LAPPEENRANTA UNIVERSITY OF TECHNOLOGY
DEPARTMENT OF ENERGY TECHNOLOGY

MASTER'S THESIS

HYDROTHERMAL CARBONIZATION OF THE TROPICAL BIOMASS

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ABSTRACT

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Degree Programme in Bioenergy Technology

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Master's thesis

2018

60 pages, 4 tables, 16 figures and 6 appendices

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Keywords: hydrothermal carbonization, tropical biomass, coffee wood, parchment, eucalyptus, bamboo

Hydrothermal carbonization is a promising method of thermochemical treatment, which allows wet biomass conversion into hydrochar; a brittle, solid and high heating value product. During this process the biomass is held at the temperature of the 180-250 ºC with a certain amount of water in the closed system for several hours. This process increases biomass hydrophobicity, lowers moisture content, increases density and heating value. These improved properties provide with extended variety of applications, such as fuel, adsorbent, and catalysts.

Even though it is abundant, tropical biomass is not yet widely used for modern, high efficiency energy purposes. New opportunities could be found after improving of its characteristics by pre-treatment, such as hydrothermal carbonization. This work is dedicated to carrying out of hydrothermal carbonization processes and analyzing HTC products of some tropical biomass, such as eucalyptus, coffee wood, coffee cherry parchment and bamboo. In addition, an examination of the influence of different temperatures on the properties of the hydrochars is made.

ACKNOWLEDGMENTS

The implementation of this Master's thesis was carried out with the support and assistance of a number of people, whom I am thankful for the inspiration and help. I want to express my gratitude to Professor Esa Vakkilainen for complete assistance, guidance and direction during me writing the Master's thesis. Moreover, I am immensely grateful to Ekaterina Sermyagina for the moral support and giving confidence to me during the study and, of course, for her preview and evaluation of the original text. In addition, I would like to express appreciation to my partner in carrying out of laboratory experiments Clara Mendoza Martinez, who helped me to adopt and gain skills in working and analyzing with the investigated samples.

Besides, I am infinitely happy to have a unique opportunity to write a Master's thesis in the Lappeenranta University of Technology. I am lucky to become a part of an international environment, to meet new friends and acquaintances and to study the development of energy field from different point of view. Studying in LUT gave me a chance to apply my knowledge in practice, work with unique equipment and gain experience in the field of biomass treatment. In addition, I want to note the contribution to my knowledge in energy sphere of my home university Moscow Power Engineering Institute (Technical University) and my supervisor Anikeev Aleksandr Viktorovich, whose authority plays an important role in my educational process.

After all, behind each person and each his or her act, there is the family and friends, who make it possible to overcome difficulties and confidently go to the goal. Therefore, I also want to express my gratitude to them and their readiness to help at any moment.

Marina Silakova

Lappeenranta,

May 2018

Table of content

List of symbols and abbreviations

ºC – degrees Celsius

CHP – combined heat and power plant

EJ – exajoule

EY – energy yield

f – reaction severity

GHG – greenhouse gases

HHV – higher heating value

HTC – hydrothermal carbonization

LHV – lower heating value

MJ – megajoule

MP – megapascal

Mtoe – million tonnes of oil equivalent

MY – mass yield

PID - proportional-integral-derivative (controller)

T – temperature in Kelvins

t – residence time

TWh – terawatt-hours

1. Introduction

There is a significant worldwide problem of climate change. The main reason is the growing amount of greenhouse gas emissions, especially in energy field. The current and future environmental stability is in danger. In addition to this problem, there is the reduction of fossil fuels availability. Some regions have poor or even no source of such feedstocks and areas, which are rich with natural resources are forced to recognize the limitation of them and the tendency to depletion. In this aspect, the price increases and dependence of some regions in fossil fuels also becomes higher.

There is an alternative for fossil fuels, which could bring positive impact on different spheres, such as environment, society and economics. The solar, wind, hydrothermal energy sources and bioenergy enable the possible ways to avoid usage of conventional types of fossil fuels. They are more environmentally friendly and have unlimited resources. Therefore, they are in spotlight of the researchers worldwide nowadays.

Biomass is an organic source, which has a huge potential for fossil fuels replacement. There are some important advantages of this source application in variety of the fields. Biomass is widely available and can be converted into different types of useful energy: heat, power and fuels for transport.

The world of the biomass is significantly diverse and the potential of some biomass species are still unexplored. It is important to know properties of different types of biomass to understand their potential, possible ways of use, and suitable methods of pretreatment.

Tropical regions have huge asset of some biomass such as coffee, bamboo, eucalyptus. This allows, assuming it as a potential material, for use in different fields, such as food, paper or textile industry or energy purposes. Moreover, there are significant amount of various by-products within the manufacturing processes at these industries. Residues and wastes have poor application at the world's scale and small variety of ways of usage. Consequently, waste utilization could bring positive impact on economic social and environmental spheres.

Generally, biomass as a raw material has rather problematic properties for energy purposes in comparison to fossil fuels, such as high moisture content, low heating value and low density. These characteristics badly influence on logistics and combustion of biomass and make it more expensive and complicated. Thus, the important field for explorations is the development of the pretreatment methods, which can improve properties of different raw materials enable new possible utilization pathways or facilitate the application of the current ones.

One of the perspective developing methods of the pretreatment is hydrothermal carbonization (HTC). This process increases the potential of the biomass usage by making material homogenous and generally improving the key properties of the feedstock - turning raw biomass into more suitable fuel for combustion.

This work is dedicated to hydrothermal carbonization of tropical biomasses. Bamboo, eucalyptus and coffee production chain residues, such as coffee bean parchment and coffee wood were treated for improving of the main properties of these biomasses. The properties of the samples and possibilities of the further usage are investigated. The influence of the process temperature on the properties of the final product was explored.

Consequently, the results of the experimental work could be further used for the subsequent researches for the biomass possibility for different purposes especially energy one, opportunity of the hydrothermal carbonization applications for these types of the tropical biomass and advantages of such treatment. This work is dedicated for the biomass properties database filling and investigation of the advanced ways of the treatment for the fuel properties increasing, such as hydrothermal carbonization.

2. Biomass overview

2.1 Current state of bioenergy

The energy consumption is increasing worldwide. The dynamic of the energy consumption in 2005-2016 by different regions is illustrated at Figure 1. According to Enerdata (2017) world energy statistics, the total world's energy consumption in 2015 was 13 393 Mtoe.

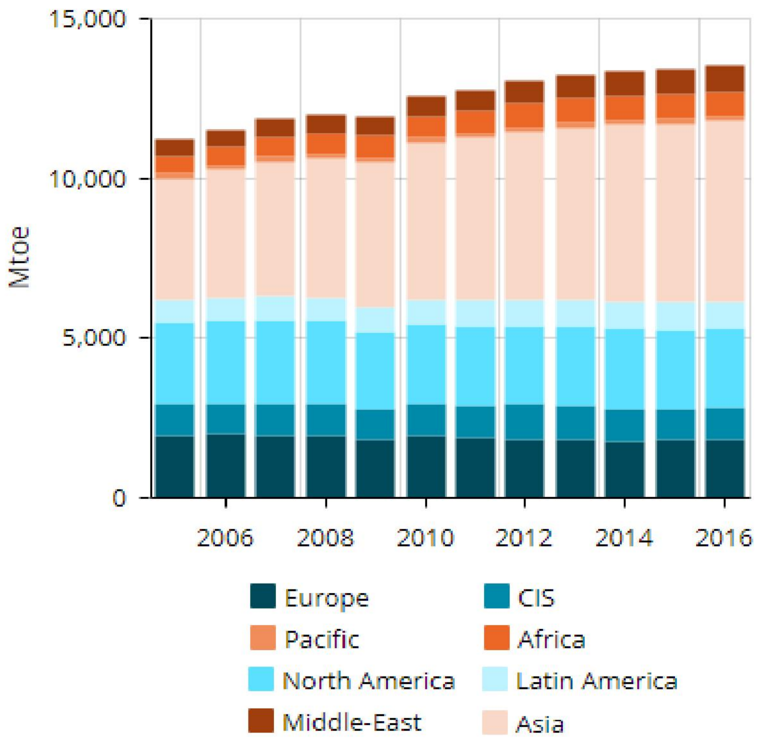

Figure 1. Total energy consumption by regions in 2005-2016(Enerdata, 2017)

The fossil fuel share in the world is 78% that makes it the most widely used resource for energy production (REN21 (2017)). The share of the renewable energy in total final energy consumption in 2015 is 19.3%. The leading countries for percentage of the renewables use for energy production are Norway (97.9%), New Zealand (84%), Colombia (82%) and Brazil (81.2%) (Enerdata (2017)). The renewables include the traditional use of biomass together with modern renewables, which are represented by novel pathways of bioenergy, geothermal, solar power and heat, wind and hydropower. According to REN21 (2017), Asia, North America and Europe are the leading regions in bioenergy production for the last 10 years. The worldwide total biomass share in it is 14.1%, from which traditional takes 9.1%. The more detailed diagram of the energy resources shares in the world's scale is shown at Figure 2.

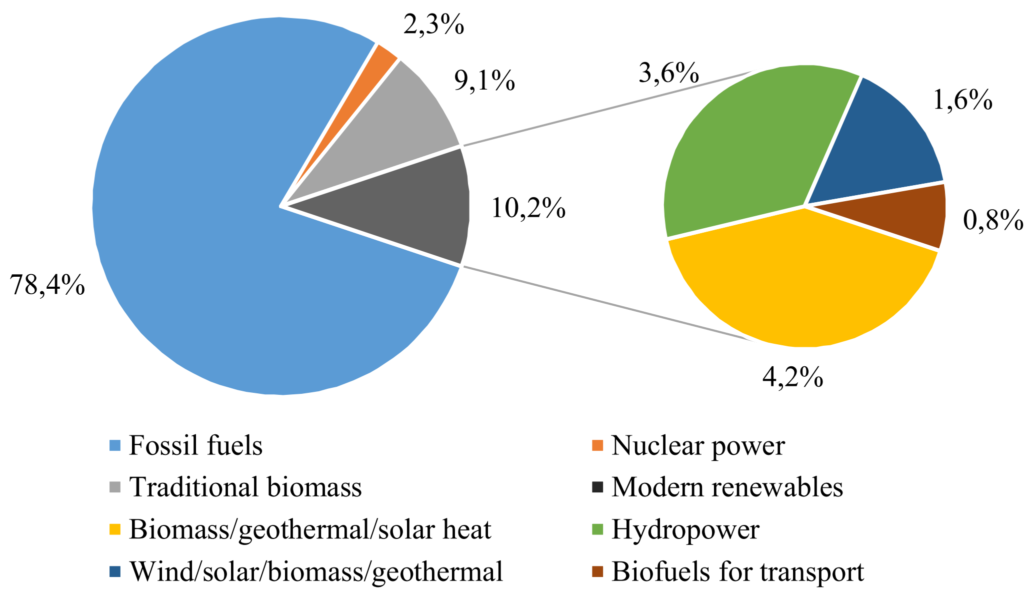

Figure 2. Share of energy resources in total energy consumption in 2015 (REN21, 2017)

Biomass presents a valuable source of renewable energy that can be used to produce heat, electricity, chemicals and transport fuels. The traditional biomass takes the biggest share of the total biomass usage in total energy worldwide consumption. The shares of biomass in 2015 in the world are given in the Figure 3. The significant part of the biomass-based energy is still used for cooking and heating in developing world. Such applications can be hardly called efficient and the biomass harvesting is mostly not sustainable. However, the modern bioenergy sector is progressing also in developing countries (REN21, 2017). Moreover, biofuels become more important; they have increased their share for 1% in 2015 in world's energy resources of total energy consumption.

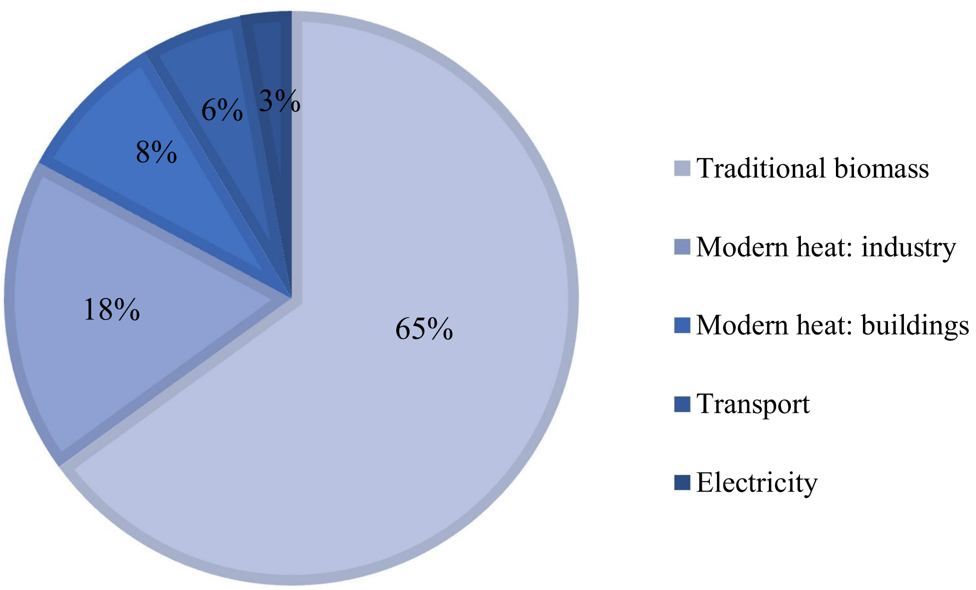

Figure 3. Biomass share in total final energy consumption in 2015

Total biomass primary energy supply was 56.2 EJ globally in 2012, with total renewable based energy equal to 75.4 EJ (IEA, WBA 2015). At the same time, electricity generation from the biomass in the world in the same year was 439 TWh, while total electricity generation from fossil and non-fossil sources was 22 752 TWh. The leading countries of the primary biomass-based energy consumption are China, India and Nigeria. Table 1 shows biomass distribution in different fields for energy supply and consumption.

Table 1. Biomass supply and consumption distribution in the leading countries in 2012 in EJ (IEA, WBA 2015)

	Final energy				**Final energy transformation**				
Country	**Primary energy**	**Electricity only**	**CHP**	**Heat only**	**Industry**	**Transport**	**Residential**	**Commercial**	**Others**
China	9,04	0,64	-	0,06	-	0,05	8,29	-	0,17
India	7,74	0,48	-	-	1,25	0,01	5,72	0,28	0,06
Nigeria	4,53	-	-	-	0,31	-	3,72	0,13	-
USA	3,71	0,59	0,33	-	1,14	1,09	0,43	0,09	0,29
Brazil	3,27	0,01	0,26	-	1,47	0,5	0,29	0,01	0,2
Indonesia	2,26	0	-	-	0,26	0,02	1,94	0,01	0
Ethiopia	1,78	-	-	-	-	0	1,42	0,01	-
Pakistan	1,25	-	-	-	0,14	-	1,09	-	-
Germany	1,17	0,21	0,3	0,07	0,12	0,12	0,27	0,05	0,24
Thailand	0,98	0,1	-	-	0,35	0,04	0,27	-	0,01
EU 28	5,73	0,77	1,24	0,24	0,97	0,62	1,64	0,12	1,07
World	56,2	3,42	2,2	0,47	7,81	2,51	34,67	0,97	2,55

Biomass itself is an organic matter. There are general types of the biomass: wood and agricultural products, solid waste. The woody biomass, including logs, chips, bark, and sawdust, nowadays provide around 40% of biomass based energy. Besides mentioned sources, any organic parts could be used for energy generation, for example, agricultural and forestry residues. Some industries, such as pulp and paper mills, utilize their own waste to produce some share of the steam and power, which are required for the operation. Nevertheless, it could not provide with necessary amounts of energy, the additional one should be bought. The solid waste could consist of the plastics, which is produced from petroleum and gas. However, solid waste combustion has potential for usable form of energy generation. This resource contain one-fourth energy potential of some types of coal. Bacteria and fungi make dead plants and animals to rot in their own purpose to survive. The waste decomposition accompanies with methane gas release. The behavior of this gas is dangerous; it is explosion and fire hazard. Methane could be collected and purified to be used for electricity generation and domestic cooking and lightning. Ethanol production is fermentation of the sugars and starches from the plants mostly, namely from the all matters that consists of cellulose, sugars and starches. Biodiesel is chemically produced from the vegetable oil, animal fat and greases, which react with alcohol. The most common source for biodiesel nowadays is soybean oil. Ethanol and biodiesel are used for the transportation purposes, in combination with the gasoline and diesel or in pure condition.

2.2 Potential of biomass

Any organic object could be converted into energy. Photosynthesis allows carbon dioxide and water transformation into sugars and oxygen with the help of the sunlight energy. These compounds provide plants with energy and nutrient materials. Sugars and cellulosic matter enforce the possibility biomass conversion into energy. Biomass is a renewable source, as far its supplies could be cultivated and there is always an asset of the waste.

The woody and herbaceous could be used for energy generation as a biomass. The key requirements for them are high yield, low cost and minimal demand for cultivation operations. For some countries, water consumption by the crops could be a limiting factor. The climate, soil, fertilizers also greatly influence the characteristics of the biomass. However, there is a biomass asset worldwide, which is not for food purposes. In addition, development potential of the forestry and agriculture provide target increase to fulfill for biomass usage for energy purposes (Bentsen *et al.*, 2010).

Undoubtedly, the main reason of the increase of biomass usage is the global climate change. This is caused by significant amount of the greenhouse gases emissions, huge part of which is a result of the fossil fuel combustion. Thus, the optimal possibility to prevent climate change is to replace fossil fuels partly or completely by renewable energy sources. The sustainable production of the biomass allows carbon dioxide emissions to be equal to capture by the new crop during the growth. Hence, this type of the renewables prevent additional carbon dioxide emission formation in the atmosphere.

The global economic growth cause the increase of the energy demand. Biomass has a potential for the covering significant part of this demand. In addition, world could run out of fossil fuels, and biomass could be available everywhere. Biomass gives the opportunity to replace fossil fuels and to make dependence on them lower. The biomass is more available worldwide; its asset in many regions exceed fossil fuels ones. This allows countries being more self-independent. In addition, the cost of biomass-based fuels is lower, what also makes it more attractive. Finally, there is a lot of waste, which is biodegradable, and by-products that could be converted to useful energy. This waste purpose allows reducing landfill taxes, expanses for waste transportation and landfills maintenance, and big areas of the land could be likewise saved.

According to previous paragraphs, the biomass usage is going to increase its share in world's energy mix. However, it requires some rules and limitations for its proper development. There is still no worldwide sustainability criteria for biomass. However, certain key issues can be formulated to characterize the sustainability in this sector. The one of them is connected with the land use. Biomass should not cause deforestation or compete with the food industry. In this option, all the natural habitats should be protected and undamaged. There is also socioeconomic factor, which influences the sustainability criteria. It is important to prevent usage of the children's labor, low employment, inadequate remuneration and careless health and impairment of education development. Talking about the environment, the key issue is to reduce air, water and soil pollution, prevent soil and forest degradation and lower the usage of the sources including water.

Fossil fuels have its wide usability because of their beneficial and stable characteristics, such as HHV, which could be twice higher than the same of biomass has. This and additionally high moisture content make storage and transportation more complicated. The difference in the quality of biomass and biofuels make it impossible to replace fossil fuel on the existing boilers and engines.

Despite to amounts of the produced energy and logistics simplicity, biomass inferiors to fossil fuels in low availability. There is a possibility to use fossil feedstock after exact extraction, while growth of the bamboo takes up to 4 years. Nevertheless, there are positive aspects such as biomass sustainability and environmentally friendly fuel. Its combustion brings no additional carbon dioxide emissions into the atmosphere.

Renewable energy resources such as hydro, wind and solar power could not cover all the energy generated by fossil fuels, as far the biggest share of these technologies allows only electricity generation. At the same time, biomass could be used at the combined heat and power (CHP) plants or at the plants with the separate generation.

In the view of efficiency biomass parameters are low (16-43%) in to comparison to wind energy conversion, but the same with wind power generation one. The released greenhouse gases are absent for all types of renewable energy, including biomass. Moreover, biomass lose to other renewable energy in water usage. Wind and solar power generation use small amounts for technical purposes, losses for hydropower generation is significant and account around 11 kg/kWh. The water, which is required for biomass crop growth is enormous and constitute 34 kg/kWh, the residue requires ten times less (Truong *et al.*, 2014).

The availability of the biomass in comparison to other renewable energy sources is rather high. It is conditioned by geological and topological requirements to generation. Such limits as sun radiation, wind speed or proper place for hydrogenation low the possibility of the usage. From this point of view, biomass could be harvested in different regions. However, talking about tropical biomass the potential area dwindles. Moreover, from technological point of view biomass electricity generation is more convenient, because its maintenance and grid operation control is simpler.

There are quite many supporting activities and targets for biomass promotion in different sectors. The long-term scenarios contains different areas of the biomass usage and complicated issues for its implementation. The main advantages of the biomass, well organized market and reliable supply chains are the key points to assume successful integration of the biomass into world's energy mix. The most prosperous countries in this implementation nowadays are Brazil, Finland, Canada, Netherlands and Sweden.

3. Tropical biomass

Forests of tropical climate zone present huge biodiversity of plants. The small-occupied territory contain up to 70% of the world's species (Pan, Y., et. al., 2013). In addition, these forests supply big variety of food and medicines. Moreover, the evolution of the species give them opportunity to prevent flooding, by steady absorbing and water releasing, restraining rivers' flows. Besides, recirculating of the nutrient matters save soil from erosion and siltation.

There always was a demand in products of tropical forestry, mostly in food industry; the development of the non-tropical countries could not totally manage to cover it. The complicatedness is in the cultivation of coffee, cocoa, and other wood and energy crop, which require special condition for growth. Nevertheless, variety of the species in tropical forestry require more diverse equipment and approaches for cultivation and servicing. Some zones on the Amazon costs could have up to hundred different species of trees, some of which are not belong to certain type.

The variety of the species provides with the range of the alternative and second-generation fuel feedstock. The sugar based material support industries, which are based on biomaterials. The potential of the tropical biomass is cultivation of the high productivity crop, which could supply market globally. In addition, in many countries, which have tropical climate, the logistic of the forestry and biomass supply well established. The industries, which have domestic scale and specializes on sugars, have good opportunity for non-food manufacturing development.

The lack of national support in some countries could become a challenge for the further development. In addition, uncertainly high price for producer and consumer makes tropical biomass market unattractive. Besides, new unknown technologies could be a barrier in the adoption of this possibility. Moreover, majority of the countries with tropical climate are properly equipped, do not have knowledge asset and exploring potential. Finally, as far there are many bordering countries with the same potential, there could appear competition. Nevertheless, it could bring and a positive impact, making the biomass price cost-competitive in the world's market.

The further development of the sector could bring positive impact of the countries' welfares. The export of the raw material and bio-based fuel could enhance financial situation, generating profit. This could, undoubtedly, stabilize regional economic position and increase social employment. In addition, it is an opportunity for national policy give attention to the agricultural and entrepreneurship sectors development and improvement. In spotlight, there is the prevention of the climate change by carbon neutral fuel usage. The government of each country, which could develop in this sphere, plays the main role in the further potential realization. It could consist of the encouraging of the long-term contracts with the investors, improvement of the supply and value chains and elaboration of the actions for the biomass support and control.

Further subchapters would be dedicated to description of some species of the tropical plants and byproducts. They are coffee tree, coffee parchment, eucalyptus and bamboo. There would be discussed their distribution in the world, most common application and usage for energy purposes.

3.1 Coffee tree

Coffee plants are usually small trees or shrubs, which are tend to flower, which belongs to *Coffea* genus. Coffee trees and their cherries are shown at the Figure 4. The drinks and other food products are made from the seeds of this plant. There is a huge variety of coffee types, which count up to 100 different species; however, the main categories are *Arabica* and *Robusta*. The most popular sort of coffee trees is Arabica; it counts up to 80% of the whole population. The next one in prevalence is 20% of *Canephora (Robusta)*. The height of the plant, which is drown in the tropical condition, could be up to 3.5 meters. The maturation and harvesting is usually in the coldest autumn or in the period of hardest and least rainfall. Coffee wood could start producing fruits on second or third year, and then its productivity could last up to 50 years. Coffee trees are fastidious: they require hills and cannot stay coldness.

Figure 4. *Coffee Arabica* with cherries (http://war-thunder-sajt.ru/fincas-matas.html)

The market of the coffee is one of the leading among other agricultural and agroindustrial goods. The green coffee production counts more than eight thousand million kilogram worldwide (Mishra, M. K., et. al., 2012). The total area occupied by coffee trees plantations is 10 million ha. This plant can grow in 80 countries with tropical and subtropical conditions. Latin America, Asia, Africa are the leading regions of the planting coffee trees. The financial market significantly depends on the coffee and by-products supply.

According to IBGE (2018), the total area covered with these two genus in Brazil, occupied 2.21 million hectares, from which up to 85%, what is 1.86 million hectares, are involved in the production. The total gross amount of these two genus of Brazil production in 2016/2017 was 2.78 million tonnes. Brazil is, undoubtedly, is the major producer and exporter of the coffee in the world.

The coffee industry has an opportunity to provide with not only residues and wastes from the coffee cherry but also with wood. According to Oliveira, J. L., et. al. (2013), 3.6 billion of the coffee trees were harvested in 2006 only in Brazil. There are also huge amounts of the coffee production waste of wood that is nearly three million tones. The available energy of the coffee wood in this country counts 50 PJ. The average weight of the old plant is 15 kg of the dry mass;

however pruning catch up to 75% of wood. Overall, energy application, in this case, allows useful utilization from social, environmental and economic point of view.

Coffee wood has relatively low moisture content (less than 20%) and rather low ash content (up to 1%) (Oliveira, J. L., et. al., 2013). At the same time, high volatile content (85%) provide high speed of burning and low stability of the flame. In addition, the density of the biomass is rather low, what make logistics more expensive and complicated. Briquette and pellets could be a good solution for this problem. In addition, the characteristics of the coffee wood shows a potential in conversion by the thermochemical treatment.

The extension of the coffee plantations and its current sizes give the reason to assume the huge potential for not only residues use but also the wood matter. It could be assumed that coffee wood has high sugar and lignin compounds content, what provide it with the energy usage potential. Nevertheless, this part usage for energy purpose requires more explorations and additional investments for careful examination.

3.2 Coffee beans parchment

The post-harvested treatment of the coffee left many byproducts, which are coffee ground, coffee husks, peel, pulp, silverskin. The coffee processing byproducts could be directly combusted or additionally treated. Pyrolysis, torrefication, gasification and hydrothermal conversion represent the possible pretreatment pathways. The products that can be obtained are biodiesel, bioethanol, biogas and biochars. The low density of the material require pellet usage to improve storage and transportation conditions.

Figure 5. Coffee cherry and its cross-section (https://gottsusa.wordpress.com/2015/12/02/for-coffee-connoisseurs/coffee-cherries-showing-beans/)

First of all, it is important to determine, where each part located in the bean structure. Figure 5 shows coffee cherry and its cross-section and the structure is explained in Fig.6. Whole cherry is covered with the skin. The parchment is the layer directly covering the bean after the silverskin. The next pressuring it segment is pulp.

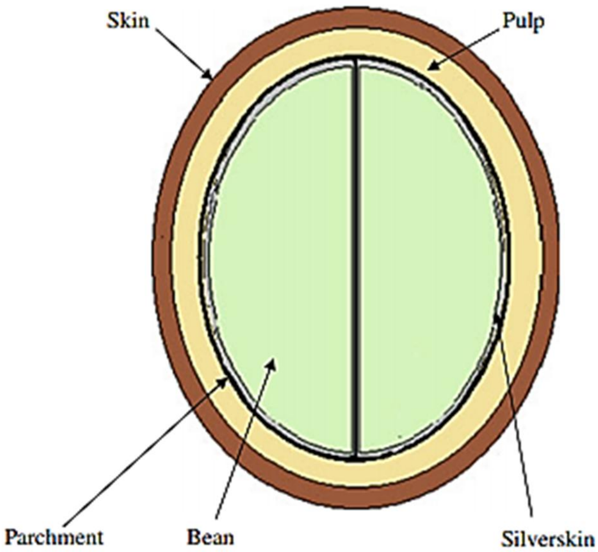

Figure 6. Cross-section of the coffee cherry with its structure (Mussatto, S. I., et. al., 2011)

The coffee residues accumulate the high amount of the volatile solids with the total amount up to 95%. The improvement of the characteristics could be reached by anaerobic digestion. The bacterial environment is under the steady condition due to stabile pH parameter. The anaerobic digestion is a good alternative for the coffee residues utilization (Lahcen, S. A. L., et. al., 2018).

During the preparation of the coffee for the food purposes it goes through several treatments. First steps are washing and drying, and then the pulp layer is taken away. This could be reached by fermentation or by regular mechanical methods. Then beans are treated by variation of technologies, which could depend on type of the species or its final purposes. However, the parchment could be got only during wet processing. In case of dry processing peel and pulp are detached together with the parchment. Thus wet technology requires drying, so beans are dried naturally or mechanically in special equipment. The next step is hulling, which takes away parchment with silverskin (Hughes, S. R., et. al., 2014). Peeling and polishing is the last step before sorting. The got green beans, as a result, are categorized by size, and other physical properties.

One of the possible ways to use coffee tree potential is usage of the husks, which amount is 22% from the total coffee weight. The gasification of this matter release some emissions, however, they are insignificant in comparison to fossil fuel level. This option seems to be suitable mostly for energy supply in the not urban region of the coffee cultivated countries. In addition, the reliably supply chain should be determined by increasing of the coffee yields (Galanakis, C. M., 2017).

The coffee bean parchment usually represents not more than 4% of the total bean weight. The average cellulose content is almost half, one third is lignin and one fifth is hemicellulose. In addition, the ash content of the coffee bean parchment is low (0.5%). These characteristics show the potential of the parchment usage. The most suitable is pressing and thermochemical treatment, in this case, anaerobic one is less reasonable. In addition, the calorific value of the coffee bean parchment has sufficiently high level, among typical wood fuels and is around 20 MJ/kg. The pulp and husk have high ash content at the level of 10% and lower HHV at 2-5 MJ/kg (Chala, B., et. al., 2015). The anaerobic conversion, gasification and briquette and pellets formation are the perspective ways of treatment coffee by-products as renewable sources of energy. The energy application allows by-products utilization for useful energy production.

3.3 Eucalyptus

Eucalyptus is a tree or a shrub, which belongs to myrtle family. There are about 700 different types of eucalyptus. This tree example is illustrated at the Figure 7. Their traditional land of growth is Australia and its islands. However, nowadays nearly 15 species are growing worldwide (Rockwood *et al.*, 2008). Among the other hardwood, Eucalyptus could be assumed as the most widely growing one. Its plantation total 18 million hectares in tropical and subtropical areas. This plant could be found in Africa, South America, Asia and Australia. Some parts of Europe and

North America are also suitable for eucalyptus. Currently, the growth of the eucalyptus plantation significantly increases. The commercial harvesting touched Congo, Indonesia, Thailand, Portugal, New Zealand and USA.

One of the benefits of eucalyptus is that it is not fastidious to the soil quality and environment instability. Moreover, these plants have high speed of growth and have resistance to insects, droughts and fires. The vegetative method of cultivation increase the efficiency of eucalyptus crop. Moreover, new researches in the field of genes improvement in tandem with gene modification cause hybrid clones with high efficiency and premium quality. Different species have different properties and characteristics; some eucalyptus are similar to wood and could be used for the same purposes.

Figure 7. *Eucalyptus rubida* in Burra, New South Wales

The most popular hybrids of Eucalyptus, which occupy up to 80% of the exciting plantations, are *Eucalyptus grandis*, *Eucalyptus urophylla*, *Eucalyptus camaldulensis*, and *Eucalyptus globulus* (Rockwood *et al.*, 2008). The most common among them is the first one in the list. It is popular for its adaptability and fast growing. The most potential from all eucalyptus are *Eucalyptus grandis* and its hybrid with *Eucalyptus urophylla*.

Integrated crop systems provide with big amounts of the eucalyptus cheaper than average market price. However, these prices are not still enough to have opportunity to be integrated into traditional market, despite the significant benefits of the advanced technologies of harvesting and genetic treatment.

There are such compounds in Eucalyptus that are important as polyphenols of the condensed and hydrolysable tannin varieties. Moreover, there are content of carbohydrate in this plant. The structure of eucalyptus allows protecting the plant from insects and small animals, from cold and ultraviolet. In addition, there are phloroglucinols, which has biological and ecological importance as antifeedants. The high amount of the polysaccharide and lignin gives to eucalyptus high advantage.

There are different application for eucalyptus usage. The most common one is production of the high quality paper. Moreover, it could be a part of fiberboard, firewood, plywood, lumber, charcoal, tannin. Honey and essential oils manufacturing are also possible application for eucalyptus usage (Rockwood *et al.*, 2008). In addition, in some regions this plant plays key role in energy source, building material and adsorbent production. In energy aspect, eucalyptus shows good properties in biofuel and biochars making. There is a significant potential for eucalyptus in bioenergy development.

The methanol and ethanol presence depends on the density of the wood and its moisture content. *Eucalyptus grandis* and *Eucalyptus urophylla* shows the most suitable properties for energy purposes. They contain the best indicator of sugars and methoxyl group despite of the low density among other wood crops. The gene control and knowledge of the lignin structure allows low lignin compound to make pulping more effective without additional financial and energy expanses. This provide bleaching and delignification with good alternative without any harm to the wood quality.

According to Rockwood (2008), eucalyptus could be a source for biofuels and byproducts. The cellulose conversion could be implemented with the 80% efficiency. Acid and enzymatic hydrolysis treat hemicellulose until the sugar formation. The fermentation allows ethanol getting. Solid wood such as eucalyptus could be used completely for district combustion. In addition, there are such options as ethanol and methanol as biofuels. The liquid after eucalyptus carbonization also could be used as a basis for fossil fuel replacement. Biooil is also produced in some countries with cost-competitive prices. The less oxygenated, more stable oils could be got from mild pyrolysis in deeper beds. However, the higher efficiency and lower prices could be achieved by direct liquefaction. In addition, bio- and thermochemical treatment allows conversion with high efficiency for the fuels and additional compounds for oil.

Gasification of eucalyptus shows such products as biofuel, energy, chemical materials and other applications. Methanol production is implemented by gasification. However, woody biomass are not prepared for such generation. Nevertheless, it is a field of the research, as far methanol is perspective transport fuel.

From the economical point of view, eucalyptus requires special management, as far the cropping for energy purposes will influence its economical and viability aspects. The bioenergy fuel is supposed to be residues from agriculture and forestry (Shepherd, M., et. al., 2011). This assumption devalue any of such source. From this point of view, eucalyptus plantations are untouched and unused resource for renewable energy.

The potential of eucalyptus cause its exploration and cultivation of its crop all over the world. It is expected that North America, East and South Asia and OECD Europe will be leading countries in eucalyptus cropping in 2025 (Sims, R. E., et. al., 2006). According to its properties, which are described above, eucalyptus shows potential as an energy source of different types. The current crop plantation could be expended for widen of the market to occupy bigger share of the energy sector. Australia is already on its way to this. There are projects for crop amounts increasing to get more heat, electricity, pharmaceutical oils and activated carbon.

The advanced treating methods provide with the short rotated crop of genetically stabile monocultures. The landscapes are safe; the same is soil, which is less harmed from the erosion, because of the rare land cultivation. Eucalyptus shows high potential among other biomass as a productive and economically viable type. Despite of the obvious requirements in water and fertilizers, the whole agricultural process is more economically beneficial.

The commercial cultivation is expected to expand in purpose of bioenergy supply. The future potential of eucalyptus is determined by high speed of growth, high adaptation abilities to conversion technologies and treatments. There is a huge potential for research of the possibilities and characteristics of the other species of this plant. Moreover, genetic modification could be improved and applied more intensively.

3.4 Bamboo

Bamboo belongs to *poaceae* (grass) family. The stem of the bamboo is strong but flexible (Figure 8). This plant has tendency to reach high sizes, for example, *Dendrocalamus brandisii* could grow up to 35 meters, with stem diameter near 25 centimeters. The speed of growing is extremely high and can reach up to 90 centimeters per day (Truong *et al.*, 2014). The productivity of this biomass is high, for example, bamboo biomass yield in China is 167 tons per hectare (Lobovikov *et al.*, 2007). Moreover, possibility of the biomass regeneration allows not being fastidious in land, thus degraded solids could also be suitable. The warm and wet environment is favorable for its growth. The excitable areas for these plants are tropical and subtropical. The bamboo covers about 36 million hectares in the world. The most common areas for it is East Asia. India, China and Indonesia lead in available bamboo asset.

Figure 8. Stems and leaves of bamboo (http://unisci24.com/187737.html)

Fast growth and some other beneficial features allow the active usage of bamboo for material production: pulp and paper industry and textiles manufacturing. Building and home decorating materials are also could be made from bamboo. In addition, Asian culture imply this plant usage for cooking purposes. Besides, light and durable quality of bamboo introduce it as a material for musical instruments. Finally, bamboo can be used as a fuel for energy purposes.

In general, bamboo contains rather low ash, high energy content (up to 22 MJ/kg) and relatively low moisture content (8-23%) (Scurlock, et. al., 2000), in comparison with other agriculture biomasses. One other beneficial feature of bamboo for bioenergy is low nitrogen and sulphur amount. At the same time, it has high alkali content, which can cause slag formation in the boiler during combustion. Kaolin could be an additional compound to prevent sintering by binding alkali.

The possibility of the bamboo usage encourages exploring its capabilities and characteristics as an energy source. Most of these researches were hold in the countries with the bamboo asset, for example, China and India. The firewood or foundation of coal production for domestic purposes is tried to be replaced by bamboo. Ethiopia and Ghana tries to reduce the usage of the woody sources by supply of the bamboo.

The most advanced country, from the energy usage point of view, is India. Bamboo asset and access to different technologies of treatment allow its usage in more efficient way. Instead of direct combustion, this type of biomass is used for co-generation of electricity and heat power. Moreover, such progressive technologies as gasification and pyrolysis are used to increase efficiency of power generation.

Despite of some benefits of bamboo, such as high HHV, there are some disadvantages. Harvesting of this plant is complicated because of the selectivity; the only shoots, which are grown enough, are taken. The total annual yield is unstable and could be in positive conditions 50 tons per ha. Moreover, the planting requires significant areas as far it is done vegetative, what increase expanses. The time of the awaiting is also high and takes several years. Finally, there is a huge competition on the bamboo market from the non-energy side.

According to analysis by Poppens *et al.* (2013) the interest to bamboo as an energy crop could cause loss of biodiversity due to mono-cultivation. In addition, there is a danger of the blooming bamboo taking over the perfect soil, which is used for the other purposes. Besides, its slow growth, biological issues and management risks threat the investments in bamboo plantations. In this case, the retardation of the harvesting, which is caused by bad weather and climate conditions, make the strong influence on the bamboo economic stability. There is no confidence in insects and disease protection. Moreover, natural disasters such as fires and droughts could reduce bamboo potential.

4. Biomass technologies

Nowadays, there are many different ways for biomass utilization. The most common way to convert energy from the biomass is thermo- and biochemical treatment. Some methods specializes into cellulose transformation, while others concentrates on microorganism formation. Figure 9 shows routes of biomass transformation into energy or fuel. The thermochemical treatments include big variety of the possible ways to use biomass, such as direct combustion to get final product, gasification and pyrolysis to receive the intermediate product (Boyle, 2004).

There are also biochemical treatments that are less used. The microbiological fermentation is used for energy and agricultural purposes. The wet and problematic feedstock could be treated in this way. These processes are anaerobic, ethanol fermentation, and methane production in landfill. The digestion, in the first option, gives available heat, methane and hydrogen gas (Sharma *et al*., 2014). The retrieved gas should be cleaned from toxics and could be used at power plants as a fuel and solid part could be an agricultural fertiliser. The ethanol is mostly use for transport purposes. The release of the methane allows faster reusing of the landfill.

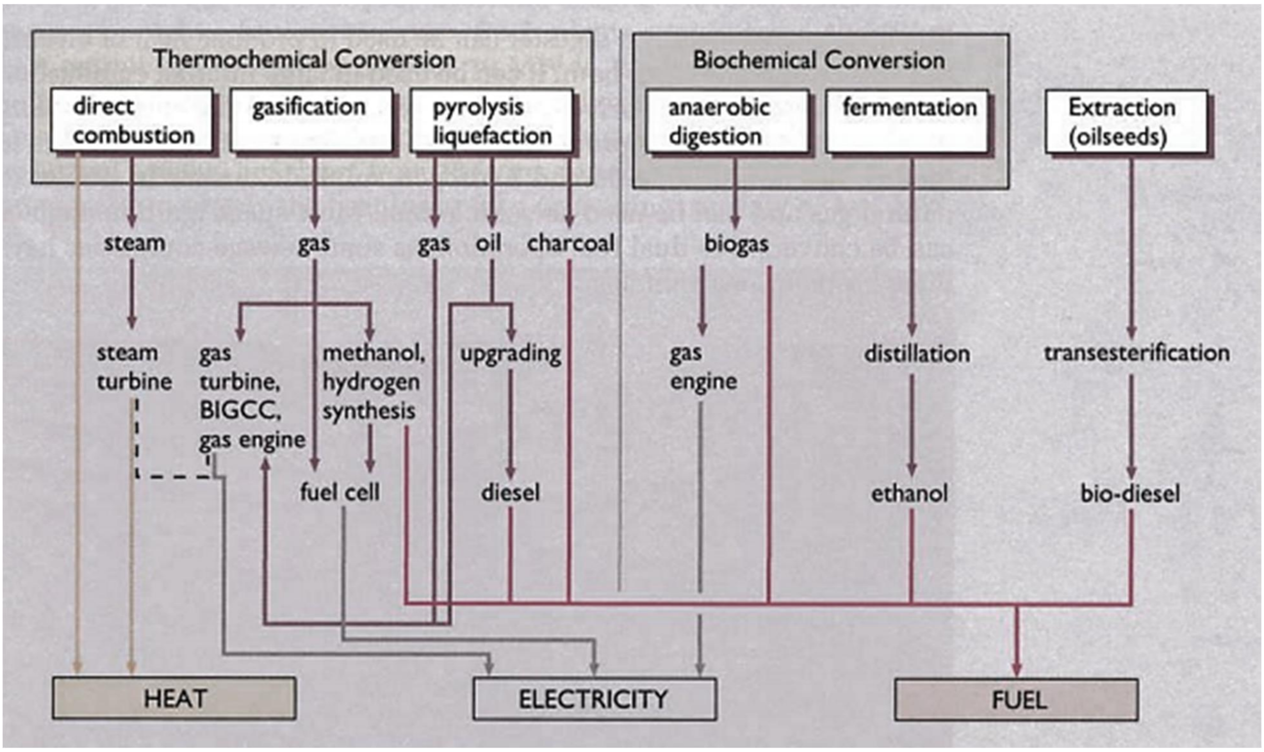

Figure 9. Possible ways to convert energy from biomass (Boyle, 2004)

The basic application for biomass in energy purposes is direct combustion for domestic purposes like cooking and heating. In addition, there is another application such as burning at the CHP plants. In this option, the oxidization is provided in the boiler to get steam with high potential to make energy due to steam turbine and district heating exchangers. In a word, it is combusted as a regular fuel at power plant in specially designed biomass-fired boilers. Moreover, biomass usage is co-firing. This could be applied on the existing boilers without any changes and efficiency losses if up to 15% of biomass is used. The higher percentage until the combustion of equal shares could be organized on the existing boilers. However, it requires additional modifications and higher quality of the biomass. The further conversion is applied on partly or fully changed boiler, which purpose is biomass combustion.

Another possible application is gasification of the solid biomass. This option is process of partial oxidation, in which low calorific gas is produced. The last one could be used for combined heat and power generation by means of gas turbine or simple combustion in the boiler. The characteristics of the final product depend on the process conditions and construction of the gasifier. The more efficient is combined gasification, which is based on coal. Fuel cell is also possible way to use gasification in the regions with shortage of fossil fuels and problems with its supply. The efficiency of combined gasification could be even higher then direct combustion.

Pyrolysis is also popular treatment of biomass nowadays. It is a process of change of the chemical composition due to thermal treatment in an inert environment. The changes in the process of pyrolysis enable to get fuel liquids, which are similar in its properties to diesel. Further development in this field is work with the high pressures, and low pressures with catalytist to get hydrogen and pyrolytic oil (Sharma *et al.*, 2014). The pyrolysis and gasification make storage and transportation cheaper. Moreover, the fuel flexibility and supply reliability increases. Nevertheless, these processes require heat input for syngas production.

Besides these main processes, there various pretreatment steps that can improve the properties of raw biomass feedstock before the final utilization: drying, densification, torrefaction, hydrothermal carbonization and so on. The carbonization is an accelerated process of charcoal formation, which is similar to natural fossil fuel creation. During the process of hydrothermal carbonization, the weak compounds are decomposed with the release of the volatiles, the carbon content is simultaneously increases due to reduction of the hydrogen and oxygen. The higher temperatures (up to 270 ºC) make environment for formation of the condensable gases.

Overall, each way of treatment have their advantages and disadvantages, which are described above. Nevertheless, thermochemical way of biomass utilization is more efficient, despite of required pre-treatments such as drying, densification torrefication, and hydrothermal carbonization. The low of the moisture content and increase of the density simplify transportation and storage and make combustion requirements more appropriate. In their turn, torrefication and hydrothermal carbonization in addition to previously described advantages increase hydrophobicity and make properties of product close to coal ones. Thus, this ways especially HTC have huge potential of usage. Hydrothermal carbonization, for its part, is described more detailed in the following subchapters.

4.1 Hydrothermal carbonization process overview

Friedrich Bergius was the first who described the process of hydrothermal carbonization (HTC) in 1913. This technology is an effective way to transform the feedstock into solid fuel with rather beneficial characteristics and calorific value comparable to brown coal. It is an opportunity to convert waste streams and biomass of lower quality to a valuable solid fuel (Oliveira *et al.*, 2013). Thus, the most preferable feedstock for the treatment is organic materials with high moisture content.

The process of hydrothermal carbonization treats the biomass mixed with water at the temperature in the range of 180-250 ºC (Román *et al.*, 2012) and corresponding saturated pressures of 2-10 MPa for a certain time. The HTC includes the parallel processes such as hydrolysis, polymerization, decarboxylation and dehydration. The basic processes of the hydrothermal carbonization resemble the torrefication (dry pyrolysis). However, the saturated conditions of the process decrease the stability of the lignocellulosic components, and the decomposition mechanisms work more intensively in comparison with torrefication (Román *et al.*, 2012). Among all lignocellulosic components, mostly the hemicelluloses are actively degrade due to their high reactivity (Hoekman *et al.*, 2011). In general, the HTC process lowers the oxygen and hydrogen contents and leads to the raise of the carbon share. This process requires saturated conditions. Figure 10 illustrates the basic schemes of the hydrothermal carbonization and pyrolysis in general.

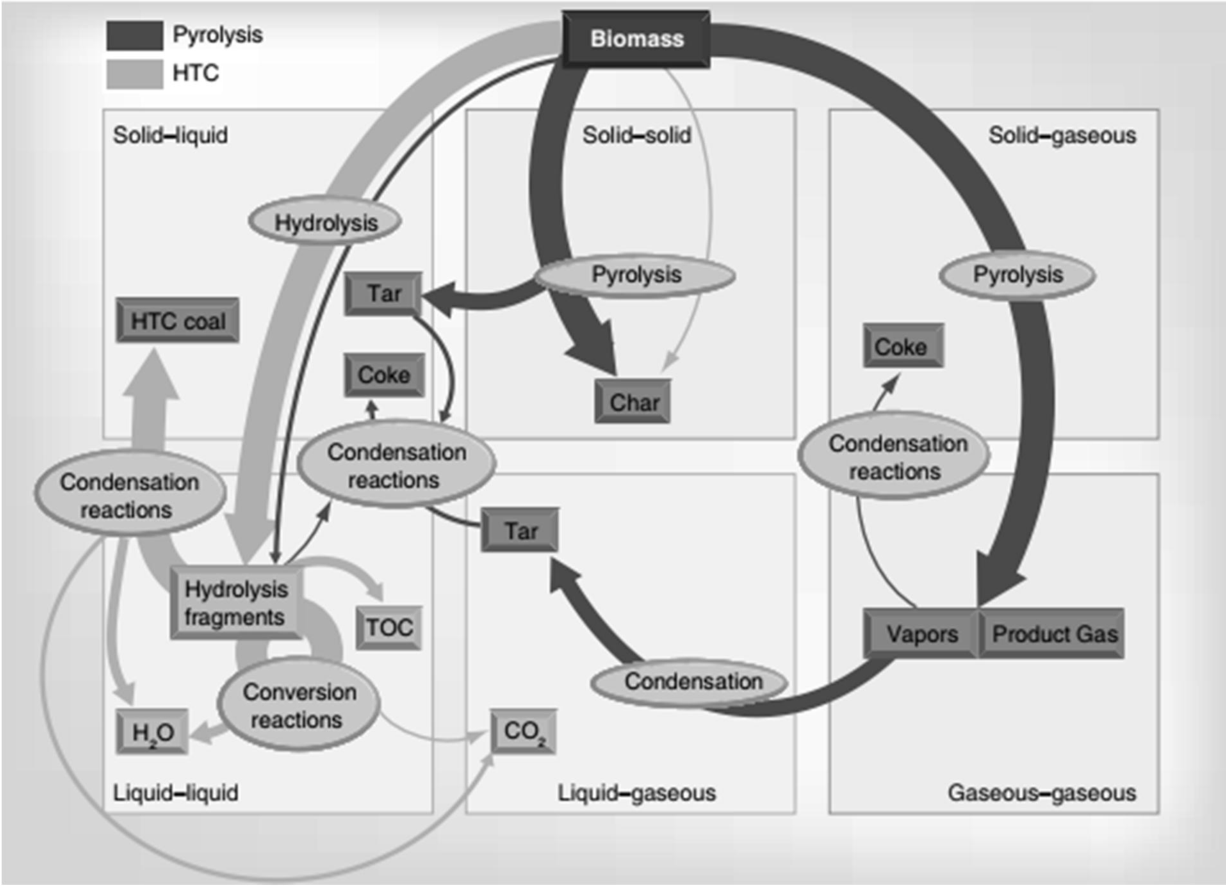

Figure 10. The scheme of the hydrothermal carbonization and dry pyrolysis (Libra *et al*., 2011)

Solids, liquids and gas are three products of hydrothermal carbonization process. The average resulting yield is shown in the Table 2 (Robbiani, Z., 2013).

Table 2 The distribution of HTC products

Product	**Weight, %**
Solid	50-80
Liquid	5-20
Gas	2-5

The produced solids (hydrochar) is the main product and characterized by higher carbon and lower oxygen content compared to the feedstock. The carbon content directly influences calorific value. The enormous benefit of the HTC that, in result of the decomposition the loss of the mass is more than the loss of energy. As a result, the product have the higher energy density. The hydrochar can be used as catalysis, energy storage, for soil amendment and carbon sequestration. However, the most common application is additional fuel or replacement of the coal in gasification process and direct combustion.

The liquid products of the HTC are usually acidic and contain both organic and inorganic compounds. Nitrogen, phosphorus and some mineral matter originated from the raw material can be also found in the produced liquids. The gas product contains 70-90% of the carbon dioxide and insignificant amount of the carbon oxide, methane and hydrogen (Ramke *et al.*, 2009).

The HTC reaction is known as exothermic one but the released heat is not enough for reaction sustenance and energy balance stabilization. Therefore, the HTC process requires external heat source to be provided. The key benefit of the HTC is the ability to convert the wet biomass into highly carbonaceous solid fuel without initial drying. In the comparison to the conventional torrefication, the process of HTC could take less time and could be suitable for wide range of the feedstock. However, the installations providing the high-pressure conditions are rather expensive and their maintenance is more sophisticated. Such pretreatment improves the storage, transportation and handling characteristics of biomass materials. In addition, the improved grinding properties and hydrophobic behavior make the hydrochar rather attractive fuel.

4.2 Influence of operating parameters

Reaction temperature is the main influencing factor of the hydrothermal carbonization. Higher temperatures lead to higher intensity of the decomposition processes. As a rule, the lowest temperature limit for the hydrolysis is around 180 °C. The carbon production is depends on reaction severity, which is calculated by following formula (Funke *et al.*, 2010). The reaction severity mostly depends on temperature and residence time.

$$f = 50 \cdot t^{0.2} \cdot e^{-\frac{3500}{T}} \qquad (1)$$

The uncertainty of the reaction velocity does not allow setting of the accurate resistance time. The duration of the process could vary between 1 and 72 hours. This time provide better severity and low organic losses. The duration influences on the results; the longer sample is treated the less weight it have and higher calorific value is (Sermyagina *et al.*, 2015). The process is taking place in a closed vessel, and the pressure is kept at the saturation level. Higher temperatures result the more intensive process of the hydrothermal liquefaction (Gollakota, A. R. K., et. al., 2017). The ratio between feedstock and water also has certain effect. The successful hydrothermal carbonization process requires the complete mixing of the solid feedstock with water. The polymerization starts faster if the biomass content is higher.

4.3 Current state of HTC technology

There are only few HTC technology manufactures on the industrial scale. There are some companies, which provide with several tons biomass conversions capacity per year. The most advanced in this field companies are AVA-CO2, SunCoal Industries and TerraNova Energy. AVA-CO2 was the first company, which has introduced the industrial size of the reactor in 2010 (AVA CO2, 2018). The manufacture capacities allows adjust equipment to the customer requirements. The services track the whole chain from the production up to commissioning at the customer's place. Moreover, used technologies are similar to existing and not complex, what allows easy maintenance and operation. Reactors of this company are capable to produce annually up to 9 thousand of hydrochar. There are also circulation and purification of the liquid residues; several possible pretreatments are also elaborated.

The SunCoal also uses the technologies, which allow meeting customer requirements (SunCoal, 2018). The CarboREN methodology treat biomass to get it in different shapes, such as powder, pellets and others. The pathway of the company is accompaniment of the equipment including feasibility material of the project and test of the facilities. The conversional capacities of the reactors of this company could reach 5 thousand tons of the feedstock. Unlike the previous ones, these reactors are of continuous type.

The reactors of TerraNova company are also of continuous type. Its undoubtful advantage is compact size of the reactor, what meet the requirement of the limited free space (TerraNova Energy, 2018). The single unit capacity allows conversion of the one and a half thousand tons per year. The special tube construction of the reactor increase its efficiency of the installation by using heat recovery.

There is also Ingelia S.L. company, which has possibility to treat 6 thousand tons of the wet raw material per year (Ingelia, 2018). The benefits of these reactors is specified recovery system. The recirculation of the heat and re-usage of water allows efficiency increasing in processes of the hydrochar formation. These reactors also provide with byproducts such as liquid, which could be used as a fertilizer, and biochemicals. Moreover, this reactor secure pellet formation.

The required investments, production costs and the future market are the main influencing factors on the HTC process development. In the designing process, there are several key issues. One of them is biomass raw material cost. Moreover, there is also an issue of the feeding process. Its type and the capacity of the equipment are defined by the size of the particles. Another influencing point is the required amounts of water. The heating demand to cover the needs of the process can be also problematic. The possible integration pathways with industrial or energy facilities can improve the situation significantly.

In addition to the heating of the feedstock, drying of the produced hydrochars should be effectively designed. The heat recuperation could improve the system. The recycling of the liquids and gases could lower the demand in the heat source, decrease the amount of waste streams and return some important nutrients into the process. Some valuable chemical compounds can be found and capture from the HTC liquid phase.

4.4 Possible HTC-coal applications

The one of the most common options for hydrochar is a combustion as a renewable source of the energy. This process does not bring additional net carbon dioxide emissions as far it compensates the ones, which were captured during the feedstock growing. The increased calorific value is also establish biocoal as a suitable fuel. It could be used at the CHP plants, industrial sites, as the main fuel, as the second fuel for co-firing or for gasification. The biomass combustion option is complex. There is a huge variety of the density, shape, moisture content and other characteristics such as ash, volatile and oxygen content. The problems of pretreatment, such as drying, requires big amounts of energy. The biocoal is solid fuel with uniform consistency and high calorific value.

The process of activation enhance the porosity and increases the surface area of the material. The high porosity and possibility to influence on the final parameters of the products could help them to satisfy huge surface with compact size conditions. These facts allows the product to take part in energy storage process, which are currently use electrodes. The biochars could replace the activated carbon and fossil material in supercapacitors and Lithium ion batteries (Titirici *et al.*, 2012). Adsorption is another possible option to use biocoal after activation or even prior. It is usually used for water purification. Highly porous activated carbons allow to adsorb various impurities from the liquids. The activated biocoal in the high-pressure conditions could capture and store methane. Activated biocoal likewise shows good potential for gas adsorption, by capacity of methane and hydrogen storage at high pressure. KOH activation and HTC treatment optimization could improve the efficiency of capture by adaptation of pore size density (Falco *et al.*., 2013). In addition, the carbon dioxide capture possibility is a positive perspective (Sevilla *et al.*, 2012). The biochars could be easily and cheaply done in big amounts what is also important for the storage material. Another possible way to use biocoal for improvement of the soil quality. The properties of the HTC-coal allows its using to bind ions and water. In this application, the porous structure of the chars, which is similar to used charcoal, is the key point. It allows keeping amounts of water in the ground. The nutrients stick in pores of the treated material and slow oxidization increase nutrient keeping capacity.

The beneficial characteristics that were already mentioned in this chapter allows HTC product usage as heterogeneous catalysts or its supports. This application also requires renewable source and good availability of the material. The selection of the reaction could be caused by nitrogen-doped and increase the catalysts potential.

4.5 HTC potentials and barriers

The HTC technology introduction enable the local economic development. This type of treatment of biomass uses the regional resources and increase of the employment. In addition, the agricultural and entrepreneurship development could be encouraged by this sort of industry introduction. Moreover, there is a possibility to cooperate with small commercial heat and power plants.

The relative novelty of the technology could be a potential barrier. The social adoption could be slowed and prevented by fear and uncertainty of new technologies. In addition, there is little understanding of the hydrothermal carbonization and possible use of its products in some regions. The problem of the people's acceptance could be solved by promoting HTC technology.

As was mentioned above, the hydrothermal carbonization production provides several important emissions reduction. The organic nature of the raw material is potential in the aspect of the greenhouse gases (GHG) abatement. The process produces the gases, which are mainly represented by carbon dioxide. However, the gaseous part is not explored as well as capture of the carbon dioxide. The acid environment and metals of liquid matter limits the whole usage as a fertiliser. In the total, the liquids have possibility to be recirculated.

The challenge of the environmental impact is in uncertainty of the current knowledge. There are products of the reaction that are still under exploring. There is still limited amount of information about the behavior of the products over time and possibilities of its decomposition and further reactions. Hydrocarbon trace gases could also bring some danger to the situation as far the influence of different GHG varies (Havukainen *et al.*, 2012). The liquid matter also should be more carefully examined and explored.

The potential of the hydrothermal carbonization in the economic aspect is significant as for the current markets of the biomass treatment are developing. Before the increase of the scale of HTC production the competitiveness would be low, what would help in the industry development. Moreover, the instability of the fossil fuel supply and growth of its cost and GHG taxes, give the possibility for the use of the biomass treatment potential. In this case, the improvement of the forestry and biomass supply chain is predetermined.

The economic disadvantage is absence of the developed HTC market, which elaboration requires investment and hard work. The implementation of the long-term guarantees could improve the economic feasibility. Alongside with fossil fuels, biomass-based fuels are forming the biocoal price in the market to create the competitive environment. The small amount of the awareness about hydrothermal carbonization in comparison to torrefication, for example, also could badly effect economic HTC image. The equipment supply chain is unstable and uncertain in the future deliveries. Moreover, the high ash content of the bio-coal could bring harm to the boilers, in which they would be combusted. This aspect could be precisely described only after years of the direct operation. Besides, content of the particle matters in the flue gases could cause additional economic expanses and challenges in environment field.

The yields and the product characteristics of the HTC process are guided by the process conditions and the feedstock properties. As a result, more knowledge is needed in order to predict and maintain the necessary outcomes of the HTC products. In the continuation of present work, the results of the bench-scale HTC experiments of several tropical biomasses will be presented and discussed.

5. Hydrothermal carbonization of the Tropical biomasses

The overview of all the materials, background of their usage and potential in the energy field were described in the previous chapter. The exact names of the species and their origin followed by the methodology and results are presented in the following. The hydrothermal carbonization was carried with four different samples of the tropical biomass: coffee tree wood, parchment of the coffee cherry, eucalyptus and bamboo.

5.1 Materials

The first sample is *Eucalyptus grandis*. The samples were taken from the plants, which is around 6 years old. The plantation, where this sample was grown is commercial and represent experimental units of the zootechny department of the Federal University of Viçosa, Minas Gerais, Brazil. The woody samples were brought from the small pieces with the thickness of 2 cm, which were taken from the top, middle and basal parts of the stems.

The samples of the wood of the coffee tree and parchment of its cherries is taken from the Minas Gerais state in the north of southeastern Brazil. These samples belong to genus of *Coffea Arábica L.* Minas Gerais is the main coffee produces in Brazil. There are were mainly grown *Coffea Arábica L.* and *Coffea Robusta*. The size of the parchment was the average that is usually got from the hulling process and equaled to less than half of centimeter.

Giant Bamboo is another sample under consideration. It was originally taken from the plantation, which is located in the Federal University of Viçosa, Minas Gerais, Brazil. The approximate age of the plant at the moment of the sample was getting was between 5 and 7 years. The small pieces of the specimen were taken from the middle and top parts of the stem and have average thickness between 2 and 3 cm.

5.2 HTC installation

The experiments of hydrothermal carbonization were carried out in batch reactor of Lappeenranta University of Technology (Lappeenranta, Finland). It was designed and constructed in this very university; and it is presented at Figure 11. The total internal volume of this installation is one liter. Its main tube is made of stainless steel and has height 705 mm and diameter 42 mm. This tube has screw closing at its bottom; and at the top, it is connected with flange. The main part of the reactor is heater, which heat the tube interactively. It is electric heater coil with the power, which is equal to 10 kW. Thick layer of insulation and steel sheet cover prevents the heat losses during the process.

The temperature is controlled of the tube by two thermocouples in the upper and lower parts. The thermocouple for upper zone is located at the 245 mm from the top, and for lower one at the 645 mm. There is also one thermocouple outside of the reactor, which controls temperature of the surface. At the top of the installation, there is a pressure sensor, which is not only measures pressure, but also forces relief valve opening, if the pressure inside exceeds 40 bars. Proportional-integral-derivative (PID) controller maintains the temperature level inside the reactor, which is required for the experiment, during the whole process. All the temperature and pressure data is automatically registered every three seconds.

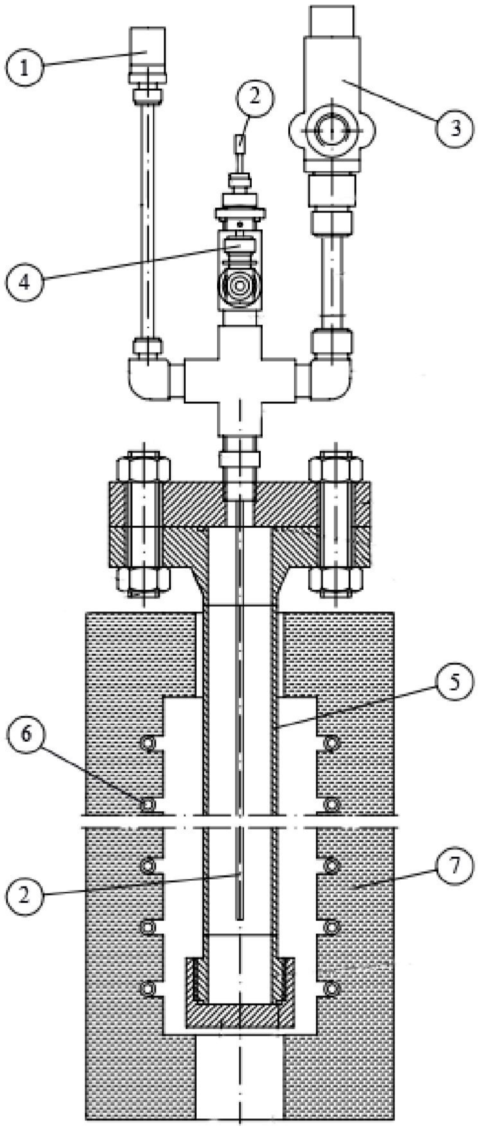

Figure 11. HTC reactor, where 1) pressure sensor; 2) thermocouples; 3) safety valve (maximum set parameters: pressure 40 bar, temperature 300 ˚C); 4) sampling valve (maximum set parameters: pressure 215 bar, temperature 315 ˚C); 5) reactor tube; 6) heater; 7) insulation.

5.3 Analytical methods

All samples were ground in an electric hammer mill with a fixed speed of 3520 rpm. The mill was linked with a sieve with opening of one centimeter. The grinding is required to ensure the uniform size distribution of the feedstock particles for higher efficiency of the HTC process. The biomass was stored in polyethylene bags at room temperature before the experiments. The milled untreated samples are presented at Figure 12.

a)

b)

c)

d)

Figure 12. Untreated samples: a) eucalyptus; b) coffee wood; c) coffee bean parchment; d) bamboo

The settings of the HTC process were the same for all studied samples. The residence time was 3 h with water-to-biomass mass ratio of 8:1. It means that 50 g of dry biomass was dispersed in 400 ml of water. The experiments were performed with the reaction temperature variation range from 180 °C to 240 °C with 20 °C step.

After the initial weighting and mixing the water and biomass, the mixture was loaded to the reactor. The temperature of the reactor was gradually increased to the required one. When the setpoint temperature was reached, it was maintained at this level for 3 hours. After the end of HTC process and cooling of the reactor to room temperature, the mixture of the solid and liquid products was taken out. Then, the solids were filtrated with Büchner funnel with Whatman glass microfiber filter paper (grade GF/A). The hydrochars were drying in the convective oven at the temperature 105±2 °C overnight. The weight of the dried and cooled hydrochars was determined and solids were put into polyethylene bags for storing at room temperature. Each experiment had at least two repetitions, and the average data from it was taken for further analysis.

5.4 Analytical methods

The proximate analysis (moisture, volatile matter, fixed carbon and ash content) and the heating value measurements were carried out for untreated biomass samples and hydrochars after the hydrothermal carbonization. Each analysis was done according to the appropriate standard procedure. At least two repetitions were done for each sample and the average value was used.

For the heating value measurements, the biomass samples were additionally grinded. For the analysis, the sawdust fraction that passed through the sieve of 40 mesh and was retained in the sieve of 60 mesh was used.

5.4.1 Higher heating value

The measurements of the higher heating value were carried out at the Parr 6400 calorimeter, following the EN 14918 (SFS, 2010b) standard for woody fuels. Produced powder after milling was pelletized with manual pellet press. The pellet was then placed into nickel crucible inserted into the calorimetric bomb installation. The pure cotton fuse, which is connected with the pellet, triggers a fire. The increase of temperature level of the water jacket surrounding the inner capsule of the calorimeter allows determination of the higher heating value.

5.4.2 Moisture content

The express moisture analyzer Sartorius 7093 was used for the moisture content evaluation. Approximately one gram of the sample was placed on the electric balance inside the moisture meter and was heated in the air atmosphere for 8 min until the constant mass is reached. The percentage of moisture content was provided automatically by the analyzer.

5.4.3 Ash content

The ash content of the biomass samples is determined according SFS EN 14775:2009 standard (SFS., 2010a). At least one gram of the sample is placed into the previously calcined and cooled down crucible. The weights of the dish and sample are weighted, and the crucible is placed into a cold muffle furnace. The temperature is gradually increased to 250 °C and to 550 °C and maintained at this level for certain time. The cooled down crucibles with ash are weighted again; its mass is recorded. The ash content on dry bases (A_d) is determined by equation (2)

$$A_d = \frac{(m_3 - m_1)}{(m_2 - m_1)} \cdot 100 \cdot \frac{100}{100 - M_{ad}} \qquad (2)$$

where m_1 - is mass of empty crucible [g]; m_2 - mass of the crucible with sample before analysis [g]; m_3 - mass of the crucible with ash [g]; M_{ad} - moisture content of the sample [%].

5.4.4 Volatile matter

SFS EN 15148:2009 standard (SFS., 2010c) contains the instructions of the procedure for volatile matter determination. According to this, not less than one gram of the well-mixed sample is put into the previously calcined and cooled down crucible, which is then closed with the lid. They all together are weighted and placed into muffle furnace at temperature 900±10 °C for seven minutes. During this time, the volatiles of the sample are released and the final mass is used to calculate their initial content. After the test, the crucibles are cooled down in dessicator and weighted. The percentage of the volatile matter on the dry basis is calculated by the following formula (3):

$$V_d = \left[\frac{100 \cdot (m_2 - m_3)}{(m_2 - m_1)} - M_{ad} \right] \cdot \left(\frac{100}{100 - M_{ad}} \right) \qquad (3)$$

where m_1 - is mass of empty crucible with lid [g]; m_2 - mass of the crucible with lid and with sample before analysis [g]; m_3 - mass of the crucible with lid and with matter after analysis [g]; M_{ad} - moisture content of the sample [%].

5.4.5 Fixed Carbon

The calculations of the fixed carbon are performed as the difference of one hundred percent and sum of the volatile matter and ash content on dry or wet basis, in the last case the moisture content should be subtracted. This parameter shows the amount of the carbon, which is connected by chemical bounds with other atoms.

5.5 Results and Analysis

The samples before treatment are analyzed for proximate analysis, heating values beforehand. The results for the eucalyptus, coffee wood, coffee beans parchment and bamboo samples are presented at the Table 3. The parameters of the higher and lower heating values are presented for dry basis, the results of the volatile and ash analysis likewise calculated on dry basis.

Table 3. Proximate analysis and heating values of the samples before treatment

Property	Unit	Eucalyptus	Coffee wood	Coffee cherry parchment	Bamboo
Moisture	%	2.7	1.7	1.8	2.1
Volatile	%	82.6641	81.2893	74.9429	81.7530
Fixed Carbon	%	14.3932	15.2090	16.5764	15.0037
Ash	%	0.2427	1.8017	6.6806	1.1433
Higher Heating Value	[MJ/kg]	19.99	20.19	18.40	19.86
Low Heating Value	[MJ/kg]	18.68	18.88	17.09	18.55

The hydrochars after the treatment of the 200 °C are illustrated at the Figure 13. The hydrothermal carbonization changes the color of the biomass to the darker one, what indicates the modification of the sample components. The composition, and color, consequently, changes more with the changes of the parameters, which influence on HTC process, such as temperature and residence time.

Appendix 2 Moisture content of the samples. The moisture content of the untreated biomass was rather small with comparison to typical values for these types of biomass, because they were initially dried in Brazil beforehand. However, for hydrothermal carbonization it does not matter, because it could treat even biomass with extremely high moisture content.

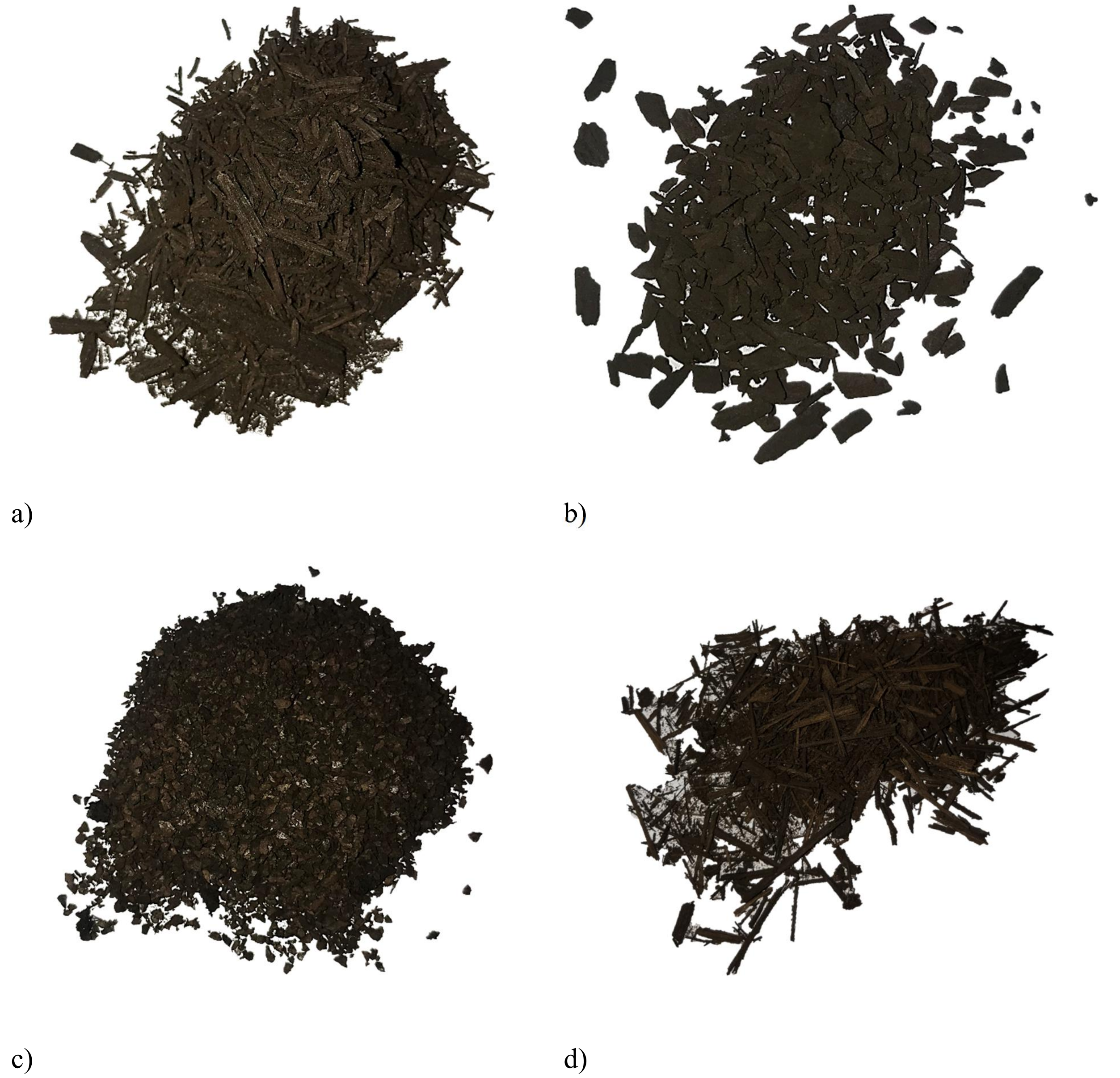

Figure 13. Hydrochar samples: a) eucalyptus; b) coffee wood; c) coffee bean parchment; d) bamboo

The moisture content of the untreated samples and hydrochars after the HTC is presented at the

The Table 4 presents the results of the proximate analysis of the biomass before and after hydrothermal carbonization. The volatile matter is shown at Appendix 6 Volatile matter of treated samples. The results present the decrease of the volatile content from 70-80% even lower than 50% with the increase of the reaction temperature. On the other hand, the amount of the fixed carbon, which data is presented at the Appendix 4 Fixed carbon of the treated samples enhances with the growth of the temperature. This parameter could reach almost four times raising at the 240 °C in comparison with untreated biomass. The more amount of the volatile matter the more effortlessly ignition occurs. Its high content increases the velocity of burning and make flame less stable. However, the higher ratio of the fixed carbon to volatile matter contribute into stabilization of the fame during the combustion process.

Table 4. The proximate analysis of samples before and after the treatment

	Temperature	Volatiles	Ash	Fixed Carbon
Parchment	Untreated	74,9429	6,6806	16,5764
	180	72,8853	1,4292	24,2355
	200	68,1775	1,4220	29,2005
	220	60,7630	1,5918	36,5202
	240	48,8460	1,6769	48,2271
Coffee wood	Untreated	81,2893	1,8017	15,2090
	180	76,5116	1,0753	21,0130
	200	73,0308	0,8536	24,9156
	220	63,4009	0,9287	33,8204
	240	52,0569	0,7996	45,1101
Eucalyptus	Untreated	82,6641	0,2427	14,3932
	180	77,9163	0,0231	20,4606
	200	64,2239	0,1317	33,5694
	220	55,0808	0,1371	42,3322
	240	46,8779	0,1621	50,8350
Bamboo	Untreated	81,7530	1,1433	15,0037
	180	73,1156	0,6563	25,1531
	200	65,7615	0,8210	32,2174
	220	55,6654	0,7429	41,8666
	240	43,8579	1,5173	52,9999

The treated biomass has lower content of the ash, however, the experiments shows that temperature increase make ash content slowly raise. The data of the ash content is presented at Appendix 5 Ash content of the samples after HTC treatment. Moreover, this parameter could be assumed be low, because it does not exceeded the 1.5%, and in majority of the cases it is lower than 1%. However, the untreated coffee bean parchment has high ash content, which is more than 6%, what could influence on the further application badly, as far salts are the considerable part of the ash content. Consequently, it is undoubtful, that all the characteristics depend on the type of the original sample and on the parameters of the experiment, such as temperature.

According to recorded mass of the biomass samples before and after hydrothermal carbonization, the mass yield of the hydrochars (MY, %) can be calculated with the equation (4):

$$MY = \frac{m_{out}}{m_{in}} \cdot 100\% \tag{4}$$

where m_{out} - mass of the dry solid matter after the HTC treatment [g]; m_{in} - mass of the dry solid untreated biomass [g].

The results of these calculations are presented at the Appendix 1 Mass Yield of the samples after HTC treatment and visually shown at Figure 14. This parameter shows which part of the sample is left after the treatment, as far the mass during the hydrothermal carbonization process goes down; the mass loss is intensified with temperature due to biomass components decomposition. The coffee bean parchment has the biggest mass losses and at the highest temperatures has only 35% of the sample left. At the same time, eucalyptus and bamboo shows extensive decrease in mass on the lower temperatures and the biggest amount after the treatment at the temperatures higher 200 °C. In addition, at the 180 °C eucalyptus shows the smallest mass loss.

In addition, there is tend for fracture at the point of 200 °C. The higher temperatures make benevolence conditions for gasification, what release carbon with volatiles. However, these losses are unavoidable (Titirici *et al.*, 2015). At any rate, the conclusion is that the type of the biomass sample predominantly influences on the mass yield, however, the change of the temperature also brings its impact on it.

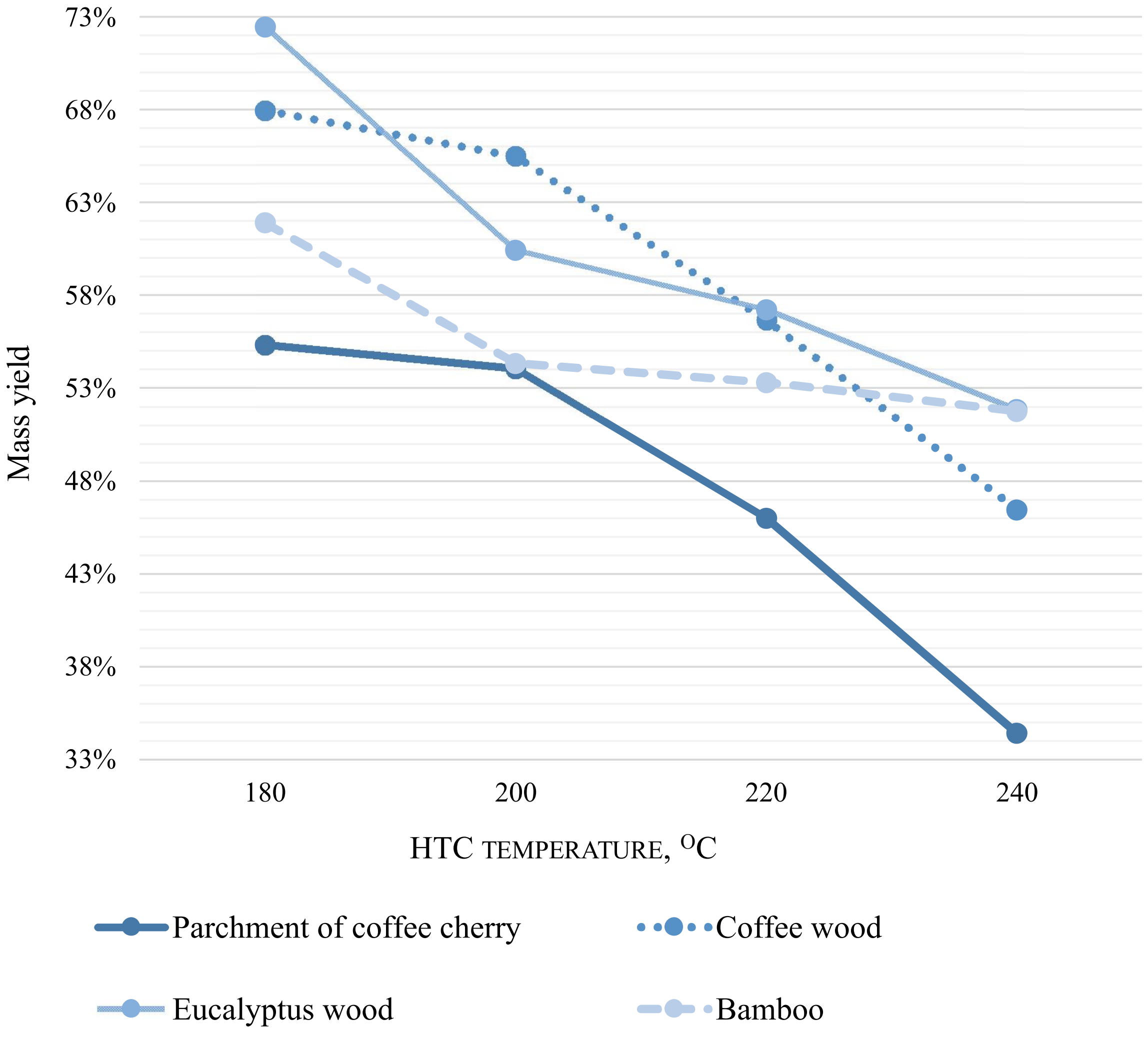

Figure 14. Mass yield after the HTC treatment

One of the most important parameters of the fuel is the heating value. The HHV values of the samples before and after HTC treatment are shown at the Appendix 3 Higher Heating Value and energy yield of the samples and illustrated at the Figure 15. The hydrothermal carbonization lead to the significant increase of the higher heating value for all samples. This parameter of the untreated biomass samples was from 19 to 20 MJ/kg and it was raising with the temperature. Thus, at the experiments with the treatment temperature 240 °C eucalyptus reached only 25 MJ/kg, when the higher heating value of the coffee bean parchment after the same treatment enhances up to 29 MJ/kg. The coffee wood and bamboo parameters are in the middle, with the increase of the heating value roughly 40%, which is average for HTC treatment on the biomass. Anyway, this characteristic is close to lignite coals and indicates the perspectives of hydrochars of these samples usage for the energy purposes along with coal.

The graph on Figure 15 presents the increase of the analyzed parameter. The biggest enhancement is reached by coffee bean parchment, which HHV changed from the lowest one among another samples to the highest one at the most high parameters treatment, this increase is more than 60%. In its turn, eucalyptus biomass shows good capability for the higher heating value increase at the temperatures of the reaction up to 200 °C, while at the higher temperatures of treatment its growth is insignificant, and totally do not exceed 30%. Nevertheless, the higher heating value is mostly depends on temperature of the hold treatment, and less on the type of the biomass.

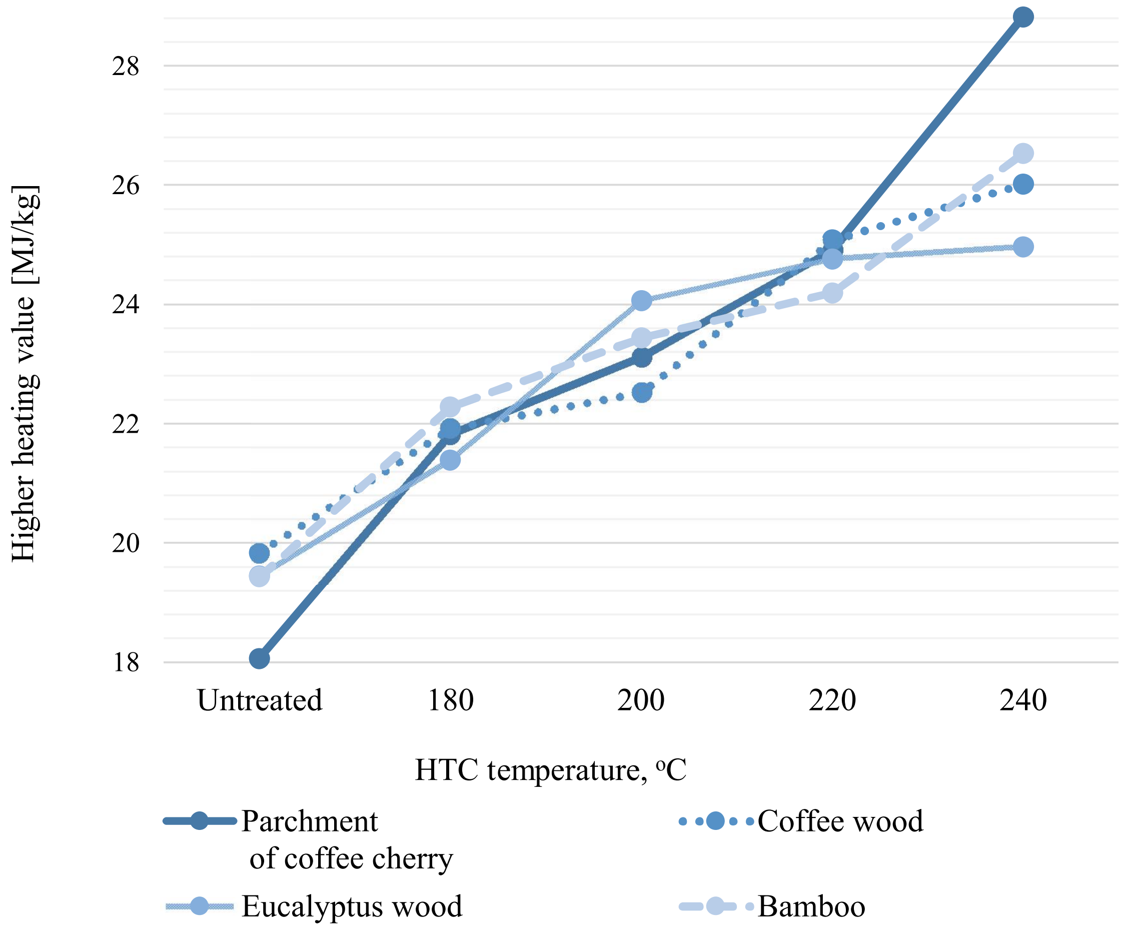

Figure 15. Higher heating value of the samples before and after treatment

The higher heating value increases because the final product has more carbon and less oxygen in its structure. In its turn, the energy densification ratio depends on the mass and more significant energy reduction. In this case, the energy yield characteristic shows the auspiciousness of the hydrothermal carbonization treatment. This parameter presents the content of the energy, which based on the change in the mass during the treatment, in comparison to untreated biomass samples characteristic. The energy yield could be determined according the equation (5), which is presented below:

$$EY = MY \cdot \frac{HHV_{dry\ out}}{HHV_{dry\ in}} \tag{5}$$

where $HHV_{dry\ out}$ - higher heating value of dry solid matter after the HTC treatment [MJ/kg]; $HHV_{dry\ out}$ - higher heating value of the dry solid untreated biomass [MJ/kg]; MY - mass yield [%].

The energy yield parameter for the sample after HTC treatment is shown at the Appendix 3 Higher Heating Value and energy yield of the samples and graphically at the Figure 16. According to this graph, the energy yield of the eucalyptus and coffee wood slightly decreases; bamboo stays almost unchanged and have uncertain behavior at different temperatures. The untreated parchment shows the lowest energy yield among the other samples mostly at each temperatures.

The energy yield is a parameter that characterizes the process and helps to compare different runs of the laboratory experiments. The lower temperatures do not cause significant energy increase and a notable mass loss, as far the temperature is not enough for decomposition. At the highest temperatures of the experiments (240 °C) the results are opposite. A lot of mass is lost and the higher heating value is likewise high. Most of the samples show comparable growth of the heating value, except parchment at lowest and highest temperatures of the experiments. However, the mass losses differs more significantly. The energy yield is balancing between these two opposing parameters. As a result, for the bamboo the mass yield is slightly decreasing; however, the heating value is increased more. These mean that the energy yield is increased with temperature. For woody samples, such as coffee wood and eucalyptus, the parameter of the energy yield change is rather similar. Moreover, the parchment reacts so vigorously, that the highest increase of the higher heating value among all the samples cannot be balanced by the mass loss.

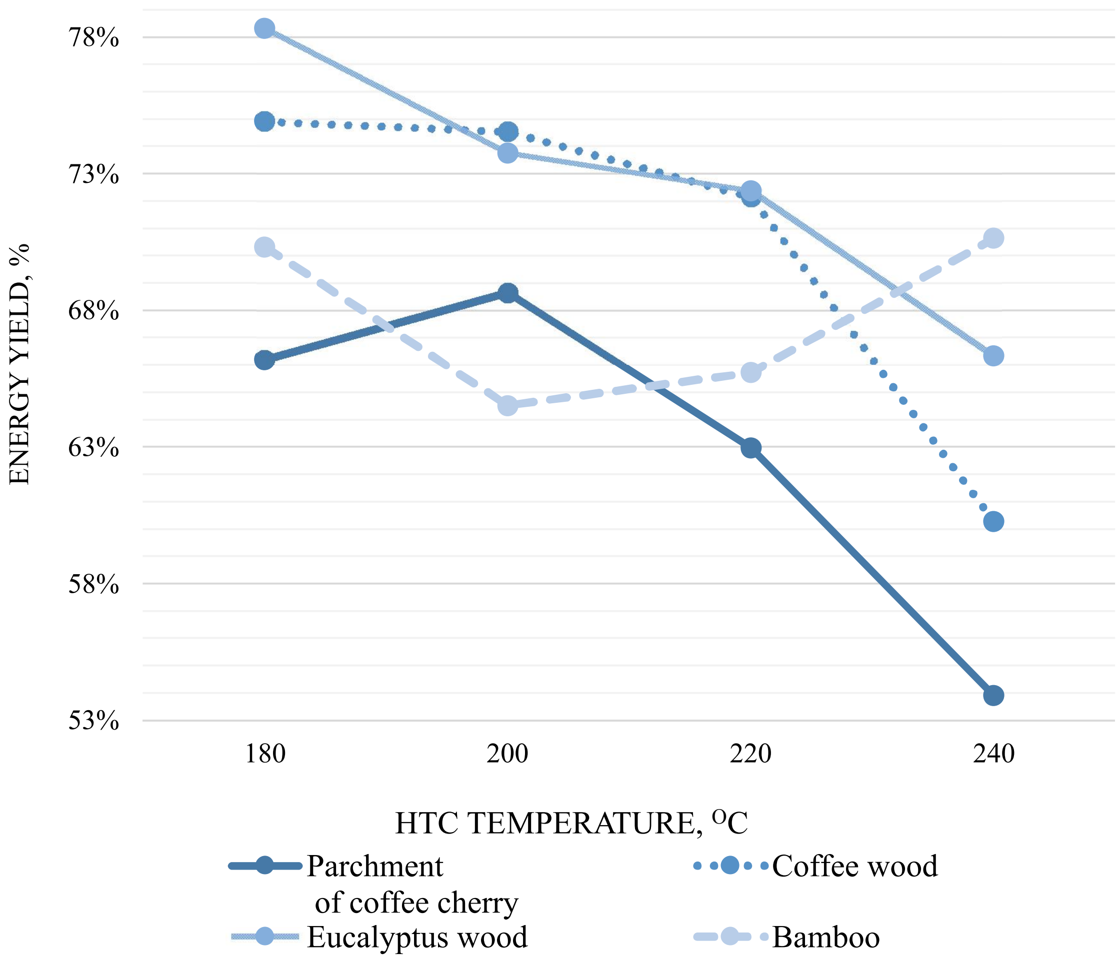

Figure 16. Energy yield of the treated samples

Consequently, the energy growth tends to increase with the higher temperatures of the hydrothermal carbonization treatment. However, the enhancement of the temperature leads to the reduction of the mass yield. This happens because of the samples decomposition, which is caused by the temperature effect. These two counter factors almost balance each other, what cause slight decrease of the energy yield in majority of cases with the temperature growth.

6. Conclusion

The problems of the climate change and exhaustion of the fossil fuels are extremely actual. The usage of the renewable sources of energy allows solving these two problems by minimizing the greenhouse gases emissions and reduction of the dependence on fossil fuels in the whole and their import. Bioenergy provides not only advantages of the alternative sources of energy but also through the development of agriculture and forestry sectors. Bioenergy is a prospective alternative to replace fossil fuels. However, biomass fuels and technologies should compete with widely used fossil fuels and it is not an easy for them to find their place in the energy mix. In order to succeed, biomass needs to improve the main characteristics, as the raw material has several properties that hinder usage. This work is dedicated to one of such methods of the treatment for enhancement of the biomass potential, which is hydrothermal carbonization.

Hydrothermal carbonization provides biomass with the increase of the energy content, improvement of the properties, which are important for the combustion, and makes this product more valuable as a fuel. In fact, it converts the biomass into material close or even equal to lignite.

There is a variety of the biomass types, which have not yet been explored. This forces to make investigations to get data about these species. Gathered information allows assessing the potential of each type and the prospective of its application. In addition, this leads to development of the existing technologies of the fuel treatment and its logistic methods and ways of combustion.

The variety and enormous asset of the biomass in the tropical regions force to learn possibility of its implementation into energy generation. In addition, industries, which are based on biomass, leave significant amounts of the residues, which is mostly not in use. However, the organic waste has noticeable potential for energy conversion.

This work analyzes the HTC potential of the coffee wood and coffee bean parchment, eucalyptus and bamboo. The materials were treated by hydrothermal carbonization at the different temperatures from 180 °C to 240 °C with 20 °C step in mixtures with water. All treated and raw samples were analyzed for moisture, volatiles, ash content and fixed carbon. In addition, the higher heating value, mass and energy yields were determined.

Coffee cherry parchment has the lowest density among the other samples, as far the coffee wood and eucalyptus have woody origin; and bamboo stem is rather dense, despite its belong to grasses. This difference even in species influences on the result of the treatment and behavior of the sample at different conditions. In addition, rather low density of the parchment do not only cause logistics problems but also require more amounts of it to produce same quantity of energy. Thus, its analysis should be carefully evaluated and assessed for this biomass appropriateness for energy purposes.

According to experiments, the influence of the treatment temperature on the key parameters could be traced. Nevertheless, the end biomass characteristics mainly depend on the type of the biomass and its primordial potential, in which hydrothermal carbonization brings some improvements.

The hydrothermal carbonization reduces the ash content and volatile matter while the fixed carbon is increased. Another positive impact on the combustion properties is the increase of the higher heating value. However, the mass yield decreases with the growth of the temperature of the treatment. The same occurs to the energy yield of the majority of the hydrochars. The eucalyptus and coffee wood shows the biggest energy yield among the experimental samples, average parameters of the higher heating value and the lowest reduction of the mass. These biomasses show good average results, which are typical for woody materials. These plants asset allows assuming their potential for the usage for energy purposes. Bamboo shows rather good improvement of the key properties after hydrothermal carbonization. Despite of its grass origin, after influence of the HTC at higher temperature bamboo has characteristics competitive to ones of the woody biomass. However, this biomass could be not in practice very suitable in usage because of its peculiar structure. The residues of the coffee, which are presented by coffee beans parchment, have uncertain results. This biomass has the highest HHV at the high temperatures, however, its mass loss during the process is significant and energy yield is low at all the temperatures of the hydrothermal carbonization treatment. In addition, low density of the parchment requires the utilization of large amounts of this biomass for energy volumes, which are close or equal to energy produced by other experimented samples.

Consequently, tropical biomass such as eucalyptus, bamboo, coffee wood and its cherry parchment show good potential to be applied for energy purposes, especially if they are treated with proper method. In addition, hydrothermal carbonization is suitable way of their treatment for the improving of the parameters, which influence on their conversion into energy. The results of the hydrothermal carbonization process could vary depending on the temperature of the reaction.

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Appendix 1 Mass Yield of the samples after HTC treatment

	Parchment of coffee cherry								Coffee wood							
Water to biomass ratio	8								8							
Residence time [h]	3								3							
Solid mass in [g]	50,92								50,86							
Solid mass in dry [g]	50,00								50,00							
Liquid mass in [g]	399,08								399,14							
Temperature [°C]	180		200		220		240		180		200		220		240	
# of experiment	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2
Solid mass out [g]	27,78	28,41	28,24	26,50	22,89	23,64	18,40	16,48	34,93	34,01	33,24	33,07	28,42	29,35	23,95	23,30
Solid mass out dry [g]	27,35	28,03	27,82	26,26	22,72	23,29	18,12	16,32	34,60	33,38	32,91	32,61	27,87	28,84	23,71	22,76
Mass yield [%]	55%	56%	56%	53%	45%	47%	36%	33%	69%	67%	66%	65%	56%	58%	47%	46%
Average mass yield	55%		54%		46%		34%		68%		66%		57%		46%	
	Eucalyptus wood								Bamboo							
Water to biomass ratio	8								8							
Residence time [h]	3								3							
Solid mass in [g]	51,39								51,07							
Solid mass in dry [g]	50,00								50,00							
Liquid mass in [g]	398,61								398,93							
Temperature [°C]	180		200		220		240		180		200		220		240	
# of experiment	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2	#1	#2
Solid mass out [g]	36,41	37,11	30,47	30,72	29,02	29,30	26,42	26,33	30,02	32,59	31,34	23,65	28,44	25,83	25,32	27,32
Solid mass out dry [g]	36,06	36,42	30,17	30,29	28,45	28,79	26,16	25,72	29,63	32,31	31,10	23,26	28,01	25,33	24,84	26,95
Mass yield [%]	72%	73%	60%	61%	57%	58%	52%	51%	59%	65%	62%	47%	56%	51%	50%	54%
Average mass yield	72%		60%		57%		52%		62%		54%		53%		52%	

Appendix 2 Moisture content of the samples

	Parchment of coffee cherry																	
	untreated		HTC-180 #1		HTC-180 #2		HTC-200 #1		HTC-200 #2		HTC-220 #1		HTC-220 #2		HTC-240 #1		HTC-240 #2	
MC [%]	1,7	1,9	2,1	1	1,8	0,9	2	1	1	0,8	0,5	1	2	1	1	2	1	1
MC average [%]	1,8		1,55		1,35		1,5		0,9		0,75		1,5		1,5		1	
	Coffee wood																	
	untreated		HTC-180 #1		HTC-180 #2		HTC-200 #1		HTC-200 #2		HTC-220 #1		HTC-220 #2		HTC-240 #1		HTC-240 #2	
MC [%]	1,6	1,8	0,9	1	0,9	2,8	1	1	1	1,8	2	1,9	1,7	1,8	1	1	1,6	3
MC average [%]	1,7		0,95		1,85		1		1,4		1,95		1,75		1		2,3	
	Eucalyptus wood																	
	untreated		HTC-180 #1		HTC-180 #2		HTC-200 #1		HTC-200 #2		HTC-220 #1		HTC-220 #2		HTC-240 #1		HTC-240 #2	
MC [%]	2,9	2,5	1	1,9	1,7	1,8	1,9	1,7	1,8	2,9	0,9	1,9	3,2	3,8	2,9	2,9	1,8	0,9
MC average [%]	2,7		1,45		1,75		1,8		2,35		1,4		3,5		2,9		1,35	
	Bamboo																	
	untreated		HTC-180 #1		HTC-180 #2		HTC-200 #1		HTC-200 #2		HTC-220 #1		HTC-220 #2		HTC-240 #1		HTC-240 #2	
MC [%]	2,2	2	0,9	1,7	1	0,7	0,6	0,9	1,8	1,5	1,3	1,7	1,9	2	1,8	2	1,8	0,9
MC average [%]	2,1		1,3		0,85		0,75		1,65		1,5		1,95		1,9		1,35	

Appendix 3 Higher Heating Value and energy yield of the samples

	HTC					
			T [°C]			
	[MJ/kg]	Untreated	180	200	220	240
Parchment of coffee cherry	HHV calorific	18,07	21,83	23,12	24,92	28,83
	HHV on dry basis	18,40	22,15	23,40	25,20	29,19
	LHV on dry basis	17,09	20,84	22,09	23,89	27,88
	Energy yield [%]		66	69	63	54
Coffee wood	HHV calorific	19,84	21,93	22,53	25,09	26,02
	HHV on dry basis	20,19	22,25	22,81	25,56	26,46
	LHV on dry basis	18,88	20,94	21,50	24,25	25,15
	Energy yield [%]		75	75	72	60
Eucalyptus wood	HHV calorific	19,45	21,40	24,07	24,77	24,97
	HHV on dry basis	19,99	21,75	24,59	25,39	25,52
	LHV on dry basis	18,68	20,44	23,28	24,08	24,21
	Energy yield [%]		78	74	72	66
Bamboo	HHV calorific	19,44	22,29	23,45	24,20	26,54
	HHV on dry basis	19,86	22,53	23,73	24,63	26,98
	LHV on dry basis	18,55	21,22	22,42	23,32	25,67
	Energy yield [%]		70	65	66	71

Appendix 4 Fixed carbon of the treated samples

Sample	Temperature [°C]	Fixed Carbon [%]
Parchment	180	24,2355
	200	29,2005
	220	36,5202
	240	48,2271
Coffee wood	180	21,0130
	200	24,9156
	220	33,8204
	240	45,1101
Eucalyptus	180	20,4606
	200	33,5694
	220	42,3322
	240	50,8350
Bamboo	180	25,1531
	200	32,2174
	220	41,8666
	240	52,9999

Appendix 5 Ash content of the samples after HTC treatment

Table 1 Ash content of the Coffee bean parchment and coffee wood after the HTC treatment

Sample	Temperature [°C]	#	Crucible mass [g]	Sample mass [g]	crucible+sample (out) [g]	Ash [%]	Average
Parchment	180	1	13,1301	1,0415	13,1453	1,4824	1,4292
		1	22,2806	1,0475	22,2996	1,8424	
		2	28,9846	1,1134	28,9958	1,0197	
		2	14,9956	1,0563	15,0099	1,3723	
	200	1	22,2473	1,0972	22,2553	0,7402	1,4220
		1	22,2829	1,0174	22,2968	1,3870	
		2	13,6081	1,0747	13,6271	1,7840	
		2	14,74	1,0053	14,7577	1,7767	
	220	1	15,0955	1,0658	15,1114	1,5031	1,5918
		1	15,7904	1,0974	15,8033	1,1844	
		2	31,4833	1,172	31,504	1,7931	
		2	23,4599	1,0925	23,4802	1,8864	
	240	1	33,6842	1,1169	33,7027	1,6816	1,6769
		1	31,4807	1,0473	31,4973	1,6092	
		2	28,9788	1,0602	28,9961	1,6483	
		2	15,0951	0,9367	15,1115	1,7685	
Coffee wood	180	1	22,2805	1,1178	22,2908	0,9303	1,0753
		1	15,7879	1,0236	15,8005	1,2428	
		2	14,9936	1,0202	15,0046	1,0985	
		2	13,1291	1,1675	13,1409	1,0298	
	200	1	22,2367	1,1248	22,2458	0,8172	0,8536
		1	14,3738	1,1262	14,3835	0,8700	
		2	13,6061	1,2268	13,6174	0,9342	
		2	14,7402	1,0743	14,7486	0,7930	
	220	1	13,8661	1,0369	13,8753	0,9049	0,9287
		1	19,2175	1,1431	19,2298	1,0974	
		2	48,1082	1,1423	48,1178	0,8554	
		2	50,7897	1,449	50,8019	0,8570	
	240	1	54,5353	1,0047	54,5432	0,8004	0,7996
		1	48,7042	1,0048	48,7131	0,9017	
		2	54,4391	1,0198	54,4452	0,6122	
		2	49,9048	1,3197	49,9162	0,8842	

Table 2 Ash content of Eucalyptus and Bamboo after the HTC treatment

Sample	Temperature [°C]	#	Crucible mass [g]	Sample mass [g]	crucible+sample (out) [g]	Ash [%]	Average
Eucalyptus	180	1	51,9879	1,337	51,9887	0,0607	0,0231
		1	51,508	1,3687	51,5083	0,0222	
		2	53,9391	1,07	53,9392	0,0095	
		2	22,2376	1,0234	22,2376	0,0000	
	200	1	17,9317	1,0597	17,9321	0,0384	0,1317
		1	17,6483	1,0489	17,6503	0,1942	
		2	17,3503	1,1395	17,352	0,1528	
		2	23,4596	1,0865	23,4611	0,1414	
	220	1	13,6057	1,0803	13,6079	0,2065	0,1371
		1	15,0945	1,0358	15,0961	0,1567	
		2	17,351	1,0744	17,3522	0,1157	
		2	17,7399	1,0468	17,7406	0,0693	
	240	1	17,5208	0,9993	17,5215	0,0721	0,1621
		1	18,1686	1,0438	18,1704	0,1776	
		2	15,7883	1,1058	15,7905	0,2017	
		2	13,606	1,0799	13,6081	0,1971	
Bamboo	180	1	14,3738	1,0545	14,3799	0,5861	0,6563
		1	23,46	1,15	23,4661	0,5374	
		2	15,7877	1,0843	15,7956	0,7348	
		2	17,7531	1,276	17,7628	0,7667	
	200	1	22,2364	1,2356	22,2478	0,9296	0,8210
		1	17,739	1,1045	17,7497	0,9761	
		2	17,7533	1,0501	17,76	0,6487	
		2	18,1688	1,0171	18,1761	0,7298	
	220	1	17,6861	1,0938	17,6948	0,8075	0,7429
		1	13,1285	1,2213	13,1364	0,6567	
		2	22,2804	1,143	22,2887	0,7406	
		2	14,3738	1,0772	14,3819	0,7669	
	240	1	19,2176	1,0301	19,227	0,9302	1,5173
		1	17,4296	1,0462	17,4416	1,1692	
		2	17,9336	1,0806	17,9569	2,1857	
		2	19,2173	1,0512	19,2358	1,7840	

Appendix 6 Volatile matter of treated samples

Table 3 Volatile matter of the treated coffee bean parchment and coffee wood

Sample	Temperature [°C]	#	Mass of crucible and lid [g]	Sample Mass [g]	Mass of crucible, lid and sample [g]	Volatiles [%]	Average
Parchment	180	1	87,1662	1,1239	87,469	72,6339	72,8853
		1	53,8872	1,0671	54,1709	72,9954	
		2	55,5477	1,0206	55,8243	72,5274	
		2	54,617	1,0508	54,8929	73,3845	
	200	1	88,5138	1,2661	88,9056	68,5833	68,1775
		1	51,5246	1,3966	51,9749	67,2664	
		2	50,4032	0,9995	50,7089	69,1369	
		2	85,5758	1,1727	85,9509	67,7235	
	220	1	77,1185	1,4473	77,6578	62,4559	60,7630
		1	84,8842	1,0284	85,2866	60,5756	
		2	80,9885	1,3041	81,5041	59,8611	
		2	91,4235	1,083	91,8485	60,1595	
	240	1	91,9464	1,1466	92,5395	47,4854	48,8460
		1	86,9736	1,0666	87,5229	47,7156	
		2	80,9895	1,0281	81,4842	51,3961	
		2	79,7957	1,0412	80,3236	48,7868	
Coffee wood	180	1	85,5567	1,1615	85,8309	76,1662	76,5116
		1	88,1766	1,0166	88,4104	76,7812	
		2	89,6456	1,0896	89,8987	76,3335	
		2	90,659	1,0248	90,8927	76,7657	
	200	1	86,4971	1,0467	86,7856	72,1588	73,0308
		1	87,0621	1,0342	87,3369	73,1603	
		2	88,0274	1,0818	88,3139	73,1403	
		2	86,2002	1,1626	86,5021	73,6636	
	220	1	90,1322	1,3199	90,5715	66,0553	63,4009
		1	83,9266	1,2557	84,3197	68,0722	
		2	82,7912	1,0298	83,2116	58,4494	
		2	83,4901	1,0966	83,91	61,0269	
	240	1	83,656	1,3912	84,3253	51,0252	52,0569
		1	84,41	1,0096	84,8929	51,3090	
		2	88,6329	1,0248	89,1074	52,6083	
		2	77,1028	1,4875	77,7817	53,2852	

Table 4 Volatile matter of the treated eucalyptus and bamboo

Sample	Temperature [°C]	#	Mass of crucible and lid [g]	Sample Mass [g]	Mass of crucible, lid and sample [g]	Volatiles [%]	Average
Eucalyptus	180	1	87,1854	1,4303	87,4956	77,9931	77,9163
		1	79,7921	1,4125	80,1027	77,6871	
		2	88,174	1,1999	88,4263	78,5987	
		2	86,4916	1,6383	86,8556	77,3861	
	200	1	83,5369	1,0621	83,9269	62,6072	64,2239
		1	91,45	1,0759	91,8338	63,6737	
		2	86,2525	1,1168	86,615	66,7601	
		2	89,8045	1,7852	90,4346	63,8548	
	220	1	84,247	1,0421	84,6978	56,1270	55,0808
		1	87,1288	1,4401	87,7746	54,5192	
		2	82,7852	1,437	83,406	55,2320	
		2	90,5357	1,1276	91,0314	54,4449	
	240	1	88,2556	1,198	88,873	46,9249	46,8779
		1	92,061	1,424	92,7916	47,1615	
		2	52,8815	1,4312	53,6263	47,2476	
		2	91,047	1,221	91,6953	46,1776	
Bamboo	180	1	84,7652	1,3656	85,1135	74,1588	73,1156
		1	90,7872	1,2494	91,0697	77,0913	
		2	87,5887	1,1439	87,9251	70,3397	
		2	83,954	1,1818	84,2953	70,8727	
	200	1	89,0915	1,192	89,4367	70,8214	65,7615
		1	89,9124	1,6756	90,4247	69,1948	
		2	83,7117	1,1063	84,137	60,9116	
		2	90,0752	1,2277	90,5326	62,1183	
	220	1	93,204	1,0612	93,6887	53,6297	55,6654
		1	90,8586	1,1552	91,3748	54,6346	
		2	87,6802	1,0373	88,118	56,9549	
		2	77,0148	1,2028	77,5167	57,4425	
	240	1	91,8949	1,0191	92,4254	46,9360	43,8579
		1	86,001	1,107	86,5757	47,0794	
		2	84,0247	1,3663	84,837	39,7339	
		2	89,9348	1,5583	90,8313	41,6821	