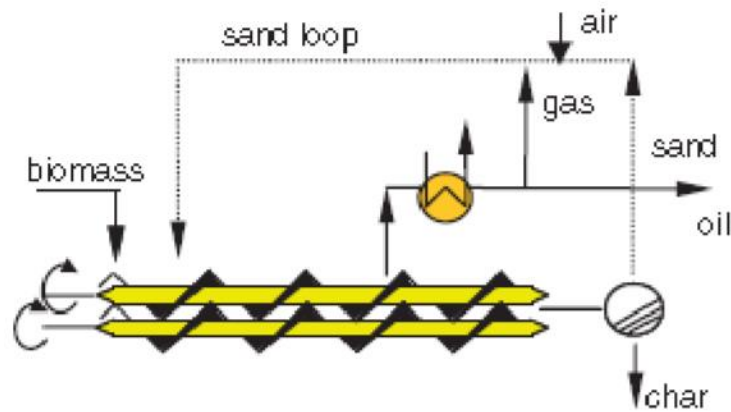
#### Screw/auger reactor

This technology is for continuous operation. It includes one or more screws that mechanically mix the input material. The reactor is indirectly heated by heating fluid. The residence time of the input material depends on the length of the reactor and the speed of rotation of the screw. This technology is financially less demanding than others

(Henrich et al. 2016). The yield of biooil may be in the range of 30 - 50 % (Zámostný and Kurc 2011). The advantage of this reactor is that steel balls can be used as a heat transfer medium (Joubert et al. 2015).

The screw reactor is used in Bioliq technology, which was developed in Germany. The pyrolysis process is carried out in a twin screw reactor where biomass with heat transfer medium is mixed, either by sand or by steel beads. The output product is slurry; slurry is a liquid product with fine semiconductor particles. This product is subsequently transformed by gasification to synthesis gas (Jílková et al. 2012).

The diagram of screw reactor is shown in the Figure 4.



**Figure 4: Diagram of screw reactor**

Source: Venderbosch and Prins 2010

Auger reactor and fluidized bed are commercially relevant technologies for agricultural applications because they regulate the amount of feedstocks through the pyrolyser. Auger reactor can be used in fast pyrolysis but it is preferable for biochar production (Roy and Dias 2017).

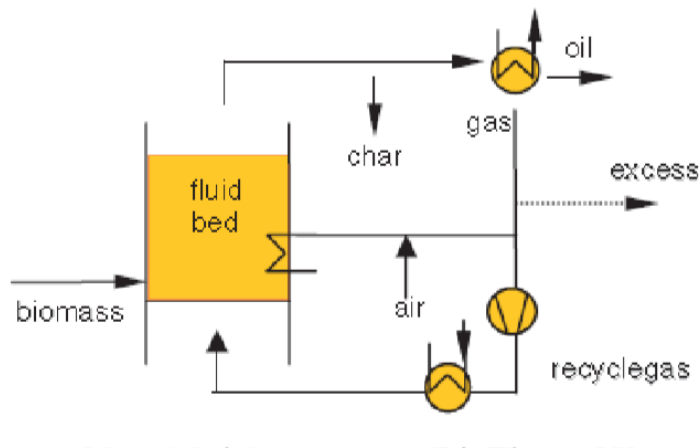
### **2.2.2. Fast pyrolysis reactors**

Reactors that are used for the fast pyrolysis are fluidized bed, rotating cones, vacuum and ablative. The most used reactors in fast pyrolysis are fluidized bed, especially bubbling fluidized bed and circulating fluidized bed (Silvestre et al. 2018).

## Fluidized bed

The fluidized bed reactors have a well-known technology and they are used in many projects to maximize the liquid product, i.e. biooil which is produced. For fluidized bed reactors an inert element is very commonly used, usually sand, for better properties of fluid and improved biomass heating (Uddin et al. 2018).

The diagram of fluidized bed reactor is shown in the Figure 5.



**Figure 5: Diagram of fluidized bed reactor**

Source: Venderbosch and Prins 2010

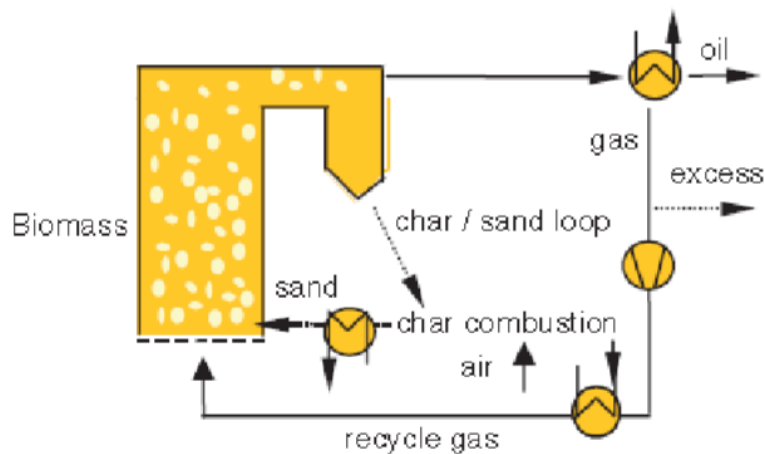
The fluidized bed reactors can be divided into two main types: bubbling and circulating.

Bubbling fluidized bed is very prevalent because it produces a high quality biooil from dry input materials. A significant feature of bubble fluidizing bed reactors is that it requires small biomass particle sizes to attain high biomass heating rate (Uddin et al. 2018).

Circulating fluidized bed reactor is comparable with bubbling fluidized bed reactor. The circulating fluidized bed is suitable for large quantities and it is commonly used for research or industrial use of fast pyrolysis of biomass. It is used in Rapid Thermal Processing technology. The main and desirable product is liquid, which is used as a source of chemicals and fuels. The yield of the liquid product can be up to 70 %.

The bed forms from a sand that is burned with semi-coke in the chamber. The semi-coke is burned and the sand is reused in the reactor. The disadvantage of this technology is that the circulating gas must be cleaned as well as mechanical wear of the device. The reactor can be divided into two main types: single circulating and double circulating (Jílková et al. 2012; Uddin et al. 2018).

The diagram of circulating fluidized bed reactor is shown in the Figure 6.



**Figure 6: Diagram of circulating fluidized bed reactor**

Source: Venderbosch and Prins 2010

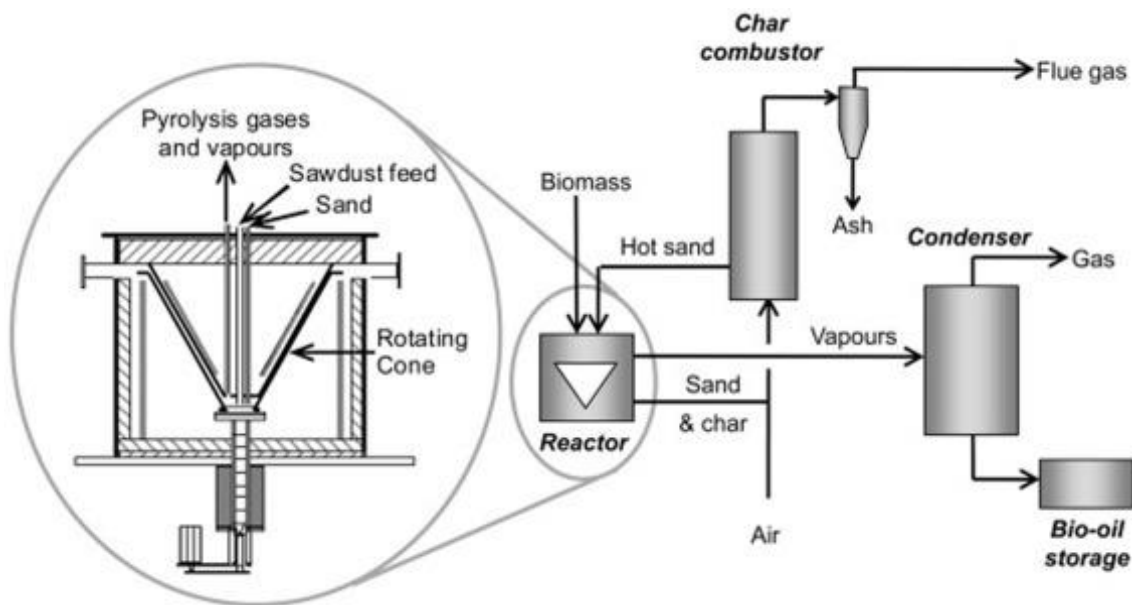
### Rotating cone

The rotating cone reactor is part of the BTG technology. This technology is developed by the Dutch Biomass Technology Group (Jílková et al. 2012). The basis of the production process is to obtain the maximum amount of biooil or pyrolysis oil (Molek 2015), which can be up to 75 % by weight of feedstock. BTG technology intensively blends biomass with hot sand in a special rotating cone reactor. In the reactor, the inlet biomass is mixed mechanically, i.e. by centrifugal forces. The use of inert gas is not used for the purpose of accidental dilution. The reactor gas is taken to a condenser where it is quenched, producing pyrolysis oil and a small amount of pyrolysis gas. The solid residue (biochar) and pyrolysis gas, is also used for energy purposes. The whole process of biomass conversion takes only a few seconds. Sand and biochar are fed into a combustion plant where the sand is heated by combustion of biochar to the

original temperature, and then the sand is reused in the reactor (BTG 2016). This technology can process the different types of biomass like wood, straw, energy crops and poultry fodder (Molek 2015).

Two pilot units are in operation in the Netherlands. A smaller unit is used to test different types of biomass as an input material and can treat 2 to 3 kg of biomass per hour. The second unit is larger and can process up to 200 kg of biomass per hour (Molek 2015). Another unit is in Malaysia. This unit can utilize coconut waste biomass, coconut dried skin and fiber. The obtained pyrolysis oil has 50 - 60 % by weight of the input biomass (Jilková et al. 2012).

The diagram of rotating cones reactor is shown in the Figure 7.



**Figure 7: Diagram of rotating cone reactor**

Source: Perkins et al. 2018

### Ablative reactor

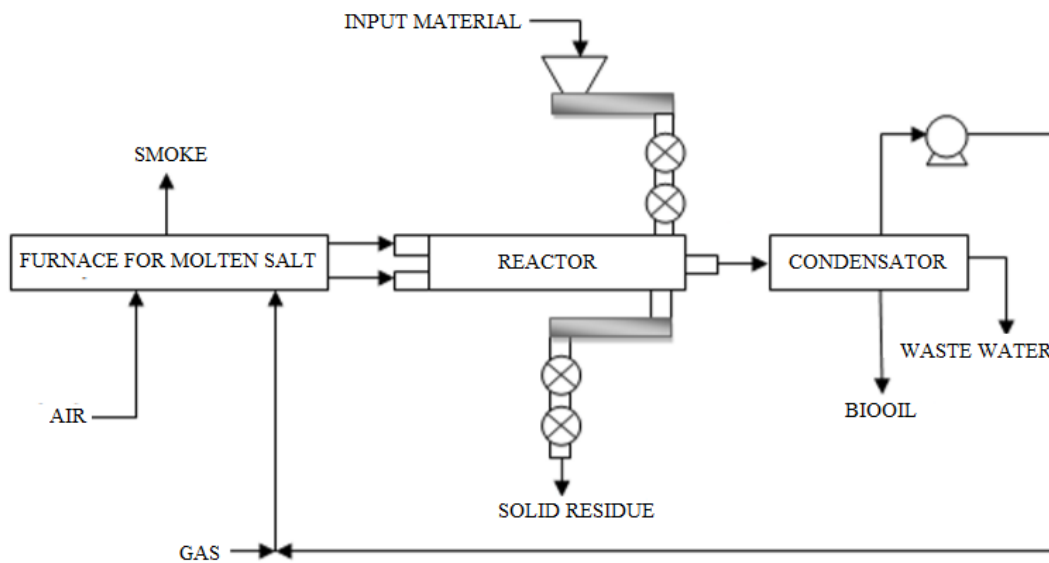
This technology is different from fluid bed in absence of a fluidizing gas. Heat energy is transmitted through wall reactors by pressing the biomass in the reactor against the walls. The input material is heated to 500 °C. These reactors have good heat

transfer with high heating rates. The reactor has high energy and cost efficiency because it does not need to heat and cool the fluidizing gases. This process of pyrolysis is used in Biomass-to-Oil technology. The yield of biooil can be as high as 75 % (Zámotný and Kurc 2011; Jílková et al. 2012; Uddin et al. 2018).

### Vacuum reactor

This process uses the Pyrovac technology developed in Canada at the University of Laval and Pyrovac. The capacity of Pyrovac is 350 kg per hour and Laval University has capacity of 30 kg per hour. This technology is combined with slow and fast pyrolysis. The biomass is first slowly heated by means of molten salts that are heated by the burning of the pyrolysis gas which is consequently produced. Then, the resulting products are quickly removed by the vacuum. This process is mechanically complicated and it needs high investment and is demanding (Jílková et al. 2012; Uddin et al. 2018).

The diagram of vacuum reactor is shown in the Figure 8.



**Figure 8: Diagram of vacuum reactor**

Source: Modified based on Jílková et al. 2012

Table 2 summarizes the type of fast pyrolysis reactors and their parameters.

**Table 2: Fast pyrolysis reactors and parameters**

<b>Reactor type</b>	<b>Status</b>	<b>Biooil [%]</b>	<b>Complexity</b>	<b>Feed size</b>	<b>Inert gas need</b>	<b>Specific size</b>	<b>Scale up</b>
Bubbling fluidized bed	Demo	75	Medium	Small	High	Medium	Easy
Circulating fluidized bed	Commercial	75	High	Medium	High	Large	Easy
Spouted fluidized bed	Pilot	70	Medium	Small	High	Medium	Easy
Entrained flow	Pilot	65	High	Small	High	Large	Easy
Rotating cone	Demo	65	High	Very Small	Low	Small	Hard
Ablative	Lab	75	High	Large	Low	Small	Hard
Vacuum	Demo	60	High	Large	Low	Large	Hard

Source: Perkins et al. 2018

### **2.3. Pyrolysis process, products and biomass as a feedstock**

The pyrolysis process is unique for each material. It depends on temperature, pressure, heating rate, reactor type, but also on the structure and composition of the input material (Vokatý 2011).

In the process of pyrolysis there are several processes that we can generally divide according to temperature intervals. At temperatures up to 150 °C, free and coarse water evaporates and desorption of adsorbed substances, the first vapors of volatile hydrocarbons may be released from the material. At temperatures of 300 to 500 °C, large amounts of water vapor are released and water vapor and carbon dioxide (CO<sub>2</sub>) resulting from the cleavage of hydroxyl and carboxyl groups. The most developed gas is methane (CH<sub>4</sub>) within this temperature range. At temperatures above 500 °C, the



production of tar vapors remains and the solid residue remains in the reactor. At temperatures above 600 °C only gaseous products emerge from the reactor, the rising temperature increases the hydrogen content and the methane content drops (Jílková et al. 2012). The output material is a solid residue and condensable and non-condensable gases. Condensable gases are converted to the desired biooil (Doumer et al. 2015).

The main temperature range in the biomass pyrolysis process is between 200 °C and 400 °C, at higher temperatures, the formation of new products still occurs, but slower and to a lesser extent (Vokatý 2011). An important part of the plant biomass pyrolysis process is the pre-drying of the biomass to a lower moisture content than 10 % (Rogers and Brammer 2012) and crushing biomass into smaller parts (Choi et al. 2012), in order to achieve a rapid heating of the input material and also to limit the amount of water in the output products, especially in the liquid products (Akhtar and Amin 2012). The technologies of biomass pyrolysis have big advantage because they can provide a higher energy output density per mass unit of fuel in comparison with raw solid biomass. Pyrolysis can be one of the ways for effective utilization of biomass especially its residues due to increasing of energy concentration of a material (Zubenko et al. 2018).

### **2.3.1. Pyrolysis products**

During the pyrolysis process three major products are formed: solid residue, pyrolysis gas and pyrolysis oil (Tripathi et al. 2016; Patel et al. 2016). Pyrolysis oil and pyrolysis gas can be used directly as fuel and these products can be refined. The properties and quantities of pyrolysis products depend on the process conditions and the input material (Molek 2015; Monlau et al. 2015).

As the temperature rises, the solid remains noticeably reduced and the gas yields increase. The largest drop occurs between 300 and 400 °C (Vokatý 2011). With longer residence times in the reactor the yield of the liquid product decreases, because of the secondary reactions. The most desirable product of pyrolysis is a liquid product, primarily by being more efficient, cost-effective handling and storage, improved

properties and higher energy density than solid fuels. The disadvantage is the higher water content (Braumakis et al. 2014).

#### 2.3.1.1. Solid residue

The process of pyrolysis creates solid residue or semi-coke. This product is very reactive and tends to self-ignite after the process. The semi-coke can go to coke at temperatures around 900 °C. Coke has almost no volatile substances (Jílková et al. 2012). The quality of solid residue is determined by its physicochemical characteristics like volatile matter, ash and carbon content, fixed carbon and calorific value. Yield of biochar decreases when temperature increasing because organic materials are combusted and higher temperature destroyed cellulose and hemicellulose (Angin 2013; Roy and Dias 2017).

By heating the wood through pyrolysis, i.e. without accessing the oxygen-containing medium, the wood does not start to burn unless the carbon burning temperature is exceeded to produce biochar (Škorpík 2011). Biochar is solid carbonaceous product, the product of slow pyrolysis. Chemically, it is mainly carbon (85 to 98 %), with a small amount of oxygen and hydrogen. Biochar provides more heat in proportion to its volume than wood or other biomass from which it can be formed. During burning the biochar only carbon dioxide is produced (Škorpík 2011).

Biochar is coal made of organic materials, usually from plant biomass (Jouiad et al. 2015). Biochar can be used for power generation, water purification, like a soil amendment or to produce activated carbon, produce pelleted fuel, or to grill food. It is also used in smiths to heat metal parts before processing (Madsen 2015). The most common usage of biochar is for soil application to improve its properties like productivity, soil microbial biomass and nutrients. The quality of biochar for use like soil amendment depends on stability and the nutrient content of biochar. This is affected by pyrolysis condition and type of input material. The big benefit has biochar from agricultural residues because it contains more nitrogen than biochar from energy crops or woody biomass due to use of fertilizer during production. This biochar with higher nitrogen content can reduce consumption of fertilizers. But the amount of biochar that

can be applied into the soil depends on number of conditions like type of soil, pyrolysis properties or climate – temperature and moisture. Biochar has a lot of benefits for crops such as nutrient recycling, water retention and it can improve soil physicochemical and biological properties (Barrow 2012; Jouiad et al. 2015; Roy and Dias 2017; Agegnehu et al. 2017).

There are several technologies for production of biochar, ranging from traditional clay charcoal pits to continuous processes that can be efficiently controlled. The yield of solid residue with traditional technology is low; it can be up to 10 %. Higher yields have brick, concrete and metal kilns, it is between 20 - 25 %. Batch retorts can achieve a yield of 30 % and continuous processes can reach 30 - 35 % yields (Duku et al. 2011).

#### 2.3.1.2. Pyrolysis gas

The main components of the pyrolysis gas are methane (CH<sub>4</sub>), carbon dioxide (CO<sub>2</sub>), hydrogen gas (H<sub>2</sub>) and carbon monoxide (CO). Pyrolysis gas is most commonly used to heat pyrolysis reactors because it contains combustible gases. It can also be used to produce energy (Nguyen et al. 2013). Further, the gas may be used to produce solvents such as acetone and methanol (Sharma et al. 2015).

#### 2.3.1.3. Liquid product

The liquid product consists of several components. It is primarily pyrolysis oil, further it can be heavy and light tar, medium oil, and carbonization gasoline or pyrolysis water. Heavy tar contains large amounts of ash and coal dust. Pyrolysis water formed from moisture contained in the input material (Molek 2015).

Pyrolysis oil is a mixture of several hundreds of substances. Alternatively, it is called pyrolysis gasoline or biooil. It is a dark brown liquid with a sharp characteristic odor (Zámotný and Kurc 2011). It is formed by the condensation of retort gases (Šejvl 2013) with the help of capacitors. It is a corrosive substance with pH in the range of 2 - 3 (Bridgwater 2012). The biooil density is slightly above 1 000 kg/m<sup>3</sup>, which is higher than gasoline (723 kg/m<sup>3</sup>) and diesel fuel (838 kg/m<sup>3</sup>) (Mohammed et al. 2015). Biooil

has a lower heating value (14 - 20 MJ/kg) than gasoline and high moisture content between 15 and 35 %. This is due to the moisture content of the input material and the conditions of the fast pyrolysis process. Biooil contain 15 - 30 % of lignin fragments (insoluble pyrolytic lignin), 10 - 20 % of aldehydes, 10 - 15 % of carboxylic acids, 5 - 10 % of carbohydrates, 2 - 5 % of phenols and other compounds (Kim et al. 2016; Yajun et al. 2018; Perkins et al. 2018).

Fast pyrolysis can produce biooil ranging from 65 % to 80 % from dry biomass and maximum amount of biooil is produce at around 500 °C. The highest yields of biooil are from woody biomass like poplar, forest residues or sawdust because it contains cellulose and hemicellulose. Biooil yield can be maximized by optimized pyrolysis temperature and particle size of input material. The quality and quantity of biooil can improve co-pyrolysis of different feedstocks (Xiu and Shahbazi 2012; Roy and Dias 2017).

This product has a many advantages like it can be combusted in industrial boilers or furnaces or can be upgraded into ethanol and biodiesel. After upgrade it can be used for vehicle technologies to replace fossil fuels. Also it can be used to generate electricity in cogeneration units or can be used in the chemical industry. A wide range of chemicals such as resins, fertilizers and others can be extracted from biooils (Kanaujia et al. 2014; Lehto et al. 2014; Patel et al. 2016). It is a stable liquid biofuel that is more easily stored and transported than biomass (BTG 2016). Biooil can be refined to fuel through two major conventional refinery hydrotreating and catalytic cracking processes (Shemfe et al. 2015).

Biooil is a desired product of pyrolysis; it is versatile and therefore has great potential due to a wide range of uses (Braumakis et al. 2014). The disadvantage of biooil is its high acidity, low thermal stability and calorific value, high viscosity, higher solids and ash content, which negatively affect the efficiency of combustion processes (Braumakis et al. 2014). The composition of pyrolysis oil differs significantly from oil-based fuels, because unlike fossil fuels, biomass contains large amounts of oxygen (Zámostný and Kurc 2011). The great potential is biooil obtained from seaweed because

it has a low content of oxygenated compounds and a relatively high calorific value up to 41 MJ/kg (Chiodo et al. 2016).

### **2.3.2. Pyrolysis feedstock**

The process of pyrolysis can process various carbon-based materials. Biomass is promising sustainable (alternative) energy source due to its availability and diversity. This is the reason why biomass is most often processed. Other materials may include tires or different types of waste like plastic waste, communal waste, municipal sludge and various hazardous wastes. Pyrolysis is one of the few biofuel technologies that can handle a whole range of biomass materials; it is an attractive option to extend the use of less desirable biomass (Prokeš 2011; Roy and Dias 2017; Uddin et al. 2018).

#### **2.3.2.1. Biomass**

In general, biomass can be defined like all biodegradable organic material and it can be derived from animals, plants, or microorganisms. The basic kinds of biomass are plants, bacteria, fungi and cyanobacteria that are capable of using solar energy (using chlorophyll) and inorganic substances such as carbon dioxide (CO<sub>2</sub>) to form proteins and carbohydrates (Weger 2009) and therefore it is a renewable energy source. For energy purposes, plant biomass is preferred, with wood being the most widely used (Zámotný and Kurc 2011). Biomass is a CO<sub>2</sub> neutral energy source. In combustion, it produces smaller amounts of greenhouse gases compared to fossil fuels (Chen et al. 2015).

Biomass has many forms, many of which are not suitable for combustion because of the high content of elements or substances that degrade the quality of combustion or generate dangerous emissions during combustion. These forms of biomass may be further processed in a manner other than combustion, for example by anaerobic fermentation for the production of biogas or by pyrolysis (Weger 2009).

Biomass is promising alternative to fossil fuels because it can produce heat, electricity, fuels or chemicals. The use of biomass as a renewable energy source has many advantages, not only for the environment, but the use of biomass converting

technology creates new jobs in the field of innovative development of agricultural waste. Conversion of biomass brings other benefits such as reducing the volume of biomass and make biomass more compacted which facilitates its transport and storage and preserves it from degradation (Van de Velden et al. 2010; Al Arni 2018). Biomass has high transport and storage costs and a lower energy density than fossil fuels (Badger and Fransham 2006).

Biomass can be classified into four categories or a combination of these, according to McKendry (2002):

- herbaceous plants and grasses,
- woody plants,
- aquatic plants
- manure.

#### Plant biomass

Plant biomass consists of organic matter, water and low ash content. Ashes are minerals from the soil (Škorpík 2011). Plant biomass is obtained for this purpose either by growing energy plants or from agricultural, food or forestry residues. Energy demands include low cost, easy harvest and high yield. Interestingly, the dry biomass of different crops has nearly the same calorific value, ranging from 17.5 to 19.5 MJ/kg (Weger 2009).

Weger (2009) divided plant biomass suitable for energy purposes into several groups:

- residual biomass from agriculture,
- residual biomass from forestry,
- biomass of energy crops.

Furthermore, Weger (2009) divides energy crops into:

- lignocellulosic crops,
- oil crops,
- starch-sugar crops.

Lignocellulosic biomass, or non-food, has great potential as it is worldwide. Above all, they are remnants of wood production, agro-waste, energy grasses, aquatic plants, algae and others. These materials have low sulfur, nitrogen and ash values, which are relatively environmentally friendly (Mohammed et al. 2015).

Earlier researches were exploring various materials during the pyrolysis process such as study of Joubert et al. (2015) has researched flooded gum (*Eucalyptus grandis*) wood under conditions of fast pyrolysis process in a fluidized bed reactor and a twin screw reactor. Jouiad et al. (2015) compared date palm (*Phoenix dactylifera*) and Rhodes grass (*Chloris gayana*), where the materials were converted to biochar by slow pyrolysis. Study by Henkel et al. (2016) researched Chinese tallow (*Triadica sebifera*) wood in the reactor by fast pyrolysis process. The Pattiya (2011) study compared the yields of biooil from manioc stem and rhizome (*Manihot esculenta*), where the materials were processed by fast pyrolysis in a fluidized bed reactor. The Yorgun and Yildiz (2015) experiment with princess tree (*Paulownia tomentosa*) wood was carried out in a fixed bed reactor using a slow pyrolysis process. Study by Chiodo et al. (2016) researched Neptune grass (*Posidonia oceanica*) during the process of slow pyrolysis. The study of Mohammed et al. (2015) used elephant grass (*Pennisetum purpureum*) in a fixed bed reactor by fast pyrolysis. And, in the study of Roberts and de Nys (2015), green seaweeds were used in the process of slow pyrolysis.

## **2.4. Economics of pyrolysis technologies**

Pyrolysis has a potential because it can produce products with higher energy value due to the thermochemical transformation. The use of pyrolysis products can reduce greenhouse gas (GHG) emissions compared to the use of fossil fuels (Akhtar and Amin 2012; Roy and Dias 2017). The use of biomass as a biofuel has gained attention in recent years through its environmental benefits. However, the expansion of biomass

depends mainly on the cost competitiveness of fuels and chemicals compared to those made from conventional fossil sources (Patel et al., 2016).

The pyrolysis process can be carried out at lower temperatures than for gasification or combustion, this affects energy costs (Demirbas 2004; Patel et al. 2016). The process of pyrolysis is energy intensive, the pre-treatment of the input material before the process, especially for fast pyrolysis. It is important to pre-dried biomass because this affects moisture content in final products. Furthermore, it is also important to crush the input material because faster heating of the material can be achieved (Rogers and Brammer 2012; Akhtar and Amin 2012; Choi et al. 2012).

The profitability of pyrolysis technologies depends on following parameters: the value of final products and whether there are renewable energy or biofuel incentive. The final products can affect costs related to feedstock type (feedstock production, collection, processing and transportation), final products yield and plant capacity (Roy and Diaz 2017). According to Badger and Fransham (2006) pyrolysis products are easier to transport, handle and store than raw input materials. Some studies reported that converting co-products such as biochar to more valuable products, e.g. activated carbon, improves profitability of pyrolysis and profitability can also be achieved by increasing scale of production (Kuppens et al. 2015; López-González et al. 2015).

The commercialization of pyrolysis technologies to produce biofuels and other products depends on the production cost of products and competitiveness with conventional fossil sources (Roy and Dias 2017).



### **3. Aims of the Thesis**

The main objective of the Thesis was to assess the energy properties of waste biomass utilized by pyrolysis process.

The specific objectives were to compare the properties of pyrolysis products (mainly solid biochar as well as pyrolysis oil) with the fuel properties of different input raw materials, and to determine the most suitable feedstocks for the energy applications.

## **4. Materials and methods**

The methodology of the Thesis is divided into two parts: methodology of the literature review and the methodology of the practical research.

### **4.1. Methodology of literature review**

The written literature review consists of three main parts, namely the basis of pyrolysis, pyrolysis technologies/reactors and pyrolysis products and suitable materials. The thesis was written according to the FTA Diploma Thesis Manual.

The following steps were taken while writing the Thesis:

The articles were found in scientific databases by using keywords such as biofuels, pyrolysis products, biooil, biochar, pyrolysis technology, slow pyrolysis, fast pyrolysis, thermochemical process, etc.

Writing of literature review was based on the study and analysis of literary sources, especially scientific articles from Scopus databases, Web of Knowledge, ScienceDirect and mainly from scientific journals such as Applied Energy, Fuel Processing Technology, Renewable and Sustainable Energy Reviews, Fuel, Journal of Analytical and Applied Pyrolysis, Biomass and Bioenergy, Bioresource Technology and others..

### **4.2. Methodology of Practical research**

Practical research was based on research methods and included these following parts:

#### **4.2.1. Materials**

Experimental materials were medicine residue, tea leaves, mushroom dreg (bacteria residue), coffee ground and bamboo chips. Each material was available and tested in three forms: initial material, biochar and pyrolysis oil (show Figure 9). Materials were brought from China through the collaboration with the Centre of

Biochar and Green Agriculture, Nanjing Agricultural University, and these experimental materials represent waste biomass or commonly available biomass in China. Particular parts of the research were done in the Laboratory of biofuels in the Faculty of Tropical AgriSciences (FTA), laboratory in the Faculty of Engineering (FE) and Research Institute of Agricultural Engineering in Prague (RIAE).



**Figure 9: Experimental materials**

Source: Author 2018

### Bamboo chips

Bamboo (*Phyllostachys pubescens*) is one of common biomass species in China with annual production of 7 million tonnes in the world (Chen et al. 2014). Compared to woody biomass, bamboo has advantages of a fast growth, lower ash content and shorter felling period. During bamboo scrimber manufacturing a lot of waste is produced. This waste can be used as fuel for burning, fodder or processed into biofuels (Zhang et al. 2017; Wang et al. 2018).

Some previous researches also examined bamboo: in the study of Guo et al. (2017) the bamboo was processed by hydrothermal carbonization, Wang et al. (2018) described bamboo properties after slow pyrolysis, Zhang et al. (2017) compared bamboo with rice husk after pyrolysis and study of Dong et al. (2018) presented data of bamboo after microwave pyrolysis.

### Coffee ground

Coffee is one of the most consumed agricultural products with over 9 billion kilograms produced worldwide. However, big quantities of coffee waste are produced by food manufacturing facilities (Kelkar et al. 2015).

Coffee ground and coffee silverskin are the main residues from coffee industry (Mussatto et al. 2011). The amount of coffee waste grows proportionally to the coffee consumption; annual global generation is around 6 million tons. This waste can be converted into alternative energy because coffee ground contains high organic compounds like lipids (Kondamudi et al. 2008; Jeguirim et al. 2014).

Study of Fermoso and Mašek (2018) described thermochemical decomposition of coffee ground residues, Kelkar et al. (2015) presented material characteristics after pyrolysis using screw-conveyor reactor, study of Bok et al. (2012) examined biooil from fast pyrolysis of coffee ground and Li et al. (2014) presented energy recovery of spent coffee ground products after pyrolysis.

### Medicine residue

Experimental material - Chinese medicine residue was a mixture of more materials, mainly composed of herbs, shellfish, insect skin, etc.

### Mushroom dreg

Mushrooms are important for degradation of organic substances in ecosystem. They have become an attractive functional food because mushroom are rich in protein, carbohydrates, essential minerals, low energy levels, and contain significant minerals. Some mushroom species are used for disease treatment in the folk medicines of China, India, Japan, and South Korea (Sun et al. 2017). The mushroom consumption is more than 24 kg per capita yearly in China, while countries of Central and Eastern have 3 kg per capita per year (Wang et al. 2017). Production of edible mushroom is continuously increasing in the world and China has becoming the biggest producer worldwide with 8.6 million tonnes (Islam et al. 2016).

Experimental material - mushroom dreg was a residual substrate after mushroom growing. It includes mainly wood chips.

### Tea leaves

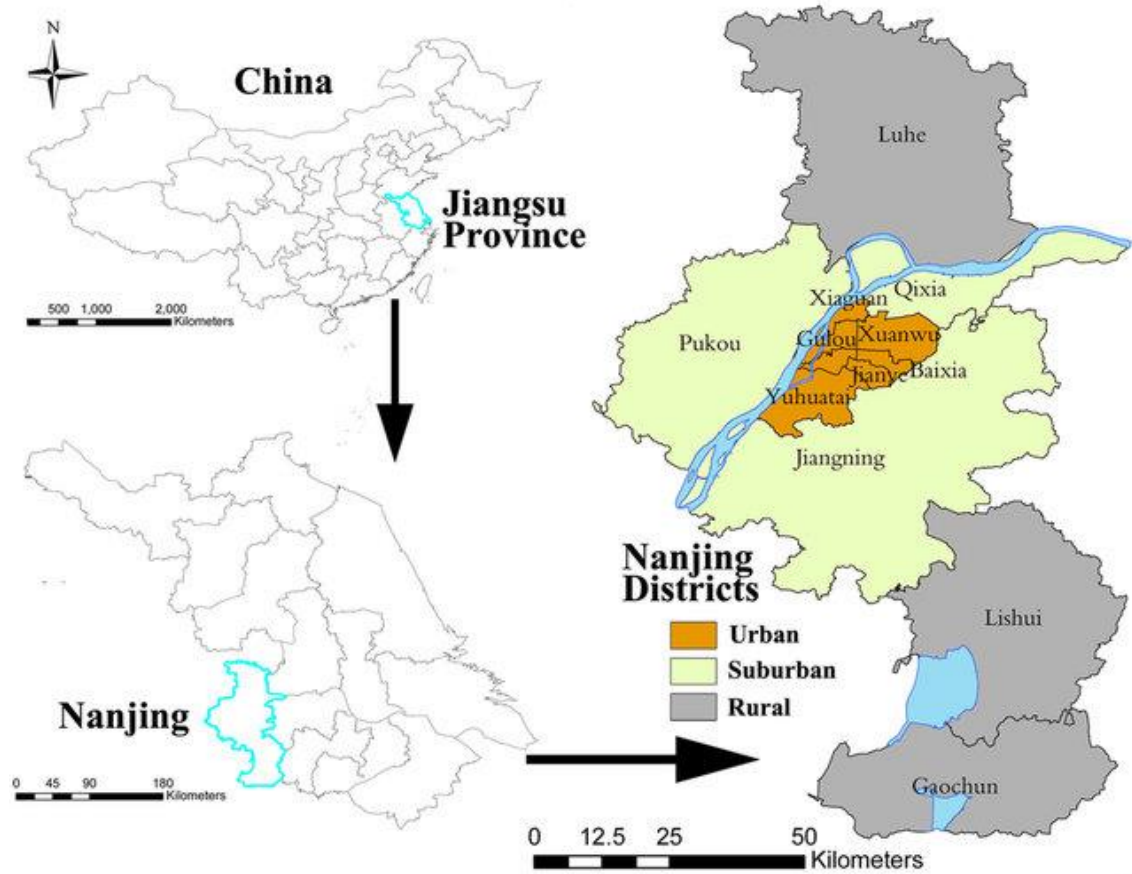
Tea plant (*Camellia sinensis*) is originated from southwest China, it is perennial evergreen bush or small tree. Tea is very popular non-alcoholic beverages in the world. In China, tea can be derived into six categories due to degree of fermentation: green tea (unfermented), white tea (slightly fermented), yellow tea (partly fermented), Oolong tea (semi-fermented), black tea (fully fermented), and dark tea (post-fermented) (Ning et al. 2017).

Tea planting in China represents approximately 55 % of the global planted area (Zhang et al. 2018). China produces 36.28 % of the global tea production and it was 2.44 million tonnes in 2016 (Meegahakumbura et al. 2016; FAO 2018). World tea consumption in 2016 was 5.5 million tonnes and 2.1 million tonnes or 38.6 % of tea consumption demanded China (FAO 2018). During the cultivation, processing, deep processing and consumption of tea, tea waste is produced and it generally includes tea leaves after drinking of tea, unused leaves, seed shells and tea oil cakes (Xie et al. 2015; Liu et al. 2017).

Experimental material - tea leaves represents the waste tea leaves after tea drinking.

#### 4.2.2. Pyrolysis process of the materials

The materials were processed by pyrolysis in China in Luhe district – Nanjing (Figure 10).



**Figure 10: Maps of Luhe district - Nanjing in China**

Source: Chen et al. 2015

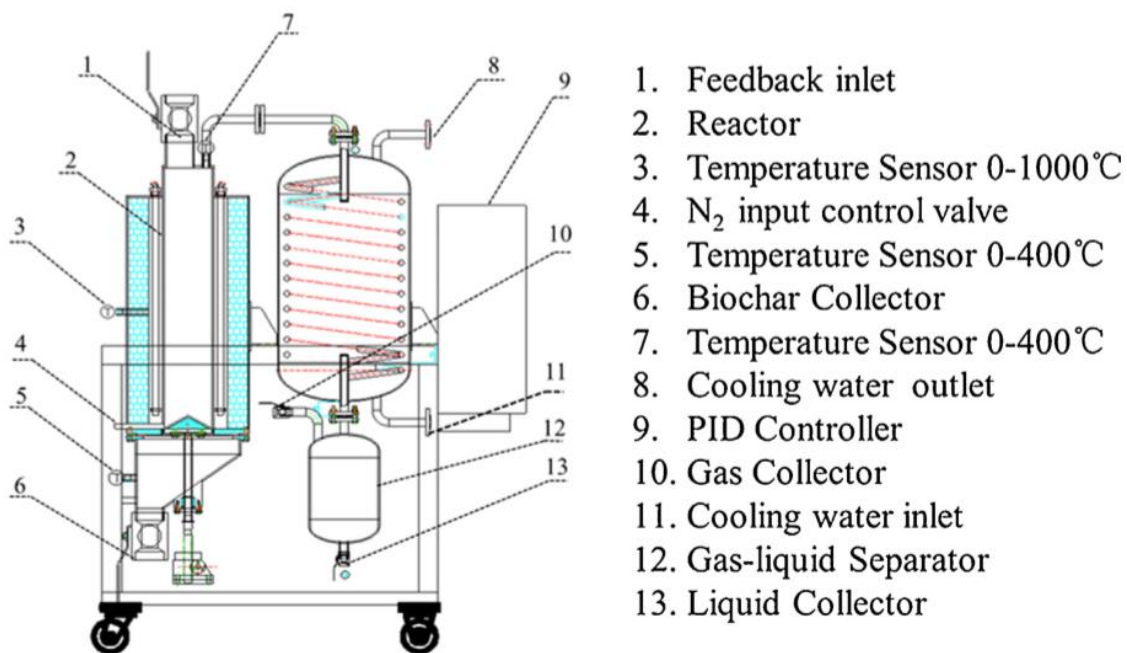
The pyrolysis process was performed by a bench scale pyrolyser (SSBP-5000 A, Huadian Environmental Protection Machinery Co Ltd, Huai-an, China). The experimental materials were pyrolysed at temperature 450 °C, the heating time was 1.5 hours and the cooling time was about 4 hours.

Before heating process the compressed nitrogen (N<sub>2</sub>) was fed into the reactor to remove oxygen (O<sub>2</sub>). The pyrolyser is shown on the Figure 11 and diagram of pyrolyser is illustrated on the Figure 12.



**Figure 11: Bench scale pyrolyser SSBP-5000 A**

Source: Ivanova 2017



**Figure 12: Diagram of bench scale pyrolyser SSBP-5000 A**

Source: Bian et al. 2016



### Preparation of the materials' samples

Firstly, raw material and biochar were crushed to the particle size lower than one mm. The materials were ground by Grinding knife mill Retsch Grindomix GM 100 in Laboratory of biofuels, FTA. The Grinding knife mill is shown on the Figure 13. The apparatus provided a fully homogenized analytical sample according to BS EN 14780 (2011): Solid biofuels - Sample preparation.



**Figure 13: Grinding knife mill Retsch Grindomix GM 100**

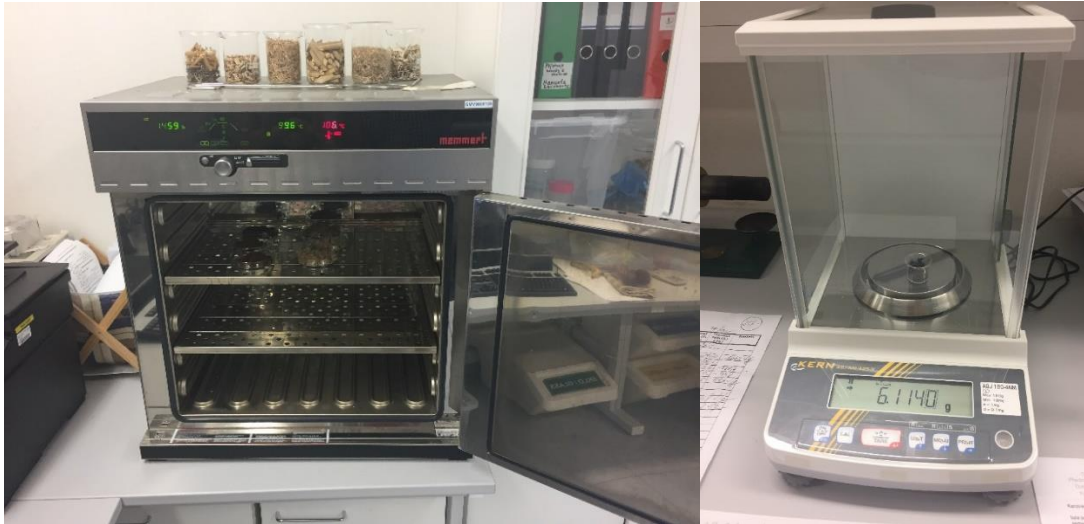
Source: Author 2018

### **4.2.3. Determination of biomass moisture content**

The moisture content of materials was measured according to the BS EN 14774-3 (2010) standards by using Memmert drying oven (model UFE 500) at the FTA laboratory at CULS. The digital laboratory balance Kern (model EW 3000-2M) with readout 0.1 mg was use for all weightings.

The oven is shown on left side and the balance on right side of the Figure 14.





**Figure 14: Memmert drying oven model UFE 500 and digital laboratory balance Kern model EW 3000-2M**

Source: Author 2018

The drying oven was heated up to 105 °C and empty dishes were put inside. When the temperature in the oven was constant, dishes were removed out and cooled to the room temperature in the desiccator. The empty dishes were weighed. The materials were put into dishes, weighed and were dried out in the oven at constant temperature 105 ± 2 °C until the weight was constant in mass.

After this process dishes with samples were removed out from the oven, cooled in a desiccator until they reached room temperature (about 15 minutes) and weighed again. The following equation was used for calculation of the moisture content of samples:

$$MC = \frac{(m_2 - m_3)}{(m_2 - m_1)} * 100 [\%]$$

where:

MC - moisture content [%]

$m_1$  - mass of empty dish [g]

$m_2$  - mass of the dish plus sample before drying [g]

$m_3$  - mass of the dish plus sample after drying [g]

#### 4.2.4. Determination of calorific value

Calorific value of samples was determined according to the standard BS EN 14918 (2009): Solid biofuels - Determination of calorific value at the laboratories of FTA and EF, CULS. The calorimeter model IKA C6000 (Figure 15) was used for the measurement of gross calorific value of liquid samples and Calorimeter LAGET model MS - 10 A (Figure 16) was used for raw materials and biochars.



**Figure 15: Calorimetr LECO AC600**



**Figure 16: Calorimetr LAGET model MS – 10 A**

Source: Author 2018

The measurements were done in a stainless steel high pressure bomb. Dried samples had weight approximately 1 g and they were placed in the high pressure bomb. The weights of samples had to be enrolled in the calorimeter. The samples were burned in the presence of oxygen in a bomb placed in the calorimeter. After complete burning of samples calorimeter model IKA C6000 automatically calculated the gross calorific value and showed on the display. Calorimeter LAGET model MS-10A showed the temperature jump on the display and the gross calorific value was calculated according to the following equation:

$$Q_{gcv} = \frac{dT_k \times T_k}{m} - Q_w - Q_p \text{ [J/g]}$$

where:

- $Q_{gcv}$  - gross calorific value [J/g]
- $dTK$  - temperature jump [°C]
- $Tk$  - constanta (9,051)
- $m$  - weight of the paper and sample [g]
- $Q_w$  - calorific capacity of wire [1 462.82 J/g]
- $Q_p$  - calorific capacity of paper [50 J/g]

Net calorific value was calculated by following formula according to standard EN 14918 (2009) Solid biofuels - Determination of calorific value:

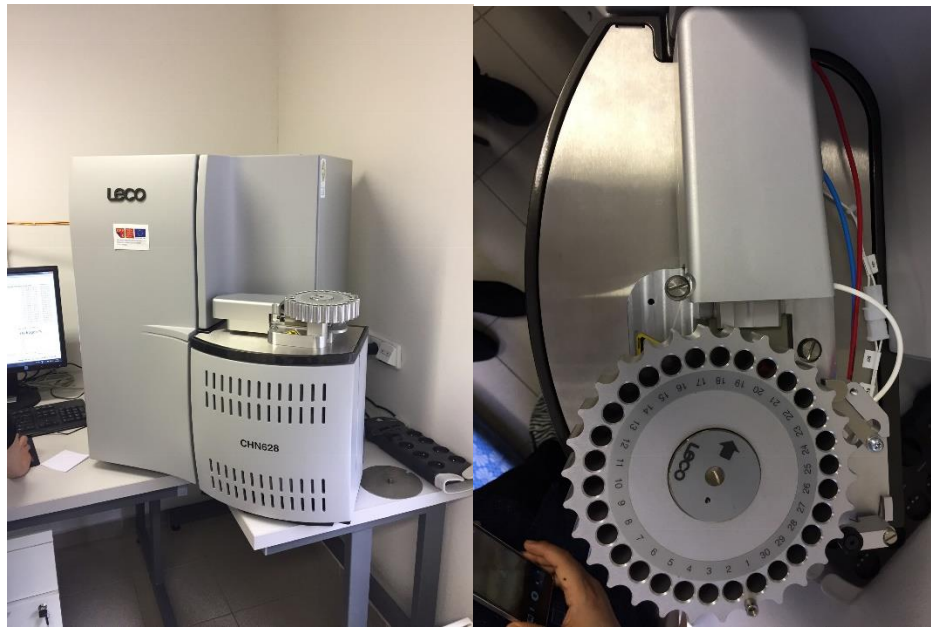
$$Q_{ncv} = Q_{gcv} - 24.42 \times (MC + 8.94 \times H) \text{ [J/g]}$$

where:

- $Q_{ncv}$  - net calorific value [J/g]
- $Q_{gcv}$  - gross calorific value [J/g]
- 24.42 - coefficient of water evaporation from the sample at 25 °C
- MC - moisture content of the sample [%]
- 8.94 - coefficient for conversion of hydrogen to water
- H - hydrogen content of the sample [%]

#### **4.2.5. Determination of content of carbon, hydrogen and nitrogen**

Determination of carbon (C), hydrogen (H) and nitrogen (N) contents of samples were determined according to standard BS EN 15104 (2011): Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen - Instrumental method at RIAE. Determination was carried out by automatic device LECO model CHN 628 series Elemental Determinator (Figure 17).



**Figure 17: Elemental determinator LECO model CHN 628 series**

Source: Author 2018

The weight of sample of dried material was as accurate as possible to 0.1 g and it was put in aluminium foils and then placed into the autoloader of the device. The samples were completely burned at temperatures up to 1 050 °C with a pure oxygen. Elemental determinator automatically calculated the results of content of carbon, hydrogen and nitrogen of samples and showed them in the computer.

#### **4.2.6. Determination of ash content**

Ash content of experimental materials was determined according to the standard BS EN 14775 (2010): Solid biofuels - Determination of ash content at FTA at CULS. The samples were burned in a Muffle furnace LAC and it is shown in the Figure 18. For

all weightings a digital laboratory balance Kern model EW 3000-2M with readout 0.1 mg was used. The ash content was calculated according to the following equation:

$$A_d = \frac{m_3 - m_1}{m_2 - m_1} \times 100 [\%]$$

where:

$A_d$  - ash content d.b. [%]

$m_1$  - mass of empty ceramic dish [g]

$m_2$  - mass of ceramic dish plus sample [g]

$m_3$  - mass of ceramic dish plus ash [g]



**Figure 18: Muffle furnace LAC**

Source: Author 2018

First, the ceramic dishes were heated up to 550 °C for at least 60 minutes and dishes were removed out of the furnace and cooled down. The ceramic dishes were place to the desiccator without desiccant to cool down to the room temperature. The cold ceramic dishes were weighed and filled with 1 g of dried material and weight again. The dishes with samples were placed into the cold furnace. The temperature was increased up to 250 °C during 30 minutes and it was kept for 60 minutes. After this the

temperature raised up again to 550 °C for 30 minutes and kept at this level of temperature for 120 minutes to achieve complete combustion (Figure 19).



**Figure 19: Samples after combustion - ash content**

Source: Author 2018

#### **4.2.7. Data processing**

The results from the experiments were processed via MS Excel. All measurements were determined triple for each material with respect to repeatability precision and summarized like arithmetic means from the measured values with standard deviation in order to quantify the range of variability of a set of data values. The obtained data were evaluated according to EN and ISO standards and compared to the standards' requirements/limits for biofuels.

## 5. Results and discussion

This chapter provides findings from the practical research according to objectives of this Thesis and compares it with the relevant findings of other authors and standards. The following tables show value of moisture content, gross calorific value and net calorific value, content of minor elements like carbon, hydrogen and nitrogen and ash content of experimental materials in three forms - raw (original material), biochar and liquid. The results were noted as arithmetic means from the measured values with standard deviation. All detailed measurements are enclosed in the Annex.

### 5.1. Moisture content of the samples

The moisture content of material was determined according to standard BS EN 14774-3 (2010). The following Table 3 shows measured moisture content of raw and biochar forms of experimental materials.

**Table 3: Moisture content of the samples**

<b>Materials</b>	<b>Moisture content [%]</b>
bamboo chips RAW	7.34 ± 0.06
bamboo chips BIOCHAR	4.29 ± 0.24
coffee ground RAW	12.17 ± 1.19
coffee ground BIOCHAR	5.35 ± 0.06
medicine residue RAW	58.36 ± 0.25
medicine residue BIOCHAR	4.16 ± 0.08
mushroom dreg RAW	40.47 ± 2.59
mushroom dreg BIOCHAR	24.45 ± 0.35
tea leaves RAW	25.38 ± 0.48
tea leaves BIOCHAR	6.21 ± 0.15

Source: Author 2019

All raw materials had a higher moisture content than biochars. The largest content of moisture had raw medicine residue but after pyrolysis this material had the lowest moisture content, a little over 4 %. The best material is bamboo, due to moisture content. The reason was a lowest content of moisture from raw materials followed by coffee ground. This is benefit because moisture content of solid biofuels should not



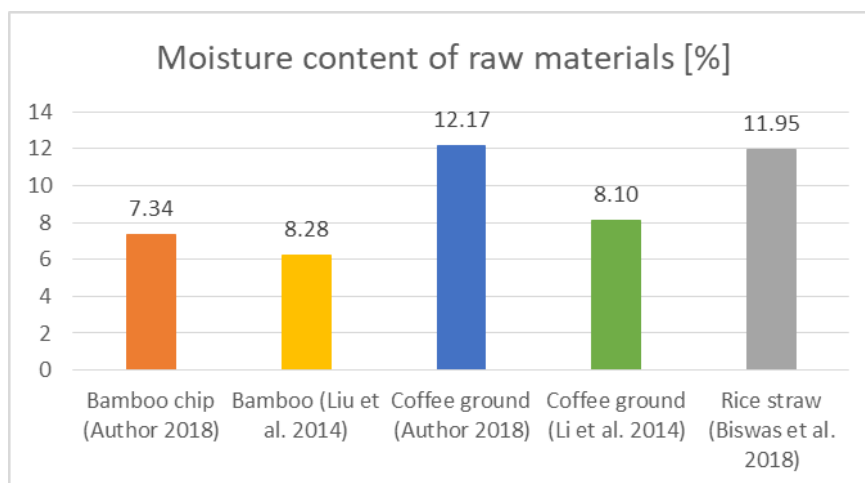
exceeds 15 %, this affect transport, storage and net calorific value of material, higher moisture content leads to lower calorific value (Chen et al. 2009; Straka 2010; Ishii and Furuichi 2014). Higher moisture content also increases risks of biological degradation or increases corrosion because of condensation of water in flue gas (Bach and Skreiberg 2016). Bamboo chips and coffee ground have advantage because they do not need to be pre-dried and process of pre-drying is economically demanding (Xu et al. 2011; Rogers and Brammer 2012). According to BS EN ISO 17225-6 (2014) these materials are also suitable for production the high quality non-wood pellets because it had moisture content less than 15 % (class B) and bamboo chip had moisture content less than 12 % (class A).

In general from the Table 3 is visible that moisture content reduced twice after pyrolysis in majority of samples (bamboo chips, coffee ground and mushroom dreg), almost five times reduction was observed in case of tea leaves material and almost fifteen times for medicine residue.

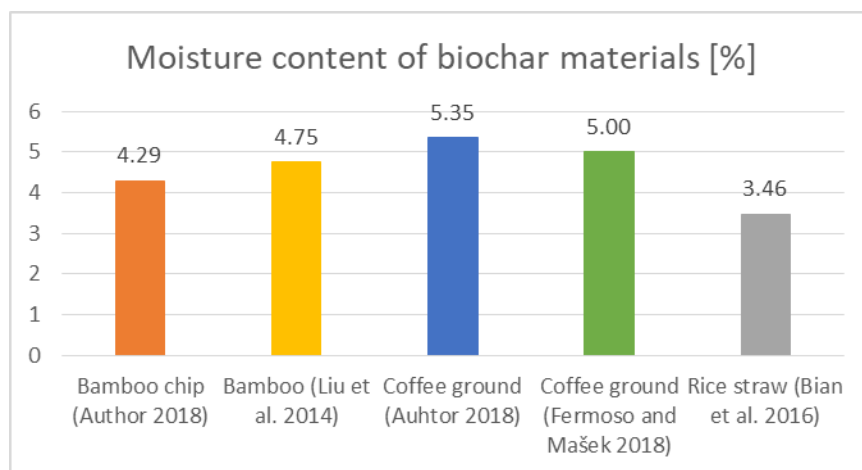
Rice straw is very common material and according to Biswas et al. (2018) it had 11.95 % moisture content. In the comparison with raw experimental materials, only bamboo chips had lower moisture value than rice straw. Rice straw derived biochar had moisture content of 3.46 % (Bian et al. 2016) and for example coal had 2.79 % (Zhu et al. 2017), this values are lower than in case of experimental materials. According to Li et al (2014) coffee ground had 8.1 % of moisture content, this is about 4 % less than experimental samples. Almost the same value of moisture had coffee ground derived biochar (5.0 %) measured by Feroso and Mašek (2018). Zhijia et al. (2012) presented similar value for raw bamboo like experimental material (average value 8.28 %) and Liu et al. (2014) presented similar average value of moisture of bamboo derived biochar 4.75 %. For comparison, woody biomass has average moisture content of 22.68 %, for example oak has 20.2 % and eucalyptus 26.4 % (Kim et al. 2013), in contrast with experimental materials these values are more similar to raw tea leaves.

Graphs 1 and 2 indicate comparison of measured moisture content of bamboo chips and coffee ground with results of other authors for the same materials, and also comparison with the most common material, which is the rice straw.





**Graph 1: Comparison of moisture content of raw materials**



**Graph 2: Comparison of moisture content of biochar materials**

## 5.2. Calorific value of the samples

Calorific values of the solid samples were determined according to standard BS EN 14918 (2009). Calorific value is the heat capacity of a material per unit weight after complete combustion. It is referred to gross calorific value (Patel et al. 2007; Llorente and Garcia 2008). Calorific value is very important parameter that define the usefulness of the material as an energy source (Tang et al. 2016). The gross calorific value (GCV) of solid sample was calculated on a basis of the temperature jump (measured by calorimeter) and GCV was needed for the net calorific value (NCV) calculation with moisture and hydrogen content of the sample. Net calorific value is referred like heat energy available after reducing the loss due to moisture of materials (Wen et al. 2017). The results of average gross and net calorific values of experimental materials as

received (a.r.) and on dry basis (d.b.) for 3 different forms of each material are presented in the Tables 4, 5 and 6.

Raw materials

**Table 4: Gross and net calorific values of the raw samples**

<b>Raw materials</b>	<b>GCV a.r. [J/g]</b>	<b>GCV d.b. [J/g]</b>	<b>NCV a.r. [J/g]</b>	<b>NCV d.b. [J/g]</b>
bamboo chips	16 701.69 ± 1.91	17 848.97 ± 32.97	15 234.39	16 414.64
coffee ground	18 584.10 ± 4.02	19 392.56 ± 24.55	16 900.61	17 684.52
medicine residue	7 582.77 ± 0.27	13 822.92 ± 166.14	4 854.28	12 794.03
mushroom dreg	10 087.36 ± 188.76	15 322.84 ± 47.65	7 928.91	13 188.22
tea leaves	13 464.64 ± 11.66	16 787.63 ± 40.12	11 633.22	14 996.32

Source: Author 2019

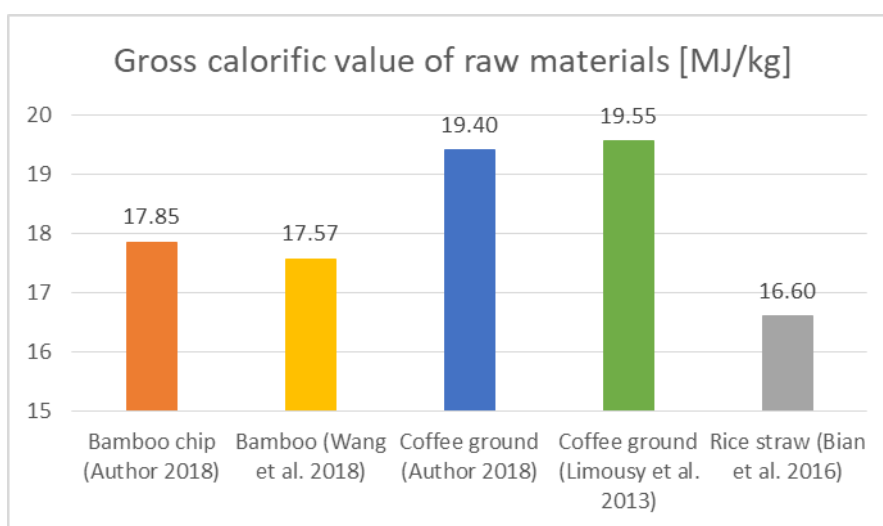
All materials had higher calorific value after drying. The biggest difference between received and dry basis had medicine residue, which can be explained by the highest moisture content of the raw material (Chen et al. 2009; Straka 2010; Ishii and Furuichi 2014) but it had still the lowest calorific value from raw materials. The biggest difference between GCV and NCV had the sample of mushroom dreg, over 2 MJ/kg, followed by tea leaves, almost 1.8 MJ/kg, and coffee ground, 1.7 MJ/kg, the smallest difference had medicine residue.

According to BS EN ISO 17225-6 (2014) for production of non-woody pellets NCV of the materials need to be higher than 14.5 MJ/kg on dry basis. The best results had coffee ground with 17.7 MJ/kg, bamboo chip with 16.4 MJ/kg and tea leaves with 15 MJ/kg. This materials fulfil NCV for production of class A of non-woody pellets.

Rice straw GCV had 16.6 MJ/kg (Bian et al. 2016), this value is almost the same like tea leaves (16.7 MJ/kg) and higher value had bamboo chip (17.8 MJ/kg) and coffee ground (19.4 MJ/kg). Wang et al. (2018), Guo et al. (2017) and Tippayawong et al. (2010) presented almost the same value of bamboo (GCV ~ 17.57 MJ/kg). According to Limousy et al. (2013) gross calorific value of coffee ground is 19.55 MJ/kg and net calorific value is 17.52 MJ/kg, these are the same values as the experimental material. Average calorific value of woody biomass is 17.85 MJ/kg, for example eucalyptus has

16.5 MJ/kg, this is almost the same value like bamboo and oak has 17.8 MJ/kg, this is similar value like coffee ground (Kim et al. 2013).

Graph 3 indicates comparison of measured calorific value of bamboo chips and coffee ground with results of other authors for the same materials, and including the comparison with the rice straw.



**Graph 3: Comparison of gross calorific values of raw materials**

Biochar materials

**Table 5: Gross and net calorific values of biochar samples**

Biochar materials	GCV a.r. [J/g]	GCV d.b. [J/g]	NCV a.r. [J/g]	NCV d.b. [J/g]
bamboo chips	27 110.86 ± 55.70	28 085.78 ± 2.70	26 303.12	27 280.75
coffee ground	21 558.55 ± 39.80	22 378.00 ± 57.51	20 519.71	21 911.10
medicine residue	15 186.35 ± 5.35	15 537.57 ± 2.51	14 530.25	14 990.76
mushroom dreg	13 255.73 ± 89.26	16 836.91 ± 41.12	12 139.07	15 679.13
tea leaves	17 916.38 ± 62.03	18 965.40 ± 26.24	17 107.61	18 130.38

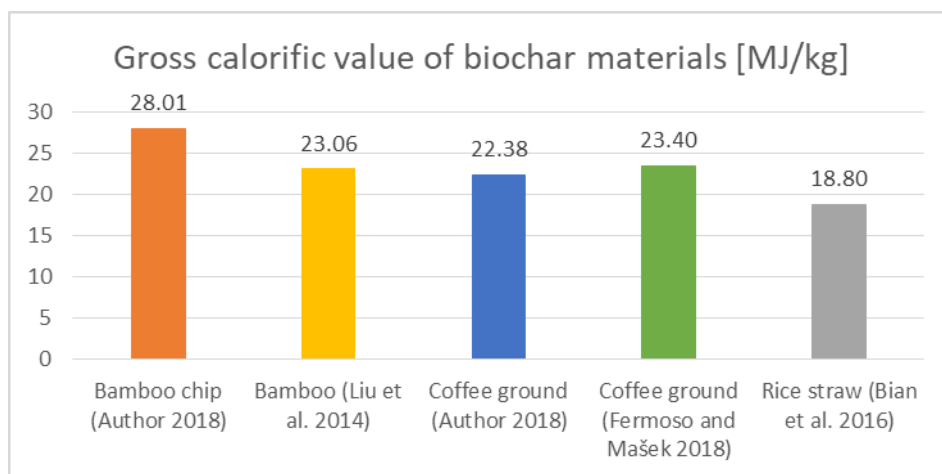
Source: Author 2019

All biochar samples had significantly higher calorific value than raw materials. The biggest value had the sample bamboo chips followed by coffee ground. Mushroom dreg had the lowest value from materials before drying; this sample also had the biggest difference between the calorific value as received and on dry basis due to the high moisture content (Chen et al. 2009; Straka 2010; Ishii and Furuichi 2014). Medicine residue had the lowest value from the tested materials on dry basis.

In general from Tables 4 and 5 is visible that NCV on d.b. grow up over 2 MJ/kg after pyrolysis in two samples (medicine residue, mushroom dreg), over 3 MJ/kg in one sample (teal leaves), over 4 MJ/kg in coffee ground sample and almost over 11 MJ/kg in case of bamboo chips.

GCV of rice straw derived biochar is 18.8 MJ/kg (Bian et al. 2016), this value is similar to tea leaves (18.97 MJ/kg). Fermoso and Mašek (2018) presented similar value of gross calorific value of coffee ground derived biochar (23.4 MJ/kg). According to Liu et al. (2014) bamboo biochar had average GCV 23.06 MJ/kg. It is lower value because it was processed under lower temperature than in this experiment. For comparison, net calorific value of coal is 25 MJ/kg (Nussbaumer 2003), only bamboo chips derived biochar had higher value over than 2 MJ/kg. Calorific value of woody biomass derived biochar is at average 31.28 MJ/kg, for example oak has 30.2 MJ/kg and eucalyptus 32.2 MJ/kg (Kim et al. 2013), and this value are much higher than the values of experimental materials.

Graph 4 shows measured values in comparison with results of other authors.



**Graph 4: Comparison of gross calorific values of biochar materials**

## Liquid materials

**Table 6: Gross calorific values of liquid samples**

<b>Liquid materials</b>	<b>GCV a.r. [J/g]</b>
bamboo chips	4 804.45 ± 35.11
coffee ground	1 947.02 ± 37.01
medicine residue	1 096.06 ± 56.52
mushroom dreg	1 086.87 ± 72.46
tea leaves	1 118.83 ± 80.46

Source: Author 2019

The highest calorific value had pyrolysis oil produced from bamboo chips followed by coffee ground. Bamboo chips showed over 2 times higher result as compared with coffee ground and 4 times more than other samples. The lowest value had mushroom dreg. The majority of the samples demonstrated similar values, over 1 MJ/kg (mushroom dreg, medicine residue and tea leaves). The Table 6 shows that the measured gross calorific values are very low, and more probably it is because of high contain water in the liquid samples. Tested liquid samples were pure pyrolysis oil directly obtained from pyrolyser without any modification, thus they need to be modified (dried or upgraded) for comparison.

Study of Li et al. (2014) presented result of coffee ground biooil 17.23 MJ/kg after modification. Similar values presented Park et al. (2019) for biooil from giant Miscanthus 17.0 MJ/kg and Kim et al. (2013) for biooil from woody biomass the average gross calorific value about 17.43 MJ/kg. Liquid fossil fuel has calorific value about 42 MJ/kg (Miao and Wu 2004; Azizi et al. 2018), biooil typical has lower value due to the high oxygen content (Perkins et al. 2018).

### **5.3. Carbon, hydrogen and nitrogen content of the materials**

Carbon, hydrogen and nitrogen content of the solid samples were determined according to standard BS EN 15104 (2011). The results are presented in Tables 7, 8 and 9 for each form of experimental materials. The carbon content of biochar materials increases with increasing temperature of the pyrolysis temperature (Biswas et al. 2018), with increasing carbon content increase also calorific value (Fernández et al. 2012). Contents of carbon and nitrogen are important in terms of emissions which are released

during combustion, especially nitrogen has direct impact on formation of nitrogen oxides (NO<sub>x</sub>) (Ivanova et al. 2018). According to standard BS EN ISO 17225-6 (2014) nitrogen content should not exceed the 2 % for class B and 1.5 % for class A solid biofuels.

### Raw materials

**Table 7: CHN content of the raw materials**

<b>Materials</b>	<b>Carbon [%]</b>	<b>Nitrogen [%]</b>	<b>Hydrogen [%]</b>
Bamboo chip	49.60 ± 0.04	0.33 ± 0.004	5.90 ± 0.05
Coffee ground	51.54 ± 0.23	3.01 ± 0.01	6.35 ± 0.03
Medicine residue	46.46 ± 0.05	2.20 ± 0.03	5.97 ± 0.01
Mushroom dreg	45.60 ± 0.18	1.07 ± 0.02	5.36 ± 0.03
Tea leaves	47.39 ± 0.17	3.52 ± 0.03	5.55 ± 0.03

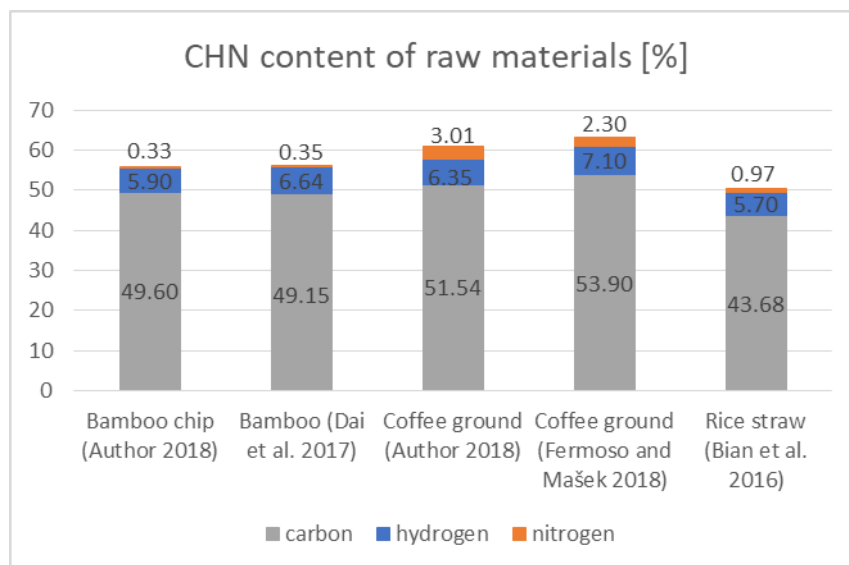
Source: Author 2019

The highest carbon content had coffee ground followed by bamboo chips. The lowest value had mushroom dreg. Coffee ground and tea leaves had higher nitrogen content due to high protein and caffeine content – over 3 % (Mussatto et al. 2011), lowest value had mushroom dreg. In majority of the samples had hydrogen content in range 5 - 6 %, just coffee ground had over 6 %.

According to the standard for production pellets of class A are suitable samples of bamboo chips and mushroom dreg due to lowest nitrogen content.

CHN content of rice straw is 43.68 % of carbon, 0.97 % of nitrogen and 5.7 % of hydrogen (Bian et al. 2016), carbon content is lower, nitrogen and hydrogen contents are similar to experimental materials. Feroso and Mašek (2018) and Li et al. (2014) presented similar values for coffee ground (53.9 % of carbon, 7.1 % of hydrogen and 2.3 % of nitrogen content). Dai et al. (2017) presented similar values for bamboo chips (49.15 % of carbon, 0.35 % of nitrogen and 6.64 % of hydrogen content). For comparison, woody biomass has average 46.93 % of carbon, 6.00 % of hydrogen and <0.2 % of nitrogen (Kim et al. 2013), experimental materials had similar values.

Graph 5 shows measured values with results of other authors.



**Graph 5: Comparison of CHN content of raw materials**

### Biochar materials

**Table 8: CHN content of the biochar materials**

Materials	Carbon [%]	Nitrogen [%]	Hydrogen [%]
Bamboo chips	77.62 ± 2.87	0.66 ± 0.11	3.22 ± 0.03
Coffee ground	62.21 ± 0.76	3.23 ± 0.05	4.16 ± 0.04
Medicine residue	44.16 ± 0.20	2.18 ± 0.01	2.54 ± 0.01
Mushroom dreg	49.98 ± 0.17	1.44 ± 0.002	2.38 ± 0.03
Tea leaves	54.28 ± 0.20	2.96 ± 0.28	3.01 ± 0.02

Source: Author 2019

The highest value of carbon had biochar produced from bamboo chips followed by coffee ground and tea leaves. The lowest value had medicine residue. The highest nitrogen content had biochar from coffee ground followed by tea leaves, and the lowest value had bamboo chips. The highest value of hydrogen had biochar from coffee ground followed by bamboo chips, and the lowest value had mushroom dreg.

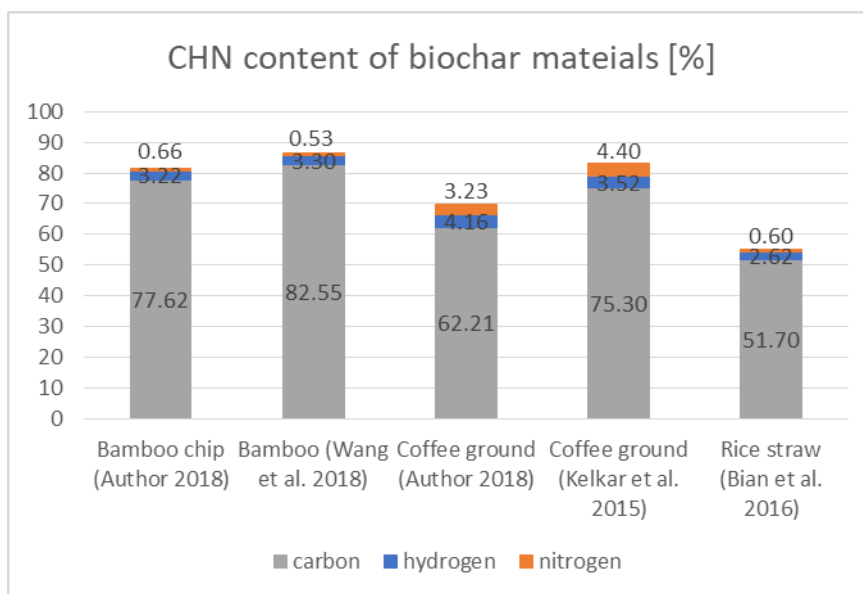
From Tables 7 and 8 is visible that carbon content increase after carbonization by pyrolysis almost in all samples except medicine residue. Carbon content of medicine residue decrease over 2.3 %. Carbon content increase in case of bamboo chips by 28.00 %, coffee ground (10.67 %), tea leaves (6.89 %) and mushroom dreg (4.38 %). Nitrogen content increase in majority of samples (bamboo chips, coffee ground, mushroom dreg), but just slightly in average over 0.31 %. The biggest increase had mushroom dreg

followed by bamboo chips. This samples can be used like soil amendment and it can improve soil conditions due to nitrogen (Agegnehu et al. 2017). Nitrogen decreased in case of medicine residue and tea leaves, the biggest decrease had tea leaves over 0.56 %. After pyrolysis hydrogen content was reduced twice in average in all samples.

CHN content of rice straw derived biochar is 51.7 % of carbon, 0.60 % of nitrogen and 2.62 % of hydrogen (Bian et al. 2016), this carbon content is lower as compared with bamboo chip, coffee ground and tea leaves. Nitrogen content is lower than in case of experimental materials and hydrogen content is lower as compared with bamboo chip, coffee ground and tea leaves. Wang et al. (2018) presented similar results of bamboo derived biochar, just carbon content had a little bit higher value (82.55 % of carbon, 0.53 % of nitrogen and 3.30 % of hydrogen). Due to Kelkar et al. (2015) coffee ground derived biochar had similar results with slightly higher carbon content (75.30 % of carbon, 4.40 % of nitrogen and 3.52 % of hydrogen). In contrast, coal has 59.55 % of carbon, 0.69 % of nitrogen and 3.56 % of hydrogen (Zhu et al. 2017), thus it has similar values like bamboo chips, but lower carbon content over 18 %. Biochar from woody biomass has average content of carbon of 88.1 %, 1.4 % of hydrogen and nitrogen was not presented due to very small amount (Kim et al. 2013). Woody biomass in comparison with bamboo chips has lower content of carbon about 10 % and hydrogen content has almost 2 % higher value.

Graph 6 shows measured values compared with results of other authors.





**Graph 6: Comparison of CHN content of biochar materials**

### Liquid materials

**Table 9: CHN content of the liquid materials**

Materials	Carbon [%]	Nitrogen [%]	Hydrogen [%]
Bamboo chip	12.27 ± 0.05	0.14 ± 0.28	10.24 ± 0.12
Coffee ground	4.41 ± 0.06	0.76 ± 0.40	10.90 ± 0.10
Medicine residue	2.66 ± 0.06	0.20 ± 0.007	10.65 ± 0.06
Mushroom dreg	2.87 ± 0.005	0.26 ± 0.004	10.68 ± 0.10
Tea leaves	2.89 ± 0.07	0.28 ± 0.005	10.86 ± 0.09

Source: Author 2019

The highest carbon content had pyrolysis oil from bamboo chips followed by coffee ground, however, bamboo had almost three times higher value. Majority of experimental materials had similar carbon content, over 2 % (medicine residue, mushroom dreg, tea leaves). The samples had showed very low nitrogen content below 1 %. Hydrogen content had all samples similar, in the range of 10.24 - 10.90 %.

Liquid fossil fuels have 83 - 87 % of carbon, 0.01 - 0.7 % of nitrogen and 10 - 14 % of hydrogen (Miao and Wu 2004; Azizi et al. 2018); experimental materials had similar results in case of nitrogen and hydrogen content but very low carbon content. The last is very likely to be explained by the fact that obtained pyrolysis oils did not pass through any additional treatment.

#### 5.4. Ash content of the samples

Ash content of raw and biochar materials were determined according to standard BS EN 14775 (2010). Ash content is an important property of solid biofuels. This can affect behaviours during combustion and calorific value, higher ash content leads to lower calorific value (Shao et al. 2012; Garcia-Maravera and Pérez-Jiménez 2015). Table 10 shows measured ash content of the samples.

**Table 10: Ash content of the materials (raw and biochar)**

Materials	Ash content [%]
bamboo chip RAW	0.49 ± 0.14
bamboo chip BIOCHAR	2.22 ± 0.10
coffee RAW	4.63 ± 0.03
coffee BIOCHAR	19.82 ± 0.11
medicine residue RAW	13.00 ± 2.04
medicine residue BIOCHAR	42.76 ± 0.08
mushroom RAW	15.24 ± 1.25
mushroom BIOCHAR	37.99 ± 0.39
tea leaves RAW	13.28 ± 0.39
tea leaves BIOCHAR	28.47 ± 0.11

Source: Author 2019

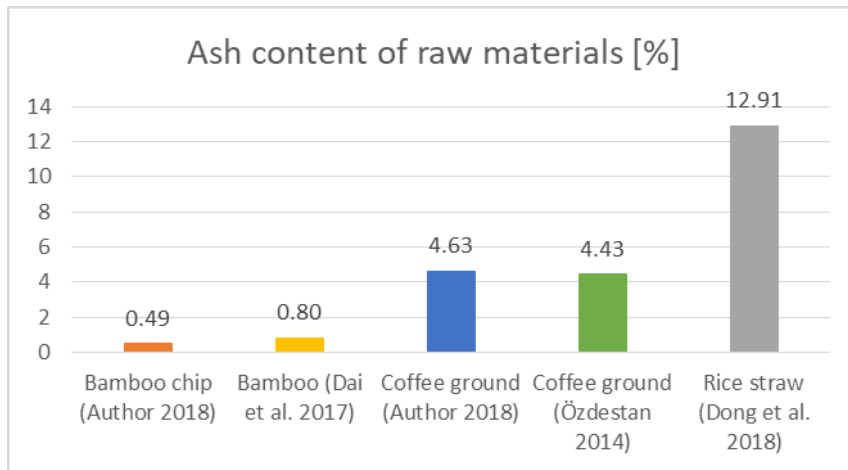
All biochar materials had a higher ash content compared to the raw materials. The lowest ash content had bamboo chips in both forms. The biggest difference between raw and biochar material had medicine residue (almost 30 %) followed by mushroom dreg with nearly 23 % difference. A little bit over 15 % had coffee ground and tea leaves. The lowest difference of ash content had bamboo chip, almost 2 %.

According to BS EN ISO 17225-6 (2014) ash content of non-woody pellets should achieve less than 6 % for class A and less than 10 % for class B pellets. The best material for pellets is bamboo chip due to lowest ash content, followed by raw coffee ground that has lower ash content than coal 4.9 % (Werther et al. 2000).

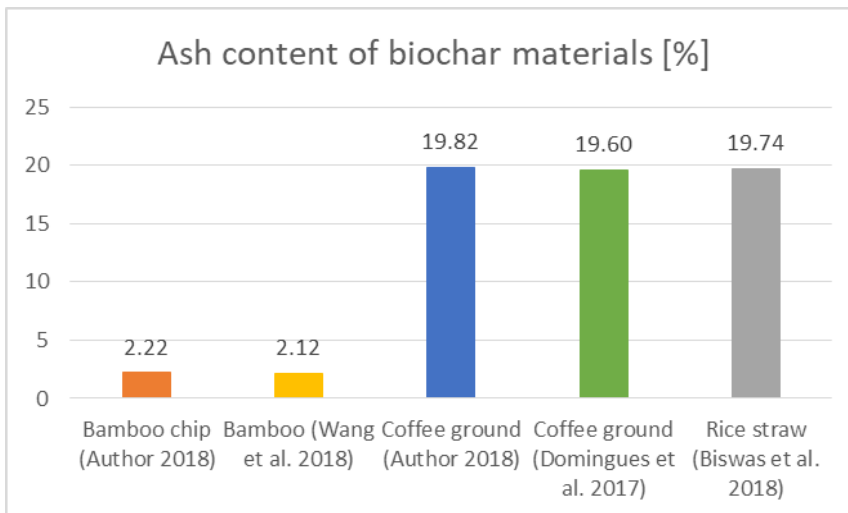
According to Dong et al. (2018) rice straw has 12.91 % of ash content, this value is similar like medicine residue and tea leaves. Rice straw derived biochar has 19.74 % (Biswas et al. 2018), similar ash content had coffee ground biochar. Dai et al. (2017) presented 0.80 % of ash content of raw bamboo that is almost two times higher than in case of experimental material. Wang et al. (2018) presented similar ash content of

bamboo derived biochar 2.12 %. Özdestan (2014) presented similar ash content of raw coffee ground (4.43 %) and Domingues et al. (2017) reported 19.60 % of ash for coffee ground biochar, almost the same value as experimental. For example, average ash content of woody biomass is 0.53 % (Kim et al. 2013), similar value had raw bamboo chips.

Graphs 7 and 8 show measured ash content and compared with results of other authors.



**Graph 7: Comparison of ash content of raw materials**



**Graph 8: Comparison of ash content of biochar materials**

## 6. Conclusion

Pyrolysis is a promising technology with substantial potential for converting a range of biomass into renewable energy that can produce a number of products: biooil, biochar and pyrolysis gas. Economic and profitability of pyrolysis process determine different factors like feedstock type and pre-treatment, yield of final products and plant/reactor capacity.

Yet the most studied Chinese material for pyrolysis process is rice waste (straw, husk) as rice is very typical biomass species and there is abundance of residues. This Thesis compares other relatively common and available waste materials that have been processed under the same conditions of pyrolysis process. Selected experimental materials are not explored much by scientific researches and if they were previously examined, it was performed under different pyrolysis conditions.

According to the experimental results it can be concluded that raw materials such as coffee ground and bamboo chips can be potentially used as a feedstock for solid biofuels (pellets/briquettes) due to their suitable and very good parameters. Both materials had relatively low moisture content, high calorific value (the highest in case of coffee grounds), high carbon content and low ash content (the lowest in case of bamboo chips). Disadvantage is that coffee ground had higher nitrogen content if compared to the standard limits, most probably due to the content of caffeine, and this can lead to the higher NO<sub>x</sub> emission during the fuel's combustion.

From all tested material, the most suitable biomass feedstock for pyrolysis is bamboo chips, as the bamboo chips based biochar had the lowest moisture and ash content, i.e. parameters that affect calorific value, as well as the lowest nitrogen content, the highest content of carbon and the highest calorific value. In general, all experimental materials in solid form got higher calorific values and significantly lower moisture content after the pyrolysis process. These are the important benefits of pyrolyzed biochars in comparison with the input materials. However, it was confirmed that after the thermochemical treatment the ash content of the fuels is increasing.

The properties of pyrolysis liquids obtained just directly from the pyrolyser were very poor and not suitable for energy application, which confirms the necessity of additional post-pyrolysis treatment.

## 7. References

- Agegnehu G, Srivastava A. K, Bird M. I. 2017. The role of biochar and biochar-compost in improving soil quality and crop performance: A review. *Applied Soil Ecology* 119: 156-170.
- Akhtar J, Amin N. S. 2012. A review on operating parameters for optimum liquid oil yield in biomass pyrolysis. *Renewable and Sustainable Energy Reviews* 16 (7): 5101-5109.
- Al Arni S. 2018 *Renewable Energy. An International Journal* 124: 197-201.
- Anex R. P, Aden A, Kazi F. K, Fortman J, Swanson R. M, Wright M. M, Satrio J. A, Brown R. C, Daugaard D. E, Platon A, Kothandaraman G, Hsu D. D, Dutta A. 2010. Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways. *Fuel* 89: 29-35.
- Angin D. 2013. Effect of pyrolysis temperature and heating rate on biochar obtained from pyrolysis of safflower seed press cake. *Bioresource Technology* 128: 593-597.
- Azizi K, Moraveji M. K, Najafabadi H. A. 2018. A review on bio-fuel production from microalgal biomass by using pyrolysis method. *Renewable and Sustainable Energy Reviews* 82: 3046-3059.
- Badger P. C, Fransham P. 2006. Use of mobile fast pyrolysis plants to densify biomass and reduce biomass handling cost-a preliminary assessment. *Biomass Bioenergy* 30: 321-325.
- Bach Q, Skreiberg Ø. 2016. Upgrading biomass fuel via wet torrefaction: a review and comparison with dry torrefaction. *Renewable and Sustainable Energy Reviews* 54: 665-677.
- Barrow C. J. 2012. Biochar: potential for countering land degradation and for improving agriculture. *Applied Geography* 34: 21-28.
- Bian R, Ma B, Zhu X, Wang W, Li L, Joseph S, Liu X, Pan G. 2016. Pyrolysis of crop residues in a mobile bench-scale pyrolyser: Product characterization and environmental performance. *Journal of Analytical and Applied Pyrolysis* 119: 52-59.

- Biswas B, Sing R, Kumar J, Singh R, Gupta P, Krishna B. B, Bhaskar T. 2018. Pyrolysis behavior of rice straw under carbon dioxide for production of bio-oil. *Renewable Energy* 129: 686-694.
- Bok J. P, Choi S. H, Choi Y. S, Park H. Ch, Kim S. J. 2012. Fast pyrolysis of coffee ground: Characteristics of product yields and crude oil quality. *Energy* 47: 17-24.
- Braimakis K, Atsonios K, Panopoulos K. D, Karellas S, Kakaras E. 2014. Economic evaluation of decentralized pyrolysis for the production of bio-oil as an energy carrier for improved logistics towards a large centralized gasification plant. *Renewable and Sustainable Energy Reviews* 35: 57-72.
- Bridgwater A. V. 2012. Review of fast pyrolysis of biomass and product upgrading. *Biomass Bioenergy* 38: 68-94.
- BS EN 14774-3. 2010. Solid biofuels - Determination of moisture content - Oven dry method - Part 3: Moisture in general analysis sample. London. BSI. 10p.
- BS EN 14775. 2010. Solid biofuels - Determination of ash content. London. BSI. 12p.
- BS EN 14780. 2011. Solid biofuels - Sample preparation. BSI Standards Publication: Bonn, Germany: 24p.
- BS EN 14918. 2010. Solid biofuels - Determination of calorific value. BSI Standards Publication: Bonn, Germany: 64p.
- BS EN 15104. 2011. Solid biofuels - Determination of total content of carbon, hydrogen and nitrogen. Instrumental methods. London. BSI. 18p.
- BS EN ISO 17225-1. 2014. Solid biofuels - Fuel specifications and classes. General Requirements - Part 1. BSI Standards Publication: Bonn, Germany: 66p.
- BS EN ISO 17225-6. 2014. Solid biofuels - Fuel specifications and classes - Part 6: Graded non-woody pellets. London. BSI. 18p.
- BTG. 2016. Biomass Technology Group. Available at <http://www.btg.cz/technologie-btg-pro-rychlou-pyrolyzu.html>: Accessed 2016-02-18.
- Carrier M, Hugo T, Gorgens J, Knoetze H. 2011. Comparison of slow and vacuum pyrolysis of sugar cane bagasse. *Journal of Analytical and Applied Pyrolysis* 90: 18-26.

- Dai L, He Ch, Wang Y, Liu Y, Yu Z, Zhou Y, Fan L, Duan D, Ruan R. 2017. Cooperative study on micro wave and convectional hydrothermal pretreatment of bamboo sawdust: Hydrochar properties and its pyrolysis behaviors. *Energy Conversion and Management* 146: 1-7.
- De Conto D, Silvestre W. P, Baldasso C, Godinho M. 2016. Performance of rotary kiln reactor for the elephant grass pyrolysis. *Bioresource Technology* 218: 153-160.
- Demirbas A. 2004. Combustion characteristics of different biomass fuels. *Progress in Energy and Combustion Science* 30: 219-230.
- Demirbas A, Arin G. 2002. An overview of biomass pyrolysis. *Energy Sources* 24 (5): 471-482.
- Domingues R. R, Trugilho P. F, Silva C. A, de Melo I. C, Melo L. C, Magriotis Z. M, Sánchez-Monedero M. A. 2017. Properties of biochar derived from wood and high-nutrient biomasses with the aim of agronomic and environmental benefits. *PLoS ONE* 12 (5): 19p.
- Dong Q, Li H, Niu M, Luo Ch, Zhang J, Qi B, Li X, Zhong W. Microwave pyrolysis of moso bamboo for syngas production and bio-oil upgrading over bamboo-based biochar catalyst. *Biosource Technology* 266: 284-290.
- Dong Q, Zhang S, Ding K, Zhu S, Zhang H, Liu X. 2018. Pyrolysis behavior of raw/torrefied rice straw after different demineralization processes. *Biomass and Bioenergy* 119: 229-236.
- Doumer M. E, Arízaga G. G. C, Agostinho da Silva D, Yamamoto C. I, Novotny E. H, Santos J. M, Oliveira dos Santos L, Wisniewski Jr. A, Bittencourt de Andrade J, Mangrich A. S. 2015. Slow pyrolysis of different Brazilian waste biomasses as sources of soil conditioners and energy, and for environmental protection. *Journal of Analytical and Applied Pyrolysis* 113: 434-443.
- Duku M. H, Gu S, Hagan E. B. 2011. Biochar production potential in Ghana—a review. *Renewable and Sustainable Energy Reviews* 15 (8): 3539-3551.
- FAO. 2018. Available at <http://www.fao.org/3/BU642en/bu642en.pdf>: Accessed 2019-4-25.



- Fermoso J, Mašek O. 2018. Thermochemical decomposition of coffee ground residues by TG-MS: A kinetic study. *Journal of Analytical and Applied Pyrolysis* 130: 358-367.
- Fernández R. G, García C. P, Lavín A. G, Bueno de las Heras J. L. 2012. Study of main combustion characteristics for biomass fuels used in boilers. *Fuel Processing Technology* 103:16-26.
- Garcia-Maraver A, Pérez-Jiménez J. A. 2015. Biomass pelletization: standards and production. Southampton: WIT Press. 194p.
- Guo S, Dong X, Thu C, Han Y, Ma F, Wu T. 2017. Pyrolysis behaviors and thermodynamics properties of hydrochar from bamboo (*Phyllostachys heterocycle cv. Pubescens*) shoot shell. *Bioresource Technology* 233: 92-98.
- Henkel Ch, Muley P. D, Abdollahi K. K, Marculescu C, Boldor D. 2016. Pyrolysis of energy cane bagasse and invasive Chinese tallow tree (*Triadica sebifera L.*) biomass in an inductively heated reactor. *Energy Conversion and Management* 109: 175-183.
- Henrich E, Dahmen N, Weirich F, Reimert R, Kornmayer C. 2016. Fast pyrolysis of lignocellulosics in a twin screw mixer reactor. *Fuel Processing Technology* 143: 151-161.
- Choi S. H, Choi Y. S, Park H. C. 2012. Fast pyrolysis characteristics of lignocellulosic biomass with varying reaction conditions. *Renew Energy* 42: 131-135.
- Chen D, Zhou J, Zhang Q. 2014. Effects of heating rate of slow pyrolysis behavior, kinetic parameters and products properties of moso bamboo. *Bioresource Technology* 169: 313-319.
- Chen J, Fan X, Jianga B, Mu L, Yao P, Yin H, Song X. 2015. Pyrolysis of oil-plant wastes in a TGA and a fixed-bed reactor: Thermochemical behaviors, kinetics, and products characterization. *Bioresource Technology* 192: 592-602.
- Chen K, Huang L, Zhou L, Ma Z, Bi J, Li T. 2015. Spatial analysis of the effect of the 2010 heat wave on stroke mortality in Nanjing, China. *Scientific Reports* 5: 10816.
- Chen L, Xing L, Han L. 2009. Renewable energy from agro-residues in China: Solid biofuels and biomass briquetting technology. *Renewable and Sustainable Energy Reviews* 13: 2689-2695.

- Chiodo V, Zafarana G, Maisano S, Freni S, Urbani F. 2016. Pyrolysis of different biomass: Direct comparison among *Posidonia Oceanica*, Lacustrine Alga and White-Pine. *Fuel* 164: 220-227.
- Ishii K, Furuichi T. 2014. Influence of moisture content, particle size and forming temperature on productivity and quality of rice straw pellets. *Waste Management* 34: 2621-2626.
- Islam T, Yu X, Xu B. 2016. Phenolic profiles, antioxidant capacities and metal chelating ability of edible mushrooms commonly consumed in China. *LWT - Food Science and Technology* 72: 423-431.
- Ivanova T, Hernández A. H. M, Bradna J, Cusimamani E. F, Montoya J. C. G, Espinel D. A. A. 2018. Assessment of Guava (*Psidium Guajava* L.) Wood Biomass for Briquettes' production. *Forests* 9: 613p.
- Jílková L, Ciahotný K, Černý R. 2012. Technologie pro pyrolýzu paliv a odpadů. *Paliva* 4: 74-80.
- Johansson A, Wiiknikka H, Sandström L, Marklund M, Öhrman O. G. W, Narvesjö J. 2016. Characterization of pyrolysis products produced from different Nordic biomass types in a cyclone pilot plant. *Fuel Processing Technology* 146: 9-19.
- Joubert J. E, Carrier M, Dahmen N, Stahl R, Knoetze J. H. 2015. Inherent process variations between fast pyrolysis technologies: A case study on *Eucalyptus grandis*. *Fuel Processing Technology* 131: 389-395.
- Jouiad M, Al-Nofeli N, Khalifa N, Benyettou F, Yousef L. F. 2015. Characteristics of slow pyrolysis biochars produced from rhodes grass and fronds of edible date palm. *Journal of Analytical and Applied Pyrolysis* 111: 183-190.
- Kanaujia P. K, Sharma Y. K, Garg M. O, Tripathi D, Singh R. 2014. Review of analytical strategies in the production and upgrading of bio-oils derived from lignocellulosic biomass. *Journal of Analytical & Applied Pyrolysis* 105: 55-74.
- Kelkar S, Saffron Ch. M, Chai L, Bovee J, Stuecken T. R, Garedew M, Li Z, Kriegel R. M. 2015. Pyrolysis of spent coffee grounds using a screw-conveyor reactor. *Fuel Processing Technology* 137: 170-178.

- Kim K. H, Kim T, Lee S, Choi D, Yeo H, Choi I, Choi J. 2013. Comparison of physicochemical features of biooils and biochar produced from various woody biomasses by fast pyrolysis. *Renewable Energy* 50: 188-195.
- Kim P, Weaver S, Labbé N. 2016. Effect of sweeping gas flow rates on temperature-controlled multistage condensation of pyrolysis vapors in an auger intermediate pyrolysis system. *Journal of Analytical and Applied Pyrolysis* 118: 325-334.
- Kondamusi N, Mohapatra S. K, Mano M. 2008. Spent coffee grounds as a versatile source of green energy. *Journal of Agricultural and Food Chemistry* 56: 11757-11760.
- Kuppens T, Van Dael M, Vanreppelen K, Thewys T, Yperman J, Carleer R, Schreurs, Van Passel S. 2015. Techno-economic assessment of fast pyrolysis for the valorization of short rotation coppice cultivated for phytoextraction. *Journal of Cleaner Production* 88: 336-344.
- Lehto J, Oasmaa A, Solantausta Y, Kytö M, Chiaramonti D. 2014. Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass. *Applied Energy* 116: 178-190.
- Li X, Strezov V, Kan T. 2014. Energy recovery potential analysis of spent coffee grounds pyrolysis products. *Journal of Analytical and Applied Pyrolysis* 110: 79-87.
- Limousy L, Jeguirim M, Dutournié P, Kraiem N, Lajili M, Said R. 2013. Gaseous products and particulate matter emissions of biomass residential boiler fired with spent coffee grounds pellets. *Fuel* 107: 323-329.
- Liu Z, Fei B, Jiang Z, Liu X. 2014. Combustion characteristics of bamboo-biochars. *Bioresource Technology* 167: 94-99.
- Liu Z, Han G. 2015. Production of solid fuel biochar from waste biomass by low temperature pyrolysis. *Fuel* 158: 159-165.
- Liu Z, Li D, Dai H, Huang H. 2017. Enhanced properties of tea residue cellulose hydrogels by addition of graphene oxide. *Journal of Molecular Liquids* 244: 110-116.
- Llorente M. J. F, Garcia J. E. C. 2008. Suitability of thermo-chemical corrections for determining gross calorific value in biomass. *Thermochim Acta* 468: 101-107.
- López-González D, Puig-Gamero M, Ación F. G, García-Cuadra F, Valverde J. L, Sanchez-Silva L. 2015. Energetic, economic and environmental assessment of the

pyrolysis and combustion of microalgae and their oils. *Renewable and Sustainable Energy Reviews* 51: 1752-1770.

Madsen M. 2015. Charcoal. Salem Press Encyclopedia of Science. Available at <http://eds.b.ebscohost.com/infodroje.czu.cz/eds/detail/detail?sid=e488e672-5bdd-4bc2-9ed9-433a0a680fcd%40sessionmgr113&vid=5&hid=120&bdata=Jmxhbmc9Y3Mmc2l0ZT11ZHMtbGl2ZQ%3d%3d#AN=89475545&db=ers>: Accessed 2016-02-18.

Mahmood A.S.N, Brammer J.G, Hornung A, Steele A, Poulston S. 2013. The intermediate pyrolysis and catalytic steam reforming of Brewers spent grain. *Journal of Analytical and Applied Pyrolysis* 103: 328-342.

Marker T. L, Felix L. G, Linck M. B, Roberts M. J. 2012. Integrated hydrolysis and hydroconversion (IH2) for the direct production of gasoline and diesel fuels or blending components from biomass, part 1: Proof of principle testing. *Environmental Progress and Sustainable Energy* 31: 191-199.

McKendry P. 2002. Energy production from biomass (part 1): overview of biomass. *Bioresour Technol* 83: 37-46.

Meegahakumbura M. K, Wambulwa M. C, Thapa K. K. 2016. Indications for Three Independent Domestication Events for the Tea Plant (*Camellia sinensis* (L.) O. Kuntze) and New Insights into the Origin of Tea Germplasm in China and India Revealed by Nuclear Microsatellites. *PLoS ONE* 11 (5): 1-14.

Miao X, Wu Q. 2004. High yield production from fast pyrolysis by metabolic controlling of *Clorella protothecoides*. *Journal of Biotechnology* 110: 85-93.

Mohammed I. Y, Abakr Y. A, Kazi F. K, Yusuf S, Alshareef I, Chin S. A. 2015. Pyrolysis of Napier Grass in a Fixed Bed Reactor: Effect of Operating Conditions on Product Yields and Characteristics. *BioResources* 10 (4): 6457-6478.

Molek T. 2015. Pyrolýza: princip, historie a současnost. *OEnergetice.cz*. Available at <http://oenergetice.cz/technologie/pyrolyza-princip-historie-a-soucasnost/>: Accessed 2015-12-13.

- Monlau F, Kaparaju P, Trably E, Steyer J. P, Carrere H. 2015. Alkaline pretreatment to enhance one-stage CH<sub>4</sub> and two-stage H<sub>2</sub>/CH<sub>4</sub> production from sunflower stalks: Mass, energy and economical balances. *Chemical Engineering Journal* 260: 377-385.
- Mussatto S. I, Machado E. M. S, Martins S, Teixeira J. A. 2011. Production, compostion, and application of coffee and its industrial residues. *Food Bioprocess Technology* 4: 661-672.
- Nguyen T. L, Hermansen J. E, Nielsen R. G. 2013. Environmental assessment of gasification technology for biomass conversion to energy in comparison with other alternatives: the case of wheat straw. *Journal of Cleaner Production* 53: 138-148.
- Ning J, Sun J, Li S, Sheng M, Zhang Z. 2017. Classification of five Chinese tea categories with different fermentation degrees using visible and near-infrared hyperspectral imaging. *International Journal of Food Properties* 20 (52): 1515-1522.
- Nguyen T. L, Hermansen J. E, Nielsen R. G. 2013. Environmental assessment of gasification technology for biomass conversion to energy in comparison with other alternatives: the case of wheat straw. *Journal of Cleaner Production* 53: 138-148.
- Nussbaumer T. 2003. Combustion and Co-Combustion of Biomass: Fundamentals, Technologies, and Primary Measures for Emission Reduction. *Energy Fuels* 17: 1510-1521.
- Özdestandan Ö. 2014. Evaluation of bioactive amine and mineral levels in Turkish coffee. *Food Research International* 61: 167-175.
- Park J. Y, Kim J, Oh Ch, Park J, Kwon E. E. 2019. Production of bio-oil from fast pyrolysis of biomass using a pilot-scale circulating fluidized bed reactor and its characterization. *Journal of Environmental Management* 234: 138-144.
- Park Y. K, Yoo M. L, Lee H. W, Park S. H, Jung S. C, Park S. S. 2012. Effects of operation conditions on pyrolysis characteristics of agricultural residues. *Renewable Energy* 42: 125-130.
- Patel M, Zhang X, Kumar A. 2016. Techno-economic and life cycle assessment on lignocellulosic biomass thermochemical conversion technologies: A review. *Renewable and Sustainable Energy Reviews* 53: 1486-1499.

- Patel S. U, Jeevan K. B, Badhe Y. P, Sharma B. K, Saha S, Biswas S, Chaudhury A, Tambe S. S, Kulkarni B. 2007. Estimation of gross calorific value of coals using artificial neural networks. *Fuel* 86: 334-344.
- Pattiya A. 2011. Bio-oil production via fast pyrolysis of biomass residues from cassava plants in a fluidised-bed reactor. *Bioresource Technology* 102: 1959-1967.
- Perkins G, Bhaskar T, Konarova M. 2018. Process development status of fast pyrolysis technologies for the manufacture of renewable transport fuels from biomass. *Renewable & Sustainable Energy Reviews* 90: 292-315.
- Poyraz Y. 2019. Specially developed methods for fuel characterization. Institute of Energy Process Engineering and Fuel Technology. Available at <https://www.ievb.tu-clausthal.de/en/equipment/specially-developed-methods-for-fuel-characterization/#c342>: Accessed 2019-02-09.
- Prokeš K. 2011. Vakuová pyrolýza a její realizace v ČR. *Biom.* Available at <http://biom.cz/cz/odborne-clanky/vakuova-pyrolyza-a-jeji-realizace-v-cr>: Accessed 2016-03-26.
- Roberts D. A, de Nys R. 2015. The effects of feedstock pre-treatment and pyrolysis temperature on the production of biochar from the green seaweed *Ulva*. *Journal of Environmental Management* 169: 253-260.
- Rogers J. G, Brammer J. G. 2012. Estimation of the production cost of fast pyrolysis bio-oil. *Biomass Bioenergy* 36: 208-217.
- Roy P, Dias G. 2017. Prospects for pyrolysis technologies in the bioenergy sector: A review. *Renewable and Sustainable Energy Reviews* 77: 59-69.
- Sharma A, Shinde Y, Pareek V, Zhang D. 2015. Process modelling of biomass conversion to biofuels with combined heat and power. *Bioresource Technology* 198: 309-315.
- Shemfe M. B, Gu S, Ranganathan P. 2015. Techno-economic performance analysis of biofuel production and miniature electric power generation from biomass fast pyrolysis and bio-oil upgrading. *Fuel* 143: 361-372.
- Shao Y, Wang J, Preto F, Zhu J, Chunbao X. 2012. Ash deposition in biomass combustion or co-firing for power/heat generation. *Energies* 5: 5171-5189.

- Silitonga A. S, Atabani A. E, Mahlia T. M. I, Masjuki, H. H, Badruddin I. A, Mekhilef S. 2011. A review on prospect of *Jatropha curcas* for biodiesel in Indonesia. *Renewable and Sustainable Energy Reviews* 15: 3733-3756.
- Silvestre W. P, Pauletti G. F, Godinho M, Baldasso C. 2018. Fodder radish seed cake pyrolysis for bio-oil production in a rotary kiln reactor. *Chemical Engineering and Processing - Process Intensification* 124: 235-244.
- Straka F. 2010. Alternativní energetické zdroje a měrné emise CO<sub>2</sub>. Available at <http://biom.cz/cz/odborne-clanky/alternativni-energeticke-zdroje-a-merne-emise-co2>: Accessed 2019-03-02.
- Sun J, Zhang J, Wang Y. Multivariate characterization of elements accumulated in *Wolfiporia extensa* mushroom from Yunnan province of China. *Journal of Environmental Science & Health, Part B -- Pesticides, Food Contaminants, & Agricultural Wastes* 52 (3): 206-213.
- Šejvl R. 2013. Energie z odpadů II. *Biom.cz*. Available at <http://biom.cz/czp/odborne-clanky/energie-z-odpadu-ii>: Accessed 2015-11-21.
- Škorpík J. 2011. Transformační technologie. Available at <http://www.transformacni-technologie.cz/biomasa-jako-zdroj-energie.html>: Accessed 2016-03-19.
- Tang J. P, Lama H. L, Azizb M. K. A, Morad N. A. 2016. Enhanced Biomass Characteristics Index in Palm Biomass Calorific Value Estimation. *Applied Thermal Engineering* 105: 941-949.
- Tippayawong N, Saengow N, Chaiya E, Srisang N. 2010. Production of charcoal from woods and bamboo in a small natural draft carbonizer. *International Journal of Energy & Environment* 5: 911-917.
- Tripathi M, Sahu J. N, Ganesana P. 2016. Effect of process parameters on production of biochar from biomass waste through pyrolysis: A review. *Renewable and Sustainable Energy Reviews* 55: 467-481.
- Uddin M. N, Techato K, Taweekun J, Rahman M. M, Rasul M. G, Mahlia T. M. I, Ashrafur S. M. 2018. An Overview of Recent Developments in Biomass Pyrolysis Technologies. *Energies* 11(11): 25p.

- Van de Velden M, Baeyens J, Brems A, Janssens B, Dewil R. 2010. Fundamentals, kinetics and endothermicity of the biomass pyrolysis reaction. *Renewable Energy* 35: 232-242.
- Venderbosch R. H, Prins W. 2010. Fast Pyrolysis Technology Development. *Biofuels, Bioproduct and Biorefining* 6: 178-208.
- Veses A, Aznar M, Martínez I, López M. J, Navarro M. V, Callén M. S, Murillo R, García T. 2014. Catalytic pyrolysis of wood biomass in an auger reactor using calcium-based catalysts. *Bioresource Technology* 162: 250-258.
- Vokatý R. 2011. Porovnávání produktů pyrolýzy měkkých druhů německého uhlí a biomasy. *Paliva* 3: 144-148.
- Weber K, Quicker P. 2018. Properties of biochar. *Fuel* 217: 240-261.
- Weger J. 2009. Biomasa jako zdroj energie. *Biom.cz*. Available at <http://biom.cz/cz/odborne-clanky/biomasa-jako-zdroj-energie>: Accessed 2015-11-21.
- Wen X, Jian S, Wang J. 2017. Prediction models of calorific value of coal based on wavelet neural networks. *Fuel* 199: 512-522.
- Wang H, Wang X, Cui Y, Xue Z, Ba Y. 2018. Slow pyrolysis polygeneration of bamboo (*Phyllostachys pubescens*): Product yield prediction and biochar formation mechanism. *Bioresource Technology* 263: 444-449.
- Wang X, Liu H, Zhang J, Li T, Wang Y. 2017. Evaluation of heavy metal concentrations of edible wild-grown mushrooms from China. *Journal of Environmental Science & Health, Part B -- Pesticides, Food Contaminants, & Agricultural Wastes* 52 (3): 178-183.
- Werther J, Saenger M, Hartge E-U, Ogada T, Siagi Z. 2000. Combustion of agricultural residues. *Progress in Energy and Combustion Science* 26: 1-27.
- Xie F, Jin L, Tu J, Le M, Wang F. 2015. Advances in Research on Comprehensive Utilization of Tea Waste. *Agricultural Science & Technology* 16 (7): 1552-1564.
- Xiu S, Shahbazi A. 2012. Bio-oil production and upgrading research: a review. *Renewable and Sustainable Energy Reviews* 16: 4406-4414.



- Xu L, Brilman D. W. F, Withag J. A. M, Brem G, Kersten S. 2011. Assessment of a dry and a wet route for the production of biofuels from microalgae: Energy balance analysis. *Bioresource Technology* 102: 5113-5122.
- Yajun W, Kang K, Zonglu Y, Guotao S, Ling Q, Lixin Z, Guan W. 2018. Effects of different heating patterns on the decomposition behavior of white pine wood during slow pyrolysis. *International Journal of Agricultural & Biological Engineering* 11 (5): 218-223.
- Yang Z, Kumar A, Huhnke R. L, Buser M, Capareda S. 2016. Pyrolysis of eastern redcedar: Distribution and characteristics of fast and slow pyrolysis products. *Fuel* 166: 157-165.
- Yorgun S, Yildiz D. 2015. Slow pyrolysis of paulownia wood: Effects of pyrolysis parameters on product yields and bio-oil characterization. *Journal of Analytical and Applied Pyrolysis* 114: 68-78.
- Zámostný R, Kurc L. 2011. Vliv podmínek a složení surovin na pyrolýzu dřevní hmoty. *Chemické listy* 105: 458-466.
- Thang J, Yang R, Chen R, Li C. Y, Peng Y, Liu Ch. 2018. Multielemental Analysis Associated with Chemometric Techniques for Geographical Origin Discrimination of Tea Leaves (*Camelia sinensis*) in Guizhou Province, SW China. *Molecules* 23: 16p.
- Zhang L, Xu C. C, Champagne P. 2010. Overview of recent advances in thermochemical conversion of biomass. *Energy Conversion and Management* 51: 969-982.
- Zhang Y, Ma Z, Zhang Q, Wang J, Ma Q, Yang Y, Luo X, Zhang W. 2017. Comparison of the Physicochemical Characteristics of bio-char Pyrolyzed from Moso Bamboo and Rice Husk with Different Pyrolysis Temperatures. *BioResource* 12 (3): 4652-4669.
- Zhijia L, Zehui J, Zhiyong C, Benhua F, Yan Y, Xing L. 2012. Dynamic mechanical thermal analysis of moso bamboo (*Phyllostachys heterocycla*) at different moisture content. *BioResource* 7(2): 1548-1557.

Zhu D, Yang H, Chen Y, Li Z, Wang X, Chen X. 2017. Fouling and Slagging Characteristics during Co-combustion of Coal and Biomass. *BioResources* 12(3): 6322-6341.

Zubenko V, Epik A, Antonenko V. 2018. Development and optimization of fast ablative pyrolysis technology in Ukraine. *Energetika* 64(1): 1-10.

## Annexes

Annex 1: Data values for determination of moisture content, gross calorific value and net calorific value, content of carbon, hydrogen and nitrogen and ash content for all experimental materials (Author 2018).

### Moisture content of raw samples

<b>MATERIAL</b>	<b>m<sub>1</sub></b>	<b>m<sub>2</sub></b>	<b>m<sub>3</sub></b>	<b>MC</b>
medicine residue	44.65	49.33	46.61	<b>58.12</b>
medicine residue	41.82	46.18	43.64	<b>58.26</b>
medicine residue	47.31	51.79	49.16	<b>58.71</b>
tea leaves	48.82	53.11	52.05	<b>24.71</b>
tea leaves	44.11	48.10	47.07	<b>25.81</b>
tea leaves	50.43	54.41	53.39	<b>25.63</b>
mushroom dreg	53.09	58.37	56.41	<b>37.12</b>
mushroom dreg	45.25	51.54	48.97	<b>40.86</b>
mushroom dreg	50.43	56.44	53.83	<b>43.43</b>
coffee ground	44.11	50.91	50.55	<b>5.29</b>
coffee ground	48.82	55.07	54.73	<b>5.44</b>
coffee ground	42.86	48.69	48.38	<b>5.32</b>
bamboo chips	53.29	58.15	57.79	<b>7.41</b>
bamboo chips	53.08	58.18	57.81	<b>7.25</b>
bamboo chips	45.25	50.14	49.78	<b>7.36</b>

### Moisture content of biochar samples

<b>MATERIAL</b>	<b>m<sub>1</sub></b>	<b>m<sub>2</sub></b>	<b>m<sub>3</sub></b>	<b>MC</b>
medicine residue	51.75	56.61	56.41	<b>4.12</b>
medicine residue	42.22	47.58	47.36	<b>4.10</b>
medicine residue	45.99	50.91	50.70	<b>4.27</b>
tea leaves	45.23	50.18	49.87	<b>6.26</b>
tea leaves	45.08	50.08	49.78	<b>6.00</b>
tea leaves	46.69	51.25	50.96	<b>6.36</b>
mushroom dreg	44.70	48.47	47.53	<b>24.93</b>
mushroom dreg	43.44	48.13	46.99	<b>24.31</b>
mushroom dreg	46.04	50.31	49.28	<b>24.12</b>
coffee ground	42.96	47.29	46.69	<b>13.86</b>
coffee ground	48.68	53.86	53.27	<b>11.39</b>
coffee ground	45.82	50.17	49.68	<b>11.26</b>
bamboo chip	45.50	51.31	51.08	<b>3.96</b>

bamboo chip	44.97	50.29	50.05	<b>4.51</b>
bamboo chip	50.85	55.40	55.20	<b>4.40</b>

where:

MC - moisture content [%]

$m_1$  - mass of empty dish [g]

$m_2$  - mass of the dish plus sample before drying [g]

$m_3$  - mass of the dish plus sample after drying [g]

Calorific value of raw materials a.r.

<b>RAW</b>	<b>m</b>	<b>dTk</b>	<b>GCV</b>
medicine residue	0.5774	0.58023	7 582.50
medicine residue	0.5806	0.58348	7 583.04
tea leaves	0.5043	0.83516	13 476.30
tea leaves	0.5340	0.88297	13 452.99
mushroom dreg	0.5660	0.75573	10 572.14
mushroom dreg	0.5950	0.75553	9 980.08
mushroom dreg	0.5140	0.66486	10 194.63
coffee ground	0.5148	1.14284	18 580.08
coffee ground	0.5528	1.22769	18 588.12
bamboo chips	0.5113	1.02885	16 699.78
bamboo chips	0.5393	1.08542	16 703.60

Calorific value of biochar materials a.r.

<b>BIOCHAR</b>	<b>m</b>	<b>dTk</b>	<b>GCV</b>
Medicine residue	0.5381	0.97784	14 934.70
medicine residue	0.5335	0.98463	15 191.71
medicine residue	0.5405	0.99691	15 181.00
tea leaves	0.5218	1.14021	18 264.91
tea leaves	0.5180	1.10841	17 854.36
tea leaves	0.5281	1.13726	17 978.41
mushroom dreg	0.5772	0.93613	13 166.48

mushroom dreg	0.5187	0.69104	10 545.37
mushroom dreg	0.5427	0.89088	13 344.99
coffee ground	0.5301	1.35358	21 598.35
coffee ground	0.5084	1.28024	21 279.14
coffee ground	0.5586	1.42144	21 518.74
bamboo chips	0.5010	1.15814	19 409.94
bamboo chips	0.5339	1.69174	27 166.55
bamboo chips	0.5064	1.59837	27 055.16

Calorific value of raw materials d.b.

<b>RAW</b>	<b>m</b>	<b>dTk</b>	<b>GCV</b>
Medicine residue	0.6008	1.01798	13 822.92
medicine residue	0.5113	0.95296	15 356.38
medicine residue	0.5094	0.96812	15 688.66
tea leaves	0.5066	1.02431	16 787.63
tea leaves	0.5024	1.02972	17 038.09
tea leaves	0.5345	1.08546	16 867.87
mushroom dreg	0.5162	0.96018	15 322.84
mushroom dreg	0.5297	0.98808	15 370.49
coffee ground	0.5495	1.2692	19 392.56
coffee ground	0.5614	1.29364	19 343.46
bamboo chips	0.6093	1.30341	17 848.97
bamboo chips	0.6061	1.30098	17 914.91

Calorific value of biochar materials d.b.

<b>BIOCHAR</b>	<b>m</b>	<b>dTk</b>	<b>GCV</b>
medicine residue	0.5172	0.97431	15 537.57
medicine residue	0.5979	1.13372	15 649.37
medicine residue	0.5543	1.05074	15 644.36
tea leaves	0.5793	1.31069	18 965.40
tea leaves	0.5606	1.26513	18 912.92
mushroom dreg	0.5432	1.10127	16 836.91

mushroom dreg	0.5106	1.02276	16 616.79
mushroom dreg	0.5703	1.15103	16 754.67
coffee ground	0.5414	1.42907	22 378.00
coffee ground	0.5533	1.49896	23 007.45
coffee ground	0.5416	1.46038	22 892.42
bamboo chips	0.5555	1.81660	28 085.78
bamboo chips	0.543	1.77899	28 091.18

where:

GCV - gross calorific value [J/g]

dTK - temperature jump [°C]

m - weight of the paper and sample [g]

Content of carbon, hydrogen and nitrogen of raw materials

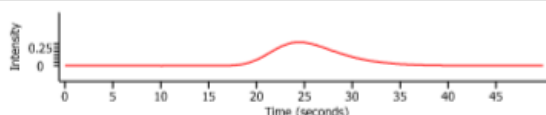
**628 SERIES**

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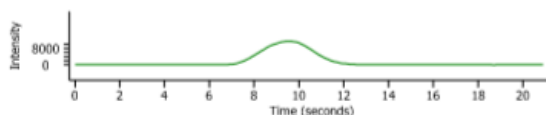
Raw dry bamboo chip

Name	Location	Mass	Comments
Raw dry bamboo chip	20	0.1088	Ivanova
Sample Moisture	Analysis Date	Method	
	12.12.2017 13:26:15	BIOPALIVO	

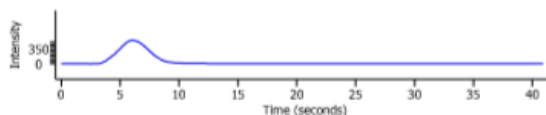
Nitrogen %  
0.32817



Carbon %  
49.605



Hydrogen %  
5.8590



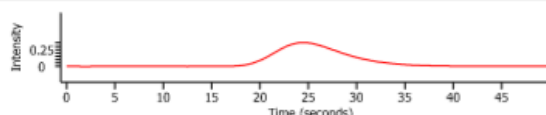
**628 SERIES**

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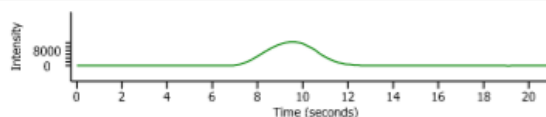
Raw dry bamboo chip

Name	Location	Mass	Comments
Raw dry bamboo chip	21	0.1194	Ivanova
Sample Moisture	Analysis Date	Method	
	12.12.2017 13:30:39	BIOPALIVO	

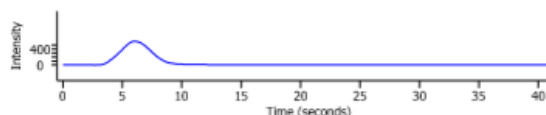
Nitrogen %  
0.33461



Carbon %  
49.555



Hydrogen %  
5.9017



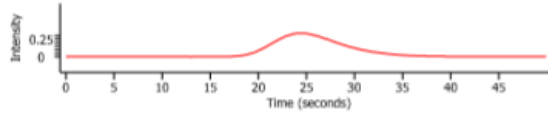
**628 SERIES**

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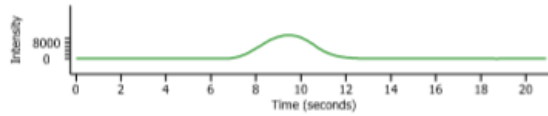
Raw dry bamboo chip

Name	Location	Mass	Comments
Raw dry bamboo chip	22	0.1124	Ivanova
Sample Moisture	Analysis Date	Method	
	12.12.2017 13:35:02	BIOPALIVO	

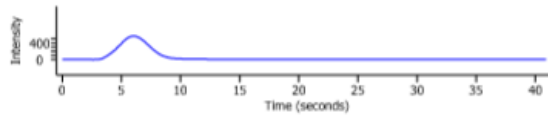
**Nitrogen %**  
0.32742



**Carbon %**  
49.629



**Hydrogen %**  
5.9509



Element	Average	Std. Deviation	RSD	Count
Mass	0.1135	0.005	4.748	3
Nitrogen %	0.33007	0.003954	1.198	3
Carbon %	49.596	0.0376	0.076	3
Hydrogen %	5.9039	0.04602	0.779	3

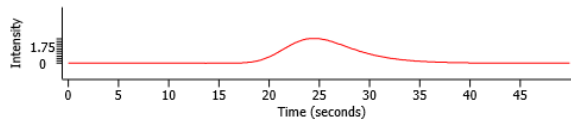
**628 SERIES**

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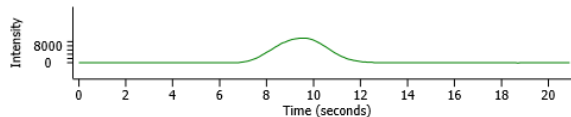
Raw dry coffea grounds 2

Name	Location	Mass
Raw dry coffea grounds 2	11	0.1073
Comments	Sample Moisture	
Ivanova		
Analysis Date	Method	
12.12.2017 12:46:44	BIOPALIVO	

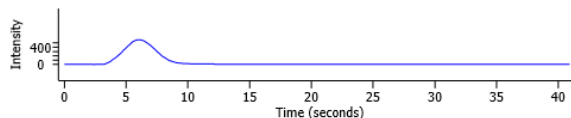
**Nitrogen %**  
3.0120



**Carbon %**  
51.661



**Hydrogen %**  
6.3139





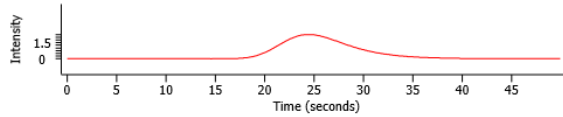
**628 SERIES**

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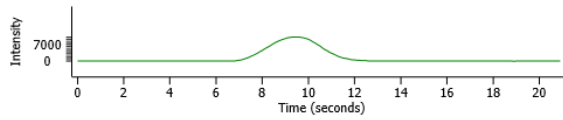
Raw dry coffea grounds 2

Name	Location	Mass
Raw dry coffea grounds 2	12	0.0934
Comments	Sample Moisture	
Ivanova		
Analysis Date	Method	
12.12.2017 12:51:07	BIOPALIVO	

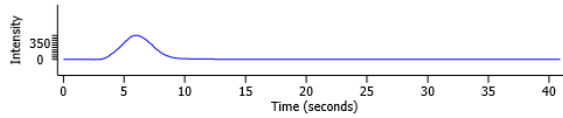
**Nitrogen %**  
3.0190



**Carbon %**  
51.686



**Hydrogen %**  
6.3799



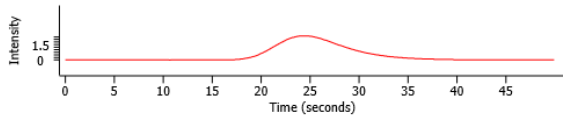
**628 SERIES**

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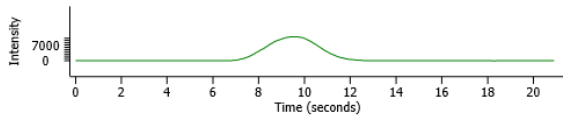
Raw dry coffea grounds 2

Name	Location	Mass
Raw dry coffea grounds 2	13	0.0987
Comments	Sample Moisture	
Ivanova		
Analysis Date	Method	
12.12.2017 12:55:29	BIOPALIVO	

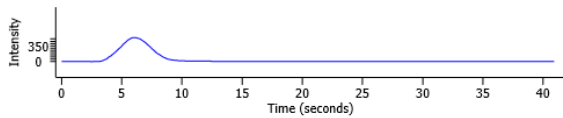
**Nitrogen %**  
2.9952



**Carbon %**  
51.270



**Hydrogen %**  
6.3432



Element	Average	Std. Deviation	RSD	Count
Mass	0.0998	0.007	7.029	3
Nitrogen %	3.0088	0.01227	0.408	3
Carbon %	51.539	0.2332	0.452	3
Hydrogen %	6.3457	0.03306	0.521	3

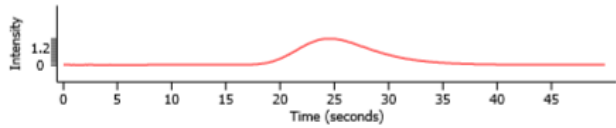
**628 SERIES**

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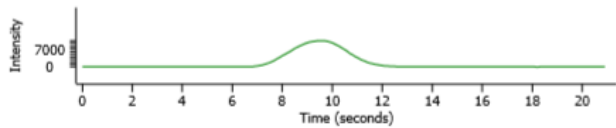
Raw dry medicine residues 5

Name		Location
Raw dry medicine residues 5 2		
Mass	Comments	Sample Moisture
0.1020	Ivanova	
Analysis Date		Method
12.12.2017 12:07:17		BIOPALIVO

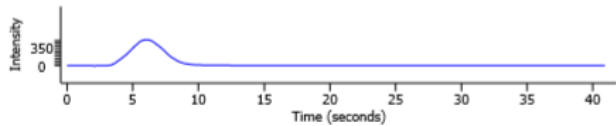
Nitrogen %  
2.2342



Carbon %  
46.408



Hydrogen %  
5.9613



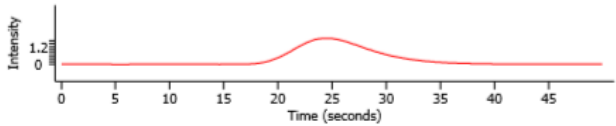
**628 SERIES**

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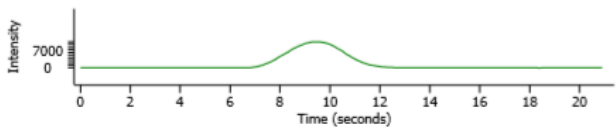
Raw dry medicine residues 5

Name		Location
Raw dry medicine residues 5 3		
Mass	Comments	Sample Moisture
0.1018	Ivanova	
Analysis Date		Method
12.12.2017 12:11:40		BIOPALIVO

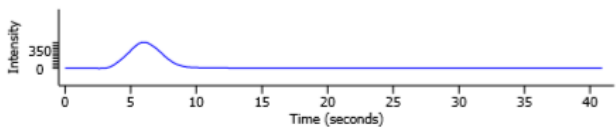
Nitrogen %  
2.1789



Carbon %  
46.459



Hydrogen %  
5.9707



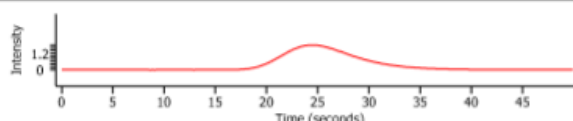
## 628 SERIES

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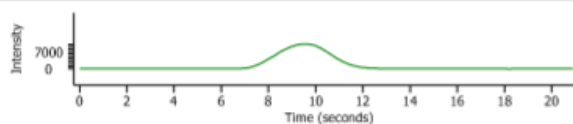
Raw dry medicine residues 5

Name		Location	
Raw dry medicine residues 5		4	
Mass	Comments	Sample Moisture	
0.1036	Ivanova		
Analysis Date		Method	
12.12.2017 12:16:02		BIOPALIVO	

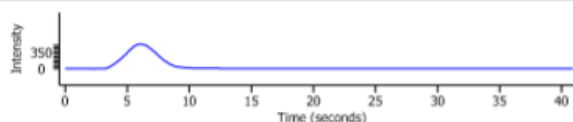
Nitrogen %  
2.1845



Carbon %  
46.515



Hydrogen %  
5.9890



Element	Average	Std. Deviation	RSD	Count
Mass	0.1025	0.0010	0.963	3
Nitrogen %	2.1992	0.03045	1.385	3
Carbon %	46.461	0.0534	0.115	3
Hydrogen %	5.9737	0.01407	0.236	3

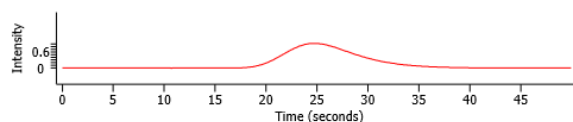
## 628 SERIES

Research institute of agriculture engineering, p.r.i.

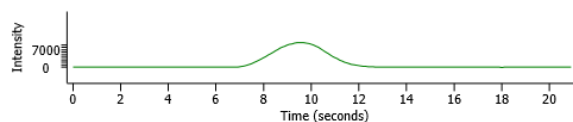
Mushroom dr

Name	Location	Mass	Comments	Sample Moisture
Mushroom dr	17	0.1040	Murcia	
Analysis Date		Method		
12.12.2017 11:00:51		BIOPALIVO		

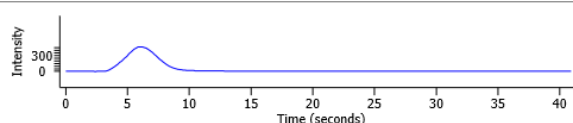
Nitrogen %  
1.0873



Carbon %  
45.716



Hydrogen %  
5.3837



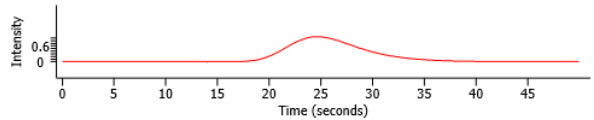
**628 SERIES**

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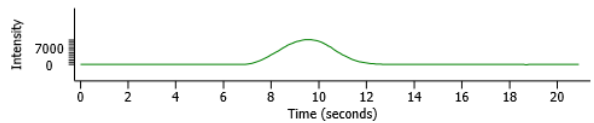
Mushroom dr

Name	Location	Mass	Comments	Sample Moisture
Mushroom dr	18	0.1070	Murcia	
Analysis Date		Method		
12.12.2017 11:05:13		BIOPALIVO		

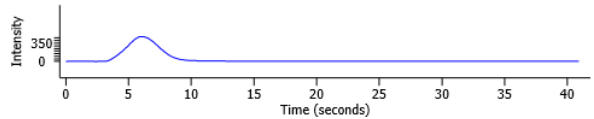
Nitrogen %  
1.0807



Carbon %  
45.396



Hydrogen %  
5.3234



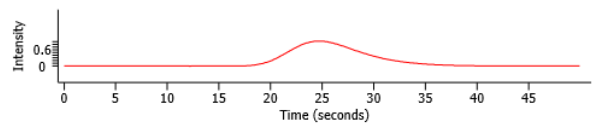
**628 SERIES**

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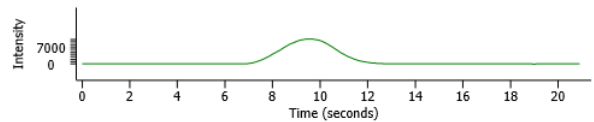
Mushroom dr

Name	Location	Mass	Comments	Sample Moisture
Mushroom dr	19	0.1068	Murcia	
Analysis Date		Method		
12.12.2017 11:10:32		BIOPALIVO		

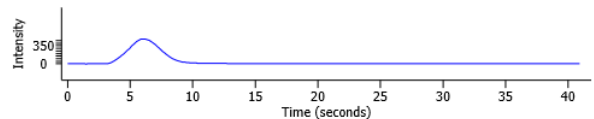
Nitrogen %  
1.0480



Carbon %  
45.697



Hydrogen %  
5.3617



Element	Average	Std. Deviation	RSD	Count
Mass	0.1059	0.002	1.583	3
Nitrogen %	1.0720	0.02104	1.963	3
Carbon %	45.603	0.1795	0.394	3
Hydrogen %	5.3563	0.03050	0.570	3

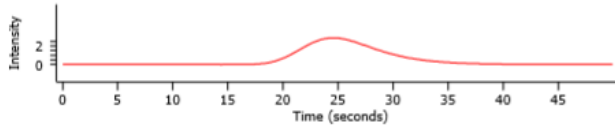
**628 SERIES**

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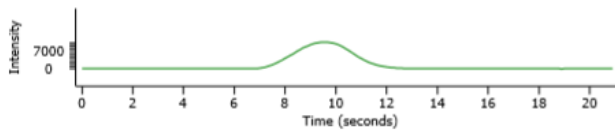
Raw dry tea leaves 6

Name	Location	Mass	Comments
Raw dry tea leaves 6	29	0.1028	Ivanova
Sample Moisture	Analysis Date	Method	
	12.12.2017 11:54:11	BIOPALIVO	

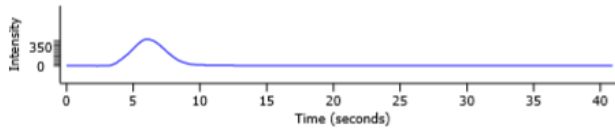
Nitrogen %  
3.4876



Carbon %  
47.529



Hydrogen %  
5.5272



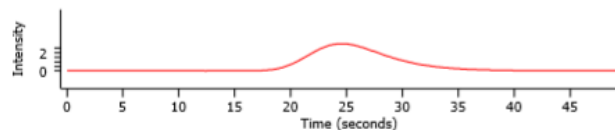
**628 SERIES**

Research institute of agriculture engineering, p.r.i.

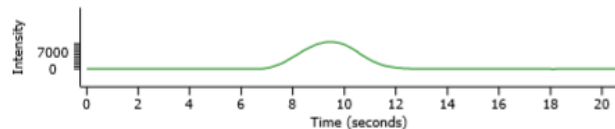
Raw dry tea leaves 6

Name	Location	Mass	Comments
Raw dry tea leaves 6	30	0.1070	Ivanova
Sample Moisture	Analysis Date	Method	
	12.12.2017 11:58:33	BIOPALIVO	

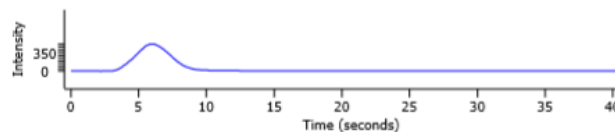
Nitrogen %  
3.5200



Carbon %  
47.195



Hydrogen %  
5.5334



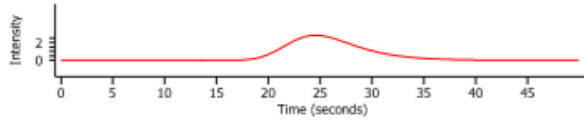
**628 SERIES**

Research institute of agriculture engineering, p.r.i.

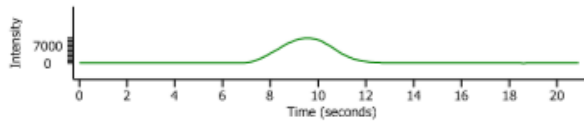
Raw dry tea leaves 6

Name	Location	Mass	Comments
Raw dry tea leaves 6	1	0.0995	Ivanova
Sample Moisture	Analysis Date	Method	
	12.12.2017 12:02:54	BIOPALIVO	

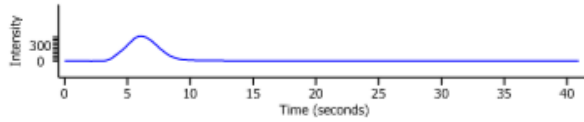
**Nitrogen %**  
3.5461



**Carbon %**  
47.440



**Hydrogen %**  
5.5817



Element	Average	Std. Deviation	RSD	Count
Mass	0.1031	0.004	3.646	3
Nitrogen %	3.5179	0.02931	0.833	3
Carbon %	47.388	0.1731	0.365	3
Hydrogen %	5.5474	0.02987	0.539	3

Content of carbon, hydrogen and nitrogen of biochar material

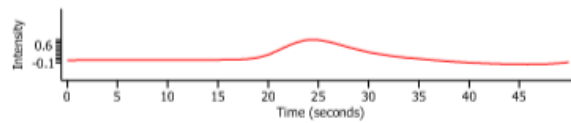
**628 SERIES**

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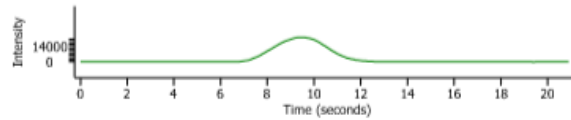
Biochar dry bamboo chip 11

Name		Location
Biochar dry bamboo chip 11		17
Mass	Comments	Sample Moisture
0.1366	Ivanova	
Analysis Date		Method
12.12.2017 13:13:04		BIOPALIVO

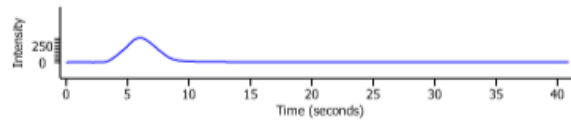
Nitrogen %  
0.54192



Carbon %  
74.938



Hydrogen %  
3.1840



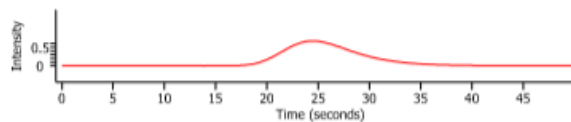
**628 SERIES**

Research institute of agriculture engineering, p.r.i.

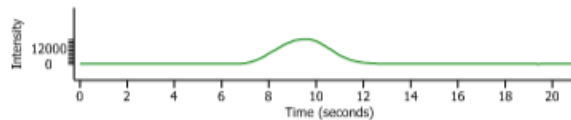
Biochar dry bamboo chip 11

Name		Location
Biochar dry bamboo chip 11		18
Mass	Comments	Sample Moisture
0.1137	Ivanova	
Analysis Date		Method
12.12.2017 13:17:28		BIOPALIVO

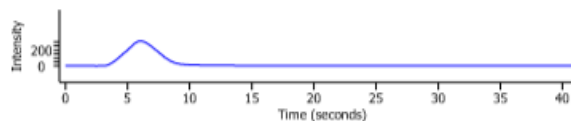
Nitrogen %  
0.70204



Carbon %  
77.296



Hydrogen %  
3.2297



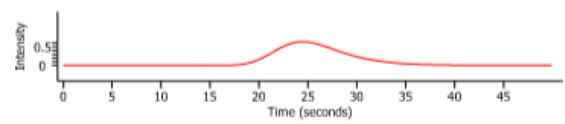
**628 SERIES**

Research institute of agriculture engineering, p.r.i.

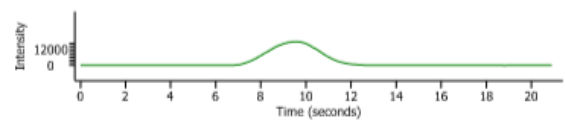
Biochar dry bamboo chip 11

Name	Location
Biochar dry bamboo chip 11	19
Mass	Comments
0.1019	Ivanova
Sample Moisture	
Analysis Date	Method
12.12.2017 13:21:51	BIOPALIVO

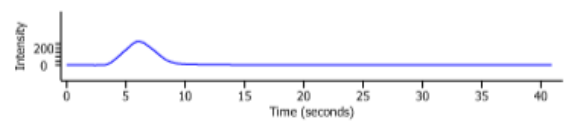
**Nitrogen %**  
0.74345



**Carbon %**  
80.649



**Hydrogen %**  
3.2322



Element	Average	Std. Deviation	RSD	Count
Mass	0.1174	0.02	15.03	3
Nitrogen %	0.66247	0.106435	16.07	3
Carbon %	77.628	2.8696	3.697	3
Hydrogen %	3.2153	0.02711	0.843	3

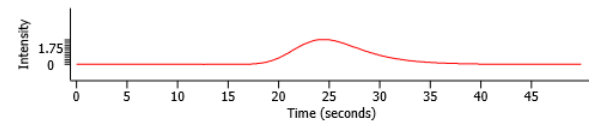
**628 SERIES**

Research institute of agriculture engineering, p.r.i.

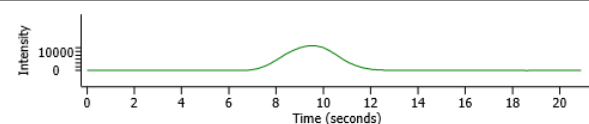
Biochar dry coffea grounds 4

Name	Location
Biochar dry coffea grounds 4	5
Mass	Comments
0.1007	Ivanova
Sample Moisture	
Analysis Date	Method
12.12.2017 12:20:25	BIOPALIVO

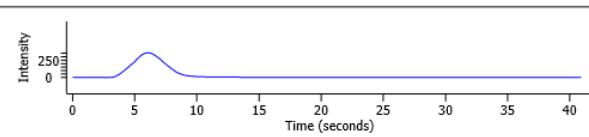
**Nitrogen %**  
3.1882



**Carbon %**  
61.485



**Hydrogen %**  
4.1909





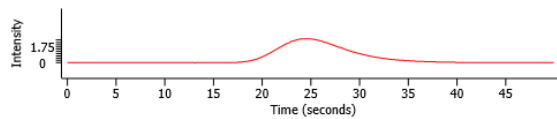
**628 SERIES**

Research institute of agriculture engineering, p.r.i.

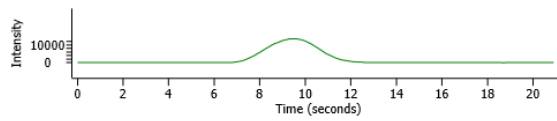
Biochar dry coffea grounds 4

Name		Location
Biochar dry coffea grounds 4		6
Mass	Comments	Sample Moisture
0.1018	Ivanova	
Analysis Date		Method
12.12.2017 12:24:48		BIOPALIVO

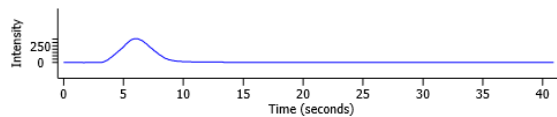
Nitrogen %  
3.2860



Carbon %  
62.999



Hydrogen %  
4.1595



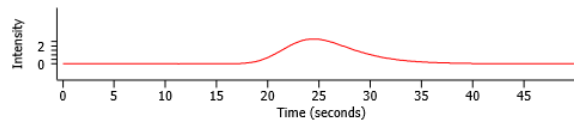
**628 SERIES**

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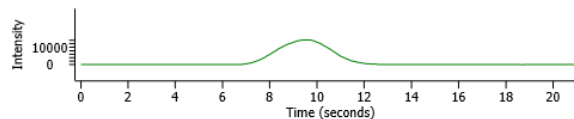
Biochar dry coffea grounds 4

Name		Location
Biochar dry coffea grounds 4		7
Mass	Comments	Sample Moisture
0.1082	Ivanova	
Analysis Date		Method
12.12.2017 12:29:10		BIOPALIVO

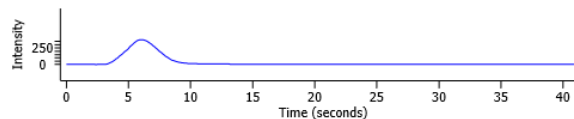
Nitrogen %  
3.2207



Carbon %  
62.139



Hydrogen %  
4.1207



Element	Average	Std. Deviation	RSD	Count
Mass	0.1036	0.004	3.911	3
Nitrogen %	3.2316	0.04983	1.542	3
Carbon %	62.208	0.7594	1.221	3
Hydrogen %	4.1570	0.03521	0.847	3

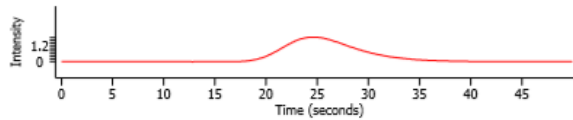
**628 SERIES**

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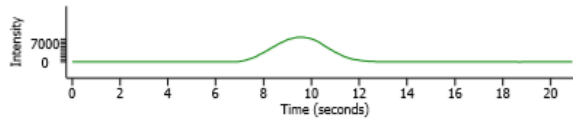
Biochar dry medicine residues 8

Name	Loc
Biochar dry medicine residues 8	23
Mass	Comments
0.1057	Ivanova
Sample Moisture	Analysis Date
	12.12.2017 11:27:
Method	
BIOPALIVO	

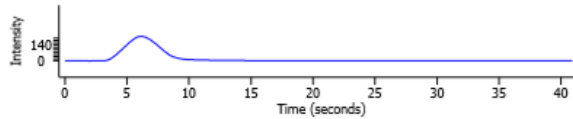
Nitrogen %  
2.1797



Carbon %  
44.140



Hydrogen %  
2.5471



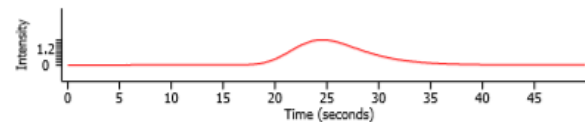
**628 SERIES**

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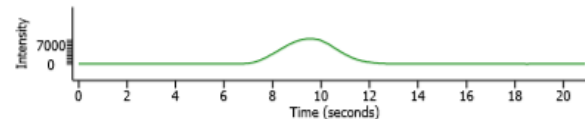
Biochar dry medicine residues 8

Name	Loc
Biochar dry medicine residues 8	24
Mass	Comments
0.1029	Ivanova
Sample Moisture	Analysis Date
	12.12.2017 11:32:
Method	
BIOPALIVO	

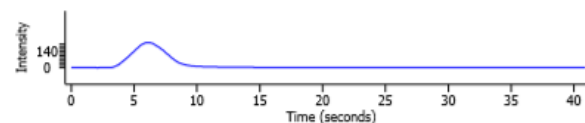
Nitrogen %  
2.1943



Carbon %  
44.366



Hydrogen %  
2.5475



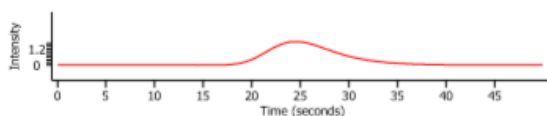
## 628 SERIES

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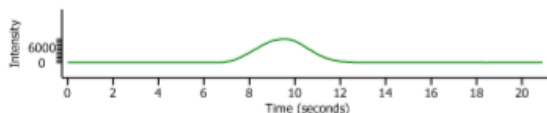
Biochar dry medicine residues 8

Name	Location
Biochar dry medicine residues 8	25
Mass	Comments
0.0996	Ivanova
Sample Moisture	Analysis Date
	12.12.2017 11:36:
Method	
BIOPALIVO	

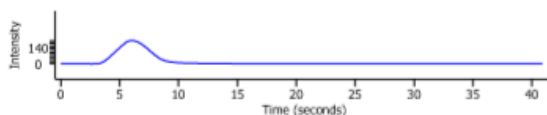
Nitrogen %  
2.1763



Carbon %  
43.961



Hydrogen %  
2.5293



Element	Average	Std. Deviation	RSD	Count
Mass	0.1027	0.003	2.972	3
Nitrogen %	2.1834	0.00958	0.439	3
Carbon %	44.155	0.2029	0.459	3
Hydrogen %	2.5413	0.01041	0.410	3

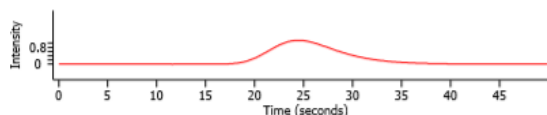
## 628 SERIES

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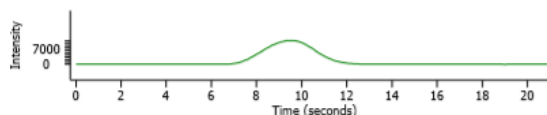
Biochar dry mushroom dreg 3

Name	Location
Biochar dry mushroom dreg 3	8
Mass	Comments
0.0969	Ivanova
Sample Moisture	
Analysis Date	Method
12.12.2017 12:33:34	BIOPALIVO

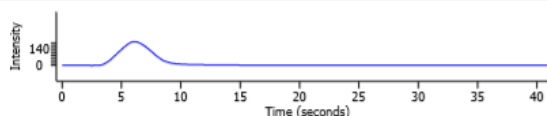
Nitrogen %  
1.4341



Carbon %  
49.919



Hydrogen %  
2.4207



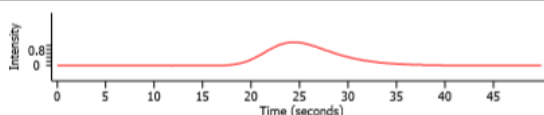
## 628 SERIES

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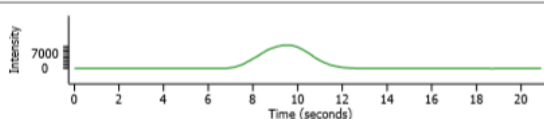
Biochar dry mushroom dreg 3

Name		Location
Biochar dry mushroom dreg 3		9
Mass	Comments	Sample Moisture
0.0995	Ivanova	
Analysis Date		Method
12.12.2017 12:37:58		BIOPALIVO

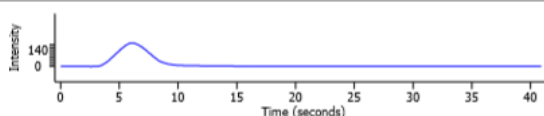
Nitrogen %  
1.4356



Carbon %  
50.175



Hydrogen %  
2.3737



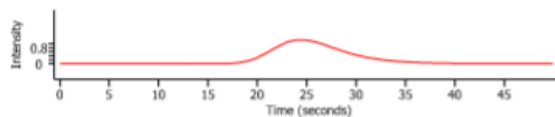
## 628 SERIES

Research institute of agriculture engineering, p.r.i.

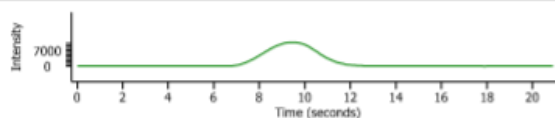
Biochar dry mushroom dreg 3

Name		Location
Biochar dry mushroom dreg 3		10
Mass	Comments	Sample Moisture
0.1012	Ivanova	
Analysis Date		Method
12.12.2017 12:42:21		BIOPALIVO

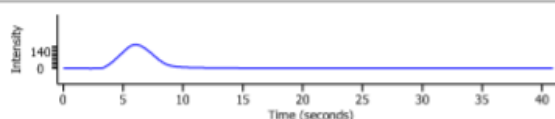
Nitrogen %  
1.4382



Carbon %  
49.854



Hydrogen %  
2.3573



Element	Average	Std. Deviation	RSD	Count
Mass	0.0992	0.002	2.183	3
Nitrogen %	1.4359	0.00206	0.143	3
Carbon %	49.983	0.1698	0.340	3
Hydrogen %	2.3839	0.03290	1.380	3

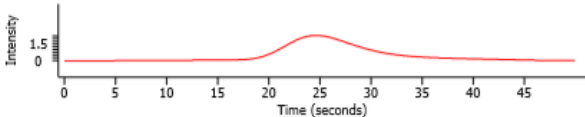
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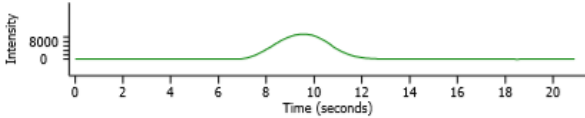
Biochar dry tea leaves 7

Name	Location	Mass
Biochar dry tea leaves 7	26	0.0998
Comments	Sample Moisture	Analysis Date
Ivanova		12.12.2017 11:41:06
Method		
BIOPALIVO		

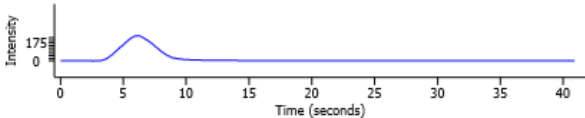
Nitrogen %  
3.2811



Carbon %  
54.110



Hydrogen %  
2.9821



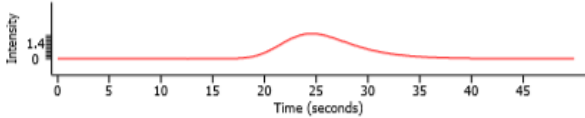
**628 SERIES**

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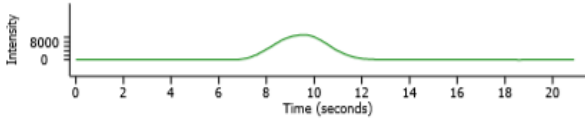
Biochar dry tea leaves 7

Name	Location	Mass
Biochar dry tea leaves 7	27	0.0969
Comments	Sample Moisture	Analysis Date
Ivanova		12.12.2017 11:45:28
Method		
BIOPALIVO		

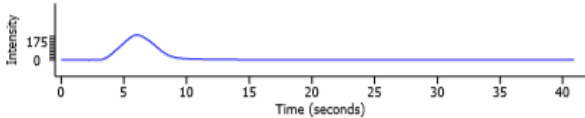
Nitrogen %  
2.8019



Carbon %  
54.499



Hydrogen %  
3.0242



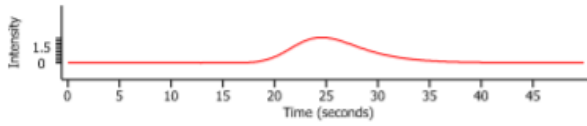
**628 SERIES**

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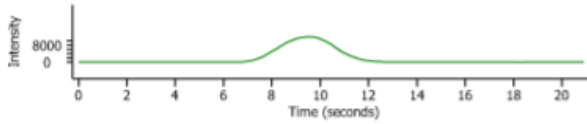
Biochar dry tea leaves 7

Name	Location	Mass
Biochar dry tea leaves 7	28	0.1050
Comments	Sample Moisture	Analysis Date
Ivanova		12.12.2017 11:49:49
Method		
BIOPALIVO		

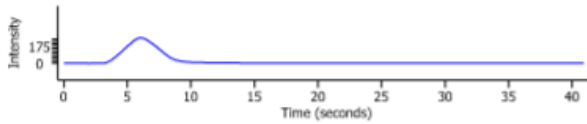
**Nitrogen %**  
2.7982



**Carbon %**  
54.239



**Hydrogen %**  
3.0112



Element	Average	Std. Deviation	RSD	Count
Mass	0.1006	0.004	4.081	3
Nitrogen %	2.9604	0.27777	9.383	3
Carbon %	54.282	0.1980	0.365	3
Hydrogen %	3.0058	0.02158	0.718	3

Content of carbon, hydrogen and nitrogen of liquid materials

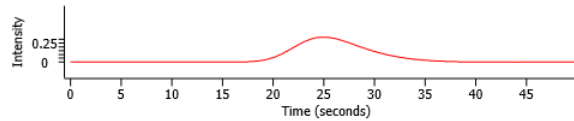
**628 SERIES**

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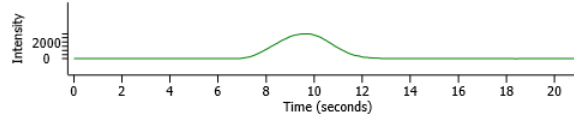
wood vinegard bamboo

Name	Location	Mass
wood vinegard bamboo	30	0.1138
Comments	Sample Moisture	Analysis Date
Ivanova		23.1.2018 10:46:23
Method		
BIOPALIVO		

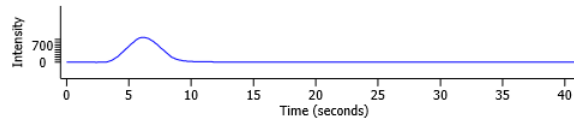
**Nitrogen %**  
0.30746



**Carbon %**  
12.328



**Hydrogen %**  
10.380



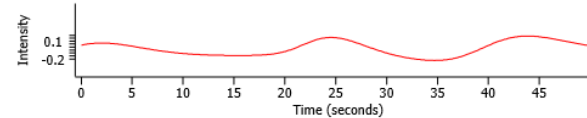
**628 SERIES**

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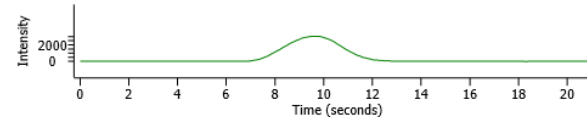
wood vinegard bamboo

Name	Location	Mass
wood vinegard bamboo	1	0.1166
Comments	Sample Moisture	Analysis Date
Ivanova		23.1.2018 10:50:42
Method		
BIOPALIVO		

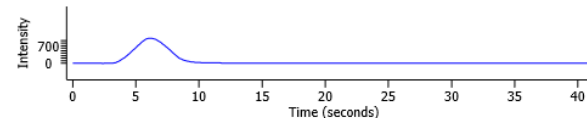
**Nitrogen %**  
-0.18412



**Carbon %**  
12.240



**Hydrogen %**  
10.167



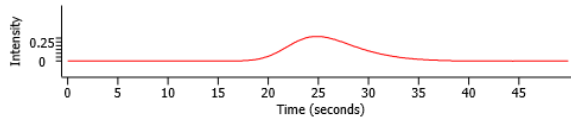
**628 SERIES**

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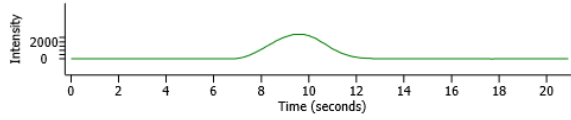
wood vinegard bamboo

Name	Location	Mass
wood vinegard bamboo	2	0.1101
Comments	Sample Moisture	Analysis Date
Ivanova		23.1.2018 10:55:03
Method		
BIOPALIVO		

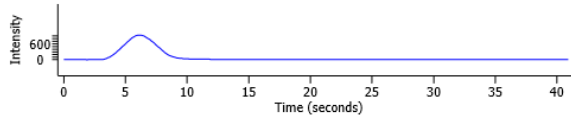
**Nitrogen %**  
0.30770



**Carbon %**  
12.251



**Hydrogen %**  
10.168



Element	Average	Std. Deviation	RSD	Count
Mass	0.1135	0.003	2.873	3
Nitrogen %	0.14368	0.283881	197.6	3
Carbon %	12.273	0.0480	0.391	3
Hydrogen %	10.238	0.1225	1.196	3

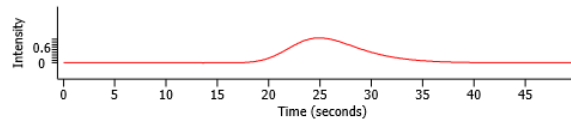
**628 SERIES**

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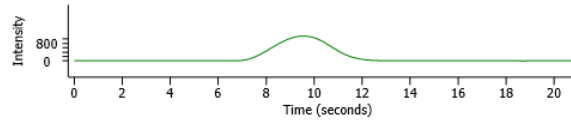
wood vinegard coffee

Name	Location	Mass	Comments
wood vinegard coffee	27	0.1158	Ivanova
Sample Moisture	Analysis Date	Method	
	23.1.2018 10:33:23	BIOPALIVO	

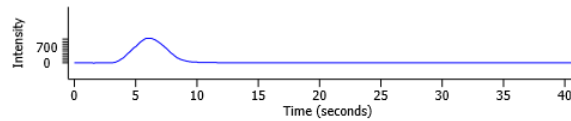
**Nitrogen %**  
0.98383



**Carbon %**  
4.4707



**Hydrogen %**  
10.821





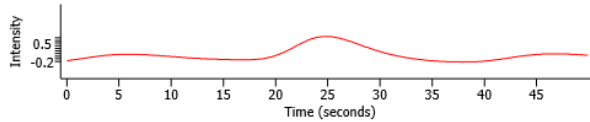
**628 SERIES**

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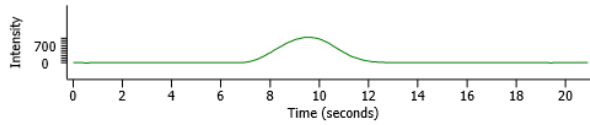
wood vinegard coffee

Name	Location	Mass	Comments
wood vinegard coffee	28	0.1073	Ivanova
Sample Moisture	Analysis Date	Method	
	23.1.2018 10:37:42	BIOPALIVO	

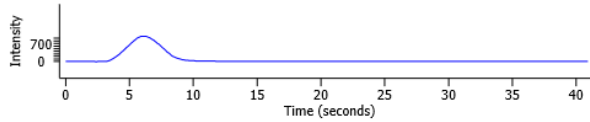
Nitrogen %  
0.30589



Carbon %  
4.4024



Hydrogen %  
11.004



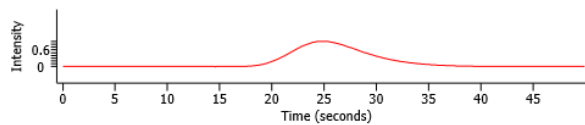
**628 SERIES**

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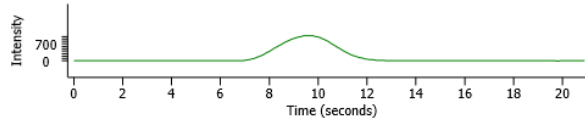
wood vinegard coffee

Name	Location	Mass	Comments
wood vinegard coffee	29	0.1081	Ivanova
Sample Moisture	Analysis Date	Method	
	23.1.2018 10:42:02	BIOPALIVO	

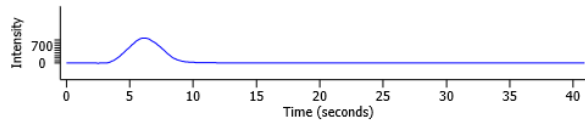
Nitrogen %  
0.99461



Carbon %  
4.3550



Hydrogen %  
10.860



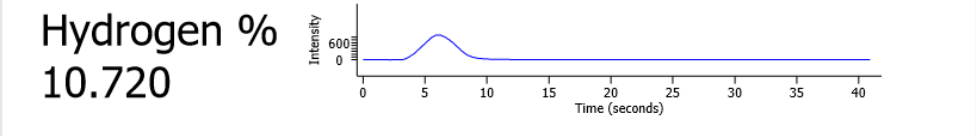
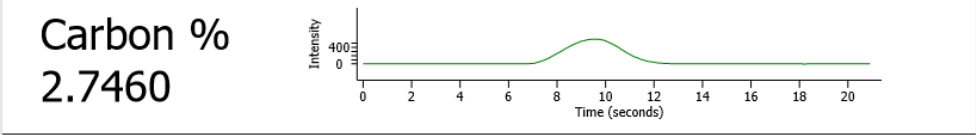
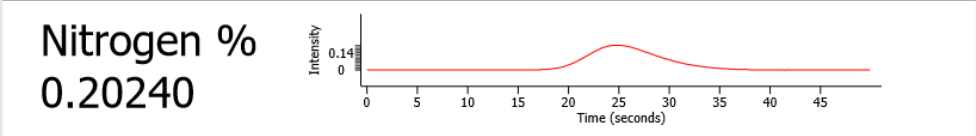
Element	Average	Std. Deviation	RSD	Count
Mass	0.1104	0.005	4.251	3
Nitrogen %	0.76144	0.394560	51.82	3
Carbon %	4.4094	0.05818	1.320	3
Hydrogen %	10.895	0.0965	0.886	3

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wood vinegard chinese medicine

Name		wood vinegard chinese medicine	7
Mass	Comments	0.0964	Ivanova
Sample Moisture	Analysis Date		23.1.2018 11:16:
Method		BIOPALIVO	

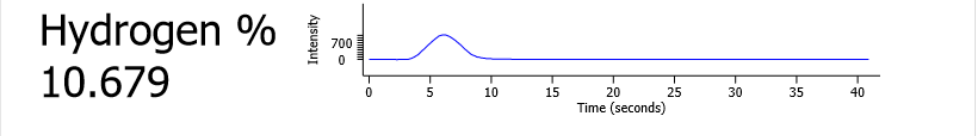
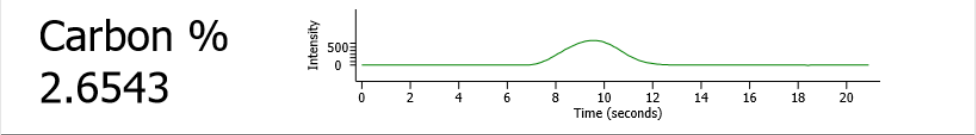
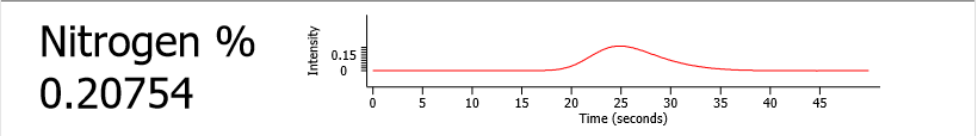


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wood vinegard chinese medicine

Name		wood vinegard chinese medicine	8
Mass	Comments	0.1138	Ivanova
Sample Moisture	Analysis Date		23.1.2018 11:21:
Method		BIOPALIVO	



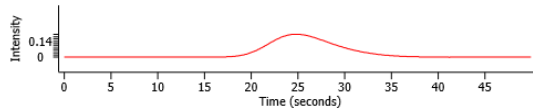
**628 SERIES**

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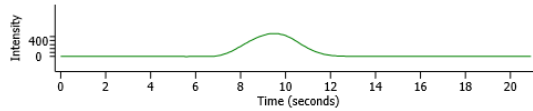
wood vinegard chinese medicine

Name		wood vinegard chinese medicine
Mass	Comments	0.0976 Ivanova
Sample Moisture	Analysis Date	23.1.2018 11:25:
Method		BIOPALIVO

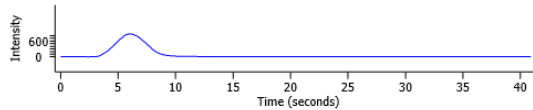
Nitrogen %  
0.19875



Carbon %  
2.6122



Hydrogen %  
10.599



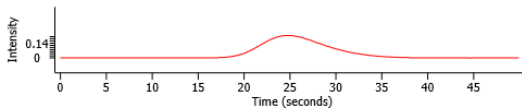
**628 SERIES**

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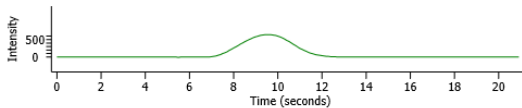
wood vinegard chinese medicine

Name		wood vinegard chinese medicine
Mass	Comments	0.1078 Ivanova
Sample Moisture	Analysis Date	23.1.2018 11:29:
Method		BIOPALIVO

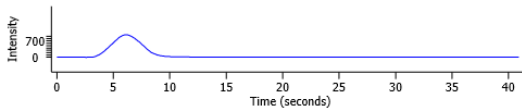
Nitrogen %  
0.19069



Carbon %  
2.6378



Hydrogen %  
10.607



Element	Average	Std. Deviation	RSD	Count
Mass	0.1039	0.008	8.036	4
Nitrogen %	0.19984	0.007091	3.548	4
Carbon %	2.6626	0.05825	2.188	4
Hydrogen %	10.651	0.0585	0.550	4

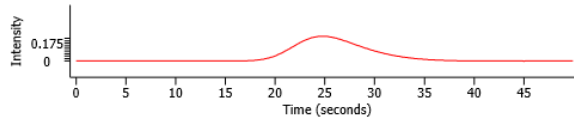
**628 SERIES**

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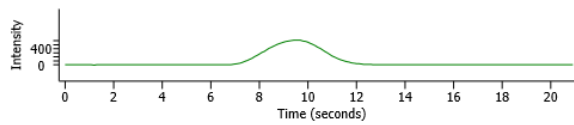
Bacteria residue

Name	Location	Mass	Comments	Sample Moisture
Bacteria residue	11	0.0954	Ivanova	
Analysis Date	Method			
23.1.2018 11:34:15	BIOPALIVO			

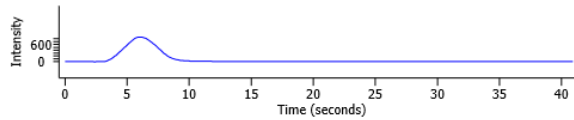
Nitrogen %  
0.26050



Carbon %  
2.8637



Hydrogen %  
10.682



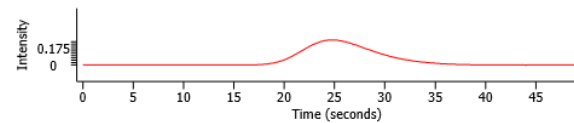
**628 SERIES**

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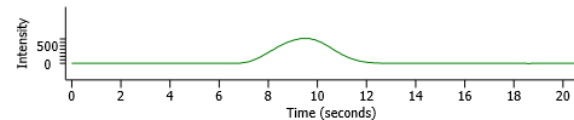
Bacteria residue

Name	Location	Mass	Comments	Sample Moisture
Bacteria residue	12	0.1103	Ivanova	
Analysis Date	Method			
23.1.2018 11:38:37	BIOPALIVO			

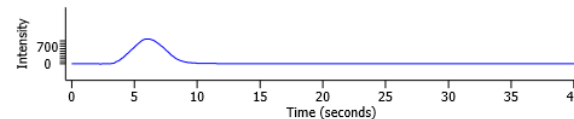
Nitrogen %  
0.25291



Carbon %  
2.8740



Hydrogen %  
10.572



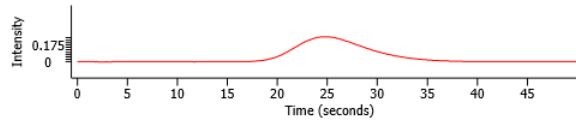
**628 SERIES**

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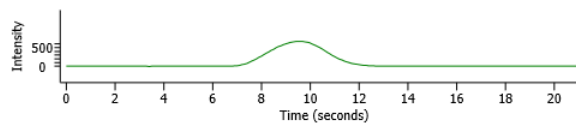
Bacteria residue

Name	Location	Mass	Comments	Sample Moisture
Bacteria residue	13	0.1038	Ivanova	
Analysis Date	Method			
23.1.2018 11:42:59	BIOPALIVO			

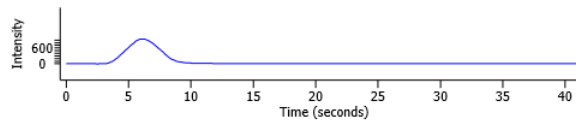
Nitrogen %  
0.26064



Carbon %  
2.8672



Hydrogen %  
10.779



Element	Average	Std. Deviation	RSD	Count
Mass	0.1032	0.007	7.241	3
Nitrogen %	0.25802	0.004423	1.714	3
Carbon %	2.8683	0.00521	0.182	3
Hydrogen %	10.678	0.1038	0.972	3

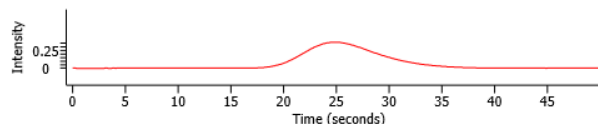
**628 SERIES**

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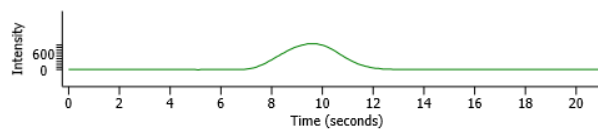
wood vinegard tea

Name	Location	Mass	Comments
wood vinegard tea	3	0.1416	Ivanova
Sample Moisture	Analysis Date	Method	
	23.1.2018 10:59:23	BIOPALIVO	

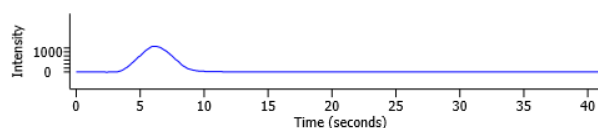
Nitrogen %  
0.27909



Carbon %  
3.0036



Hydrogen %  
10.905



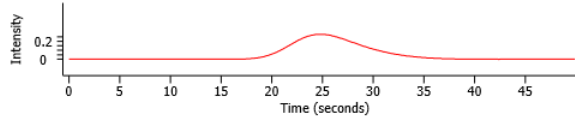
**628 SERIES**

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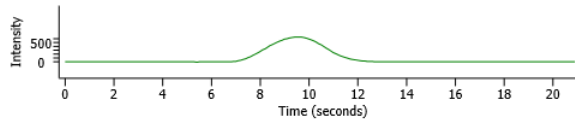
wood vinegard tea

Name	Location	Mass	Comments
wood vinegard tea	4	0.1004	Ivanova
Sample Moisture	Analysis Date	Method	
	23.1.2018 11:03:43	BIOPALIVO	

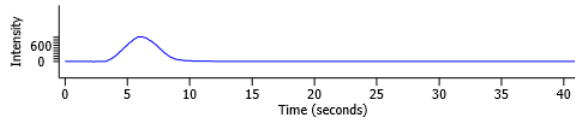
Nitrogen %  
0.28362



Carbon %  
2.8605



Hydrogen %  
10.955



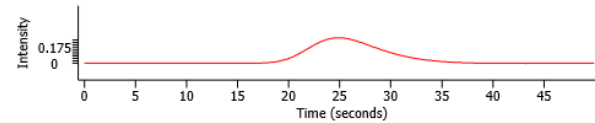
**628 SERIES**

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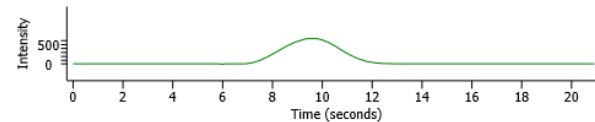
wood vinegard tea

Name	Location	Mass	Comments
wood vinegard tea	5	0.1025	Ivanova
Sample Moisture	Analysis Date	Method	
	23.1.2018 11:08:05	BIOPALIVO	

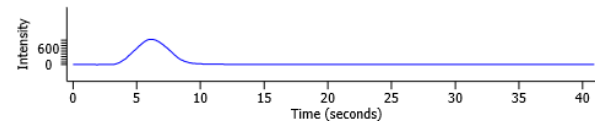
Nitrogen %  
0.27327



Carbon %  
2.8492



Hydrogen %  
10.773



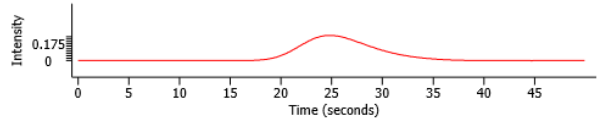
# 628 SERIES

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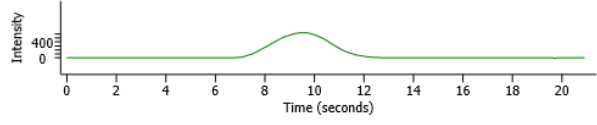
wood vinegard tea

Name	Location	Mass	Comments
wood vinegard tea	6	0.0983	Ivanova
Sample Moisture	Analysis Date	Method	
	23.1.2018 11:12:26	BIOPALIVO	

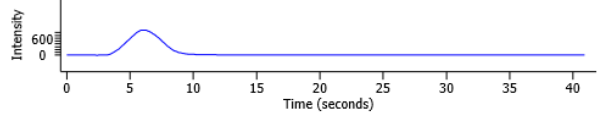
**Nitrogen %**  
0.27447



**Carbon %**  
2.8619



**Hydrogen %**  
10.792



Element	Average	Std. Deviation	RSD	Count
Mass	0.1107	0.02	18.67	4
Nitrogen %	0.27761	0.004730	1.704	4
Carbon %	2.8938	0.07343	2.537	4
Hydrogen %	10.856	0.0880	0.811	4

Ash content

Bamboo chips	m1	m2	m3	sample	ash [g]	ash [g/kg]	Ad
RAW	21.8856	23.1562	21.8937	1.2706	0.0081	0.3497	0.6374
RAW	22.3522	23.8313	22.3602	1.4791	0.0080	0.3356	0.5408
RAW	26.4794	28.0551	26.4841	1.5757	0.0047	0.1675	0.2982
BIOCHAR	26.0801	27.2881	26.1062	1.2080	0.0261	0.9564	2.1605
BIOCHAR	25.7951	26.8844	25.8183	1.0893	0.0232	0.8629	2.1298
BIOCHAR	24.5967	25.7470	24.6239	1.1503	0.0272	1.0564	2.3646

Coffee ground	m1	m2	m3	sample	ash [g]	ash [g/kg]	Ad
RAW	17.7046	19.0884	17.7692	1.3838	0.0646	3.3842	4.6683
RAW	18.6598	20.0675	18.7248	1.4077	0.0650	3.2390	4.6174
RAW	17.1067	18.644	17.1773	1.5373	0.0706	3.7867	4.5924
BIOCHAR	20.3077	21.6029	20.5658	1.2952	0.2581	11.9474	19.9274
BIOCHAR	24.8621	26.2149	25.1282	1.3528	0.2661	10.1507	19.6703
BIOCHAR	20.8094	22.4762	21.1407	1.6668	0.3313	14.7400	19.8764

Medicine residue	m1	m2	m3	sample	ash [g]	ash [g/kg]	Ad
RAW	21.6754	22.7512	21.7842	1.0758	0.1088	4.7821	10.1134
RAW	18.4737	19.7759	18.6628	1.3022	0.1891	9.5621	14.5215
RAW	15.6338	17.0143	15.8322	1.3805	0.1984	11.6607	14.3716
BIOCHAR	18.0685	19.1789	18.5441	1.1104	0.4756	24.7980	42.8314
BIOCHAR	26.8698	28.3485	27.5028	1.4787	0.633	22.3292	42.8078
BIOCHAR	16.7506	17.9642	17.2682	1.2136	0.5176	28.8128	42.6499

Mushroom dreg	m1	m2	m3	sample	ash [g]	ash [g/kg]	Ad
RAW	18.2379	19.2667	18.3876	1.0288	0.1497	7.7698	14.5509
RAW	20.2219	21.2432	20.3954	1.0213	0.1735	8.1673	16.9881
RAW	16.7141	17.8962	16.8816	1.1821	0.1675	9.3595	14.1697
BIOCHAR	20.3523	21.5726	20.8226	1.2203	0.4703	21.8008	38.5397
BIOCHAR	16.1478	17.7311	16.7450	1.5833	0.5972	33.6809	37.7186
BIOCHAR	18.4871	19.7199	18.9519	1.2328	0.4648	23.5700	37.7027



Tea leaves	m <sub>1</sub>	m <sub>2</sub>	m <sub>3</sub>	sample	ash [g]	ash [g/kg]	Ad
RAW	21.5154	22.6531	21.6613	1.1377	0.1459	6.4406	12.8241
RAW	25.3662	26.5867	25.5276	1.2205	0.1614	6.0707	13.2240
RAW	18.0800	19.2497	18.2412	1.1697	0.1612	8.3741	13.7813
BIOCHAR	24.1773	25.4995	24.5535	1.3222	0.3762	14.7532	28.4525
BIOCHAR	25.3791	26.6749	25.7499	1.2958	0.3708	13.9007	28.6155
BIOCHAR	25.0309	26.7477	25.5174	1.7168	0.4865	18.1884	28.3376

where:

Ad - ash content d.b. [%]

m<sub>1</sub> - mass of empty ceramic dish [g]

m<sub>2</sub> - mass of ceramic dish plus sample [g]

m<sub>3</sub> - mass of ceramic dish plus ash [g]