Biochar production by biomass pyrolysis for various applications

Sara Solís

Luleå University of Technology

Highlights

- Contemplate biomass as a renewable source of energy
- Research concerning pyrolysis for char production
- Investigation about how to optimize char production
- Analyzing various parameters to determine the more suitable option
- Summarize all the results

Abstract

Nowadays, there is a challenge to replace the use of fossil fuels and to reduce the greenhouse gases emissions. One possible solution is the renewable energies; in this paper was studied the thermo-chemical conversion of biomass.

It is investigated how to increase char production for different applications; as a sustainable acquired raw material to steel production.

Several experiments made on the laboratory are utilized in the project; experiments with pure wood chips of fir, bio-oil and also an impregnation process of the pure chips and tar both with bio-oil. Then some experiments to calculate some properties as the High Heating Value, the content of Carbon, Hydrogen and Oxygen and finally some calculations of the mass and energy yield.

After all the experiments were done, it was realized that as long as the temperature is increased in the pyrolysis process, the time consumption is less; weight is a clearly factor of how the piece get the final weight; with constant temperature it is going to have the same fraction of initial wood mass, it is going to decomposed the same amount; increasing the temperature gives less mass yield for every sample; impregnation gives the same mass yield than pure chips; doing twice pyrolysis you obtain almost the same piece at the second stage; impregnated char with oil and char have almost the same mass and energy yields; it is only possible to impregnated 40% (40-oil/60-wood); pyrolysis at more temperature gives biochar with more HHV; with more temperature, it is obtained more content of Carbon and less of Hydrogen and Oxygen.

A good possible final option can be Wood+Bio-oil at 340°C.

Keywords

Biomass; Pyrolysis; Wood; Char; Tar

Table of contents

List of figures

List of tables

1. *Introduction*

The overall aim of this project is study the biochar production for steel mill process.

It can be distinguish between two modern steel productions: Blast Furnace and Electric Arc Furnace Steelmaking. Both processes produce steel from iron ore together with recycled steel scrap. Nowadays, it is more used the blast furnace technology, but it is expected to increase the usage of the arc furnace technology. **[1]**

Figure 1 shows the schematic processes of the two different technologies:

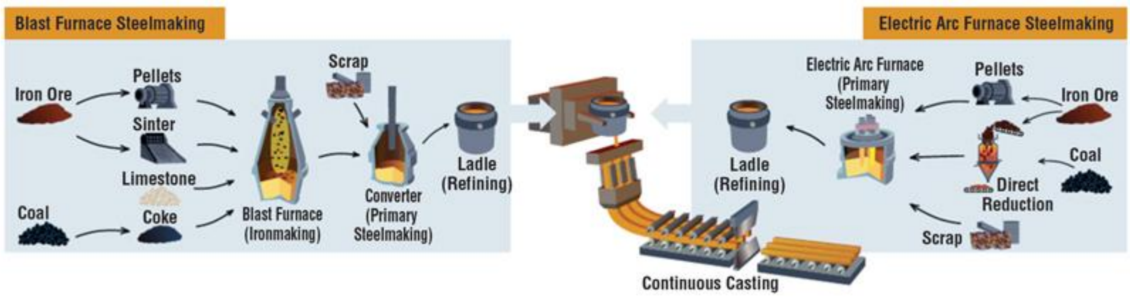


Figure 1: Schematic representation of the steelmaking processes

Coke is essential raw material in the Blast Furnace for the steel process. It is very porous and rich in carbon element and it is the product of mineral coal from pyrolysis.

Coke has different purposes in a Blast Furnace: it works as a fuel, a reducing agent and also it allows the hot gases to flow upwards because of its porosity and strength.

Some characteristics are desired to coke: relatively low reactivity (to be able to reach the bottom of the furnace without reacting too much with the gas flow), enough strength (at high temperatures to support the load of the material above), low moisture, ash and sulfur content.

To decrease the coke consumption and increase the production rate of the iron, pulverized coal is injected supplementary with the hot air. The amount of coke that can be replaced by pulverized coal depends basically on the coal quality and the dimensions of the Blast Furnace. **[2]**

Our role is to develop a production technology for biorchar that are suitable for the specification required from steel industry.

The objective of this thesis is to investigate the effect of pyrolysis condition on biochar yield and its physical and chemical properties.

2. *Literature review*

2.1 Pyrolysis

Pyrolysis is a thermo-chemical process where organic materials are decomposed at high temperature and without oxygen, see Figure 2.

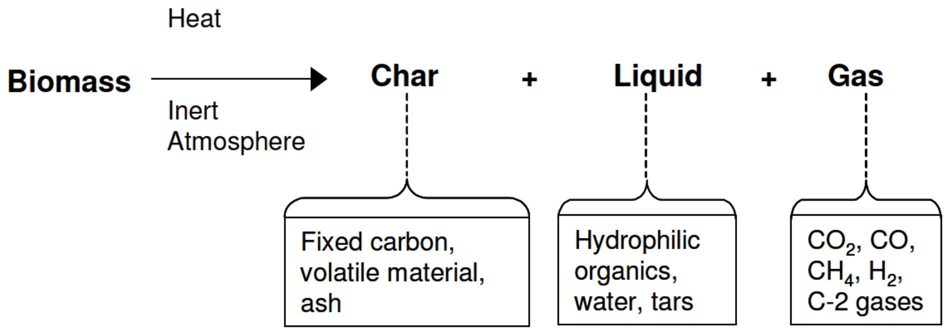


Figure 2: Representation of Pyrolysis Process

Biomass is fuel which is developed from organic materials, it is a renewable and sustainable source of energy and it is used to create electricity or other forms of power. **[3]**

Char is the main product that it is obtained of wood after pyrolysis. It can be used as a fuel replacing the fossil coal in the steel production.

There are some liquids acquired in the pyrolysis process as hydrophilic organics, water and one of the most important is tar because it can block, erosion and corrosion the pipes and valves. Hence, there are diverse methods to tar reforming as used Nickel as a catalyst in the pyrolysis process.

The gases originated in this procedure are mainly CO_2, CO, CH_4, H_2 and C-2. These gases are often referred to as syngas or synthesis gas. **[4]**

The main difference of pyrolysis from gasification and combustion is that pyrolysis is a process without oxygen while gasification needs some controlled oxygen and the combustion process is with atmospheric oxygen.

And also, more dissimilarities are the primary products that are obtained in the different processes, the product and energy recovery and finally the secondary products that are obtained as it is showed in Figure3:

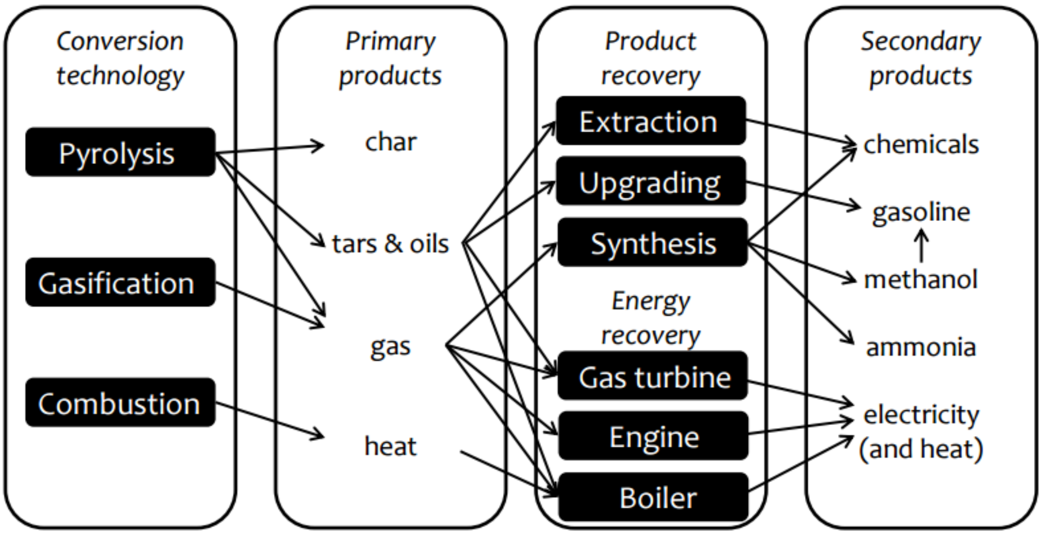


Figure 3: Products, process and equipment for different technologies

2.2 Slow vs. Fast pyrolysis

In *slow pyrolysis* (300°C-500°C) there are high yields of char (as much as 40 wt-%) but it also produce a relatively low-value energy product, pyrolysis gas of modest heating value.

Fast *pyrolysis* (500°C-900°C) maximizes the production of bio-oil with biochar and pyrolysis gas as lower-yielding coproducts. Fast pyrolysis in comparison with the slow one, produces higher value energy product but with a higher cost in investment.

The main differences between slow and fast pyrolysis are the heating rates and maximum reaction temperatures. Slow pyrolysis requires several minutes or even hours, while fast pyrolysis is complete in as little as two seconds. **[5]**

2.3 Effect of reaction parameters

At the moment that we want to study the pyrolysis process, it is important to study first the effects of main parameters.

2.3.1 Biomass type

Firstly, we are going to start with biomass type. Depending on the biomass type, the growth environment and the harvesting time, it is going to obtain different constituents with dissimilar mass ratios, reaction pathways, thermo-chemical characteristics, products and structural.

In this project, the biomass used is fir wood. By instance, if the fir contains more cellulose and hemicelluloses, this contribute to obtain bio-oil; while with lignin yields, there will be more proportion of solid char.

2.3.2 Biomass pretreatment

The biomass feedstock normally requires any method of pre-treatment before its pyrolysis.
The technologies for biomass pretreatment can be divided into five main categories: physical (milling/grinding and extrusion), thermal (torrefaction, steam explosion/liquid hot water pretreatment and ultrasound/microwave irradiation), chemical (treatment with acids, bases and ionic liquids), biological (fungal, microbial consortium and enzymatic) and above combined pretreatments.

In this document, it is going to experiment with impregnation wood with bio-oil.

2.3.3 Reaction conditions

Atmosphere

Biomass pyrolysis is usually done under inert atmosphere. But other gases can be also introduced to modify the pyrolysis process.
One possible option is the steam because it improves the yield of organic oxygen by preventing to extent the cracking reactions in the gas phase. But in this project, it is not used steam.
There are some effects of the following gases N2, CO2, CO, CH4 and H2 that have been studied; as have more bio-oil yields; increase the surface area or better chemical composition.
For that reason, the project was made with Nitrogen atmosphere.

Temperature

Pyrolysis temperature is one of the most important parameters to take into account due to it significantly modifies the distribution and properties of products. As it was mentioned by talking about slow and fast pyrolysis, with low temperatures, it is obtained bio-oil yield and with higher temperatures, the bio-oils and char products are converted in to gas. **[6]**
For that reason, it is going to experiment with lower temperatures, in order to study the char production.

Heating rate

Heating rate is also a fundamental parameter that defines the type of biomass pyrolysis too (flash, fast, and slow pyrolysis).
If it has a fast heating rate, the fragmentation of the biomass will be quicker and yield more gases and produce less char.

Vapor residence time (Removal time)

Shorter residence time favors bio-oil production because of the quick removal of organic vapors from reactors which minimizes the secondary reactions.

Pressure

The most significant consequence of pressure in char is the change of the physical structure. If the pressure is increased, the charcoal yield is going to increase but the reactivity is going to decrease. **[7]**

2.4 Increase the amount of char

There are several different approaches to increase the amount of char. In this paper it is going to be explained some of them:

Starting with removing ash before pyrolysis; pre-treat biomass can be done in different ways including with water, surfactant and acid:
It is known that water remove the majority of alkali metals from biomass and it is better if they are agitated. For high inorganic content biomass, water washing is more suited.
Strong acids is another good option because they decrease the amount of hemicellulose and cellulose, so increasing lignin.
One desirable way is to use surfactant with water because it removals better inorganic material and is cheaper. **[8]**

Second option is to absorb tar on the biomass at low temperature. Adsorption capacity depends on the particles size of the carbon materials. It is going to be easier to remove light tar compounds when the pieces have larger surface area and smaller particle size. **[9]**

Another option is tar deposit, coking on tar at high temperature (900 °C) with Ni with MgO as a catalyst. **[10]**

And finally, also absorb tar on char at low temperature but at these temperatures it is obtained a high level of tar in the gas. **[11]**

We decided to try to increase the amount of char by oil impregnation. Later on, the experiments and results are shown.

3. Method

3.1 Experimental equipment

The experiments were done on the TGA (Thermo Gravimetric Analyzer),(see Figure 4); a fixed bed reactor made of stainless steel with an inner diameter of 90 cm and a length of 113 cm and was fully instrumented with monitoring and control of gas flow and temperature.

The pyrolysis temperature was externally heated by an electrical furnace, heating at a rate of 2 °C min^{-1} to the desired temperature (300, 320, 340, 360, 380, 400, 425 and 450°C).

The reactor system was continually purged with nitrogen at 7liters/min. Nitrogen was used as the carrier gas and to keep the atmosphere inert.

TGA works with measuring change weight of materials as a function of time with constant temperature.

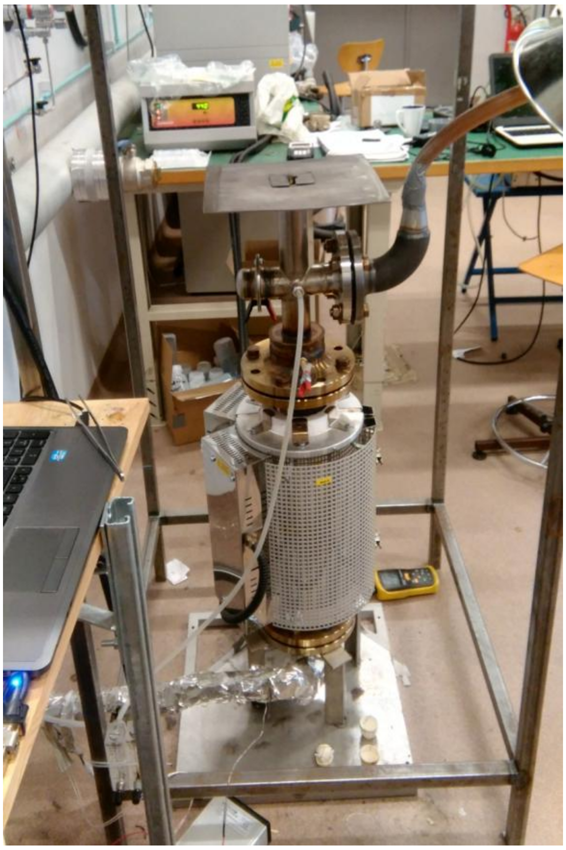


Figure 4: Picture of the TGA

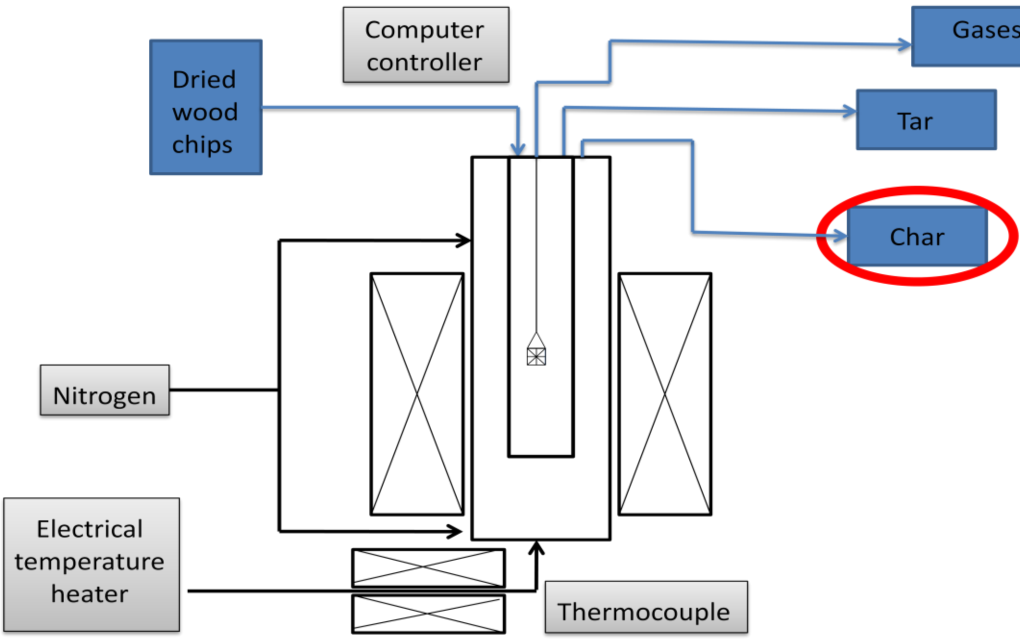


Figure 5: Schematic representation of pyrolysis process in the TGA

3.2 Procedure

First of all, TGA was prepared by purging with Nitrogen, setting the desired temperature and making the scale of the weight zero.
Our different inputs were pure wood, wood with oil, char with oil and oil.
The particle weights used were around 2-7grams and 0.5-1.5 grams for oil.
Wood chips of fir were dried overnight at a temperature of 105 °C.
For each temperature, three samples of each category were taken.
One by one, the sample was put in a little basket and introduced in the TGA.
Thanks to the computer controller, the weight of the sample was known in every moment and the mass yield and time consumption was calculated from the biochar. All the procedure is represented in Figure 5.
Once the sample didn't decompose more, it was taken and kept for upcoming experiments.

With our range of temperatures, it was basically to obtain biochar but also some gasses that were directly through an exhaust available in the laboratory.

3.3 Samples

There are four kinds of samples used in this thesis:

- Wood chips: little pieces of fir (about 4 x 2 x 2cm), from the pure wood it is obtained char after pyrolysis.
- Bio-oil/tar: from the liquid state it is obtained a porous sponge
- Wood impregnated by bio-oil: using various percentages of the rate wood/oil, from a piece of wood impregnated it is obtained char with some bumps in several cases.
- Char impregnated by bio-oil: from some samples of char (wood pyrolysised at the optimal temperature) it is obtained char.

4. *Results and discussion*

This paper is going to show all the different kinds of experiments made on the TGA:

4.1 Wood chips

First, it is started with simply wood chips that were dried over the night at 105°C through pyrolysis process at different temperatures: 300, 320, 340, 360, 380, 400, 425 and 450°C.

From the wood chip it is obtained char which is a product of the incomplete combustion of the biomass in pyrolysis, see Figure 6.

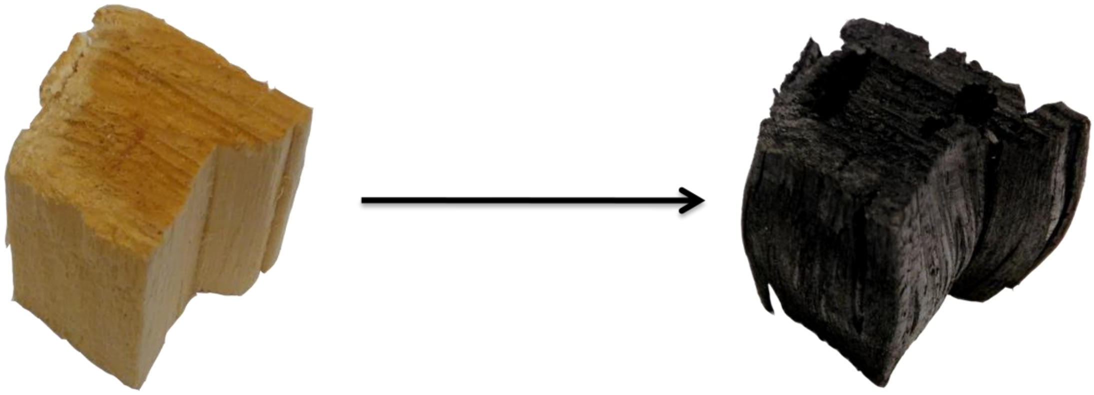
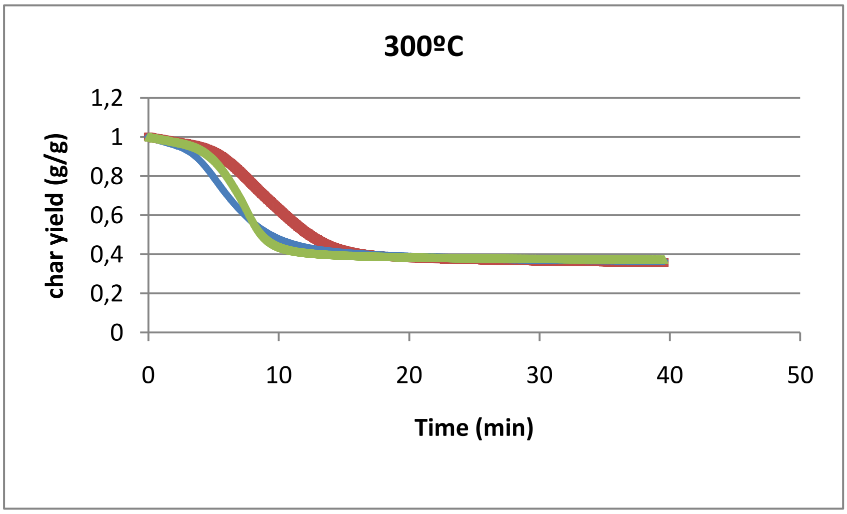


Figure 6: Picture of wood chip after pyrolysis and char before pyrolysis

TGA directly gives you the weight when the reaction occurs. With that, it is made some comparison graphs of the char yield and the time consumption. By instance, at 300°C with three different samples (Figure 7):



Figures 7: Graph of char yield and time consumption of wood chips at 300°C

From 100% of the piece (1 of char yield at the graph), it is showed how it is decreasing the amount of weight until the reaction is finished.
This is an example at 300°C with the three different samples that we put it one by one.

With all the experiments done of the wood chips at the different temperatures, we can clearly see that the temperature are connected with the conversation time (Figure 8): with 300°C pyrolysis takes around half an hour while for 450°C the process is made in less than ten minutes. Also you can see how it is obtain less amount of char when you increase the temperature.

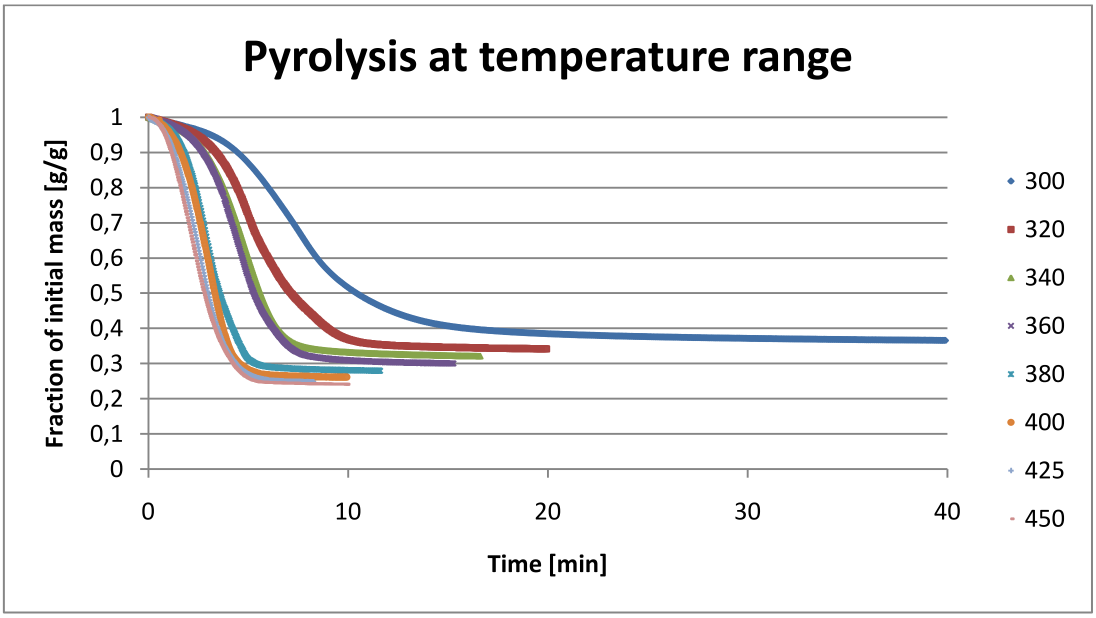


Figure 8: Graph of pyrolysis time depending on the temperature

One important factor to taken into account is the sample weight, in the following graph (Figure 9) it is showed how it is reached the final weight depend of it: the more heaviness the piece, the more time it is going to take to reach its final weight. But it is always to decompose the same amount of wood at a fixed temperature.

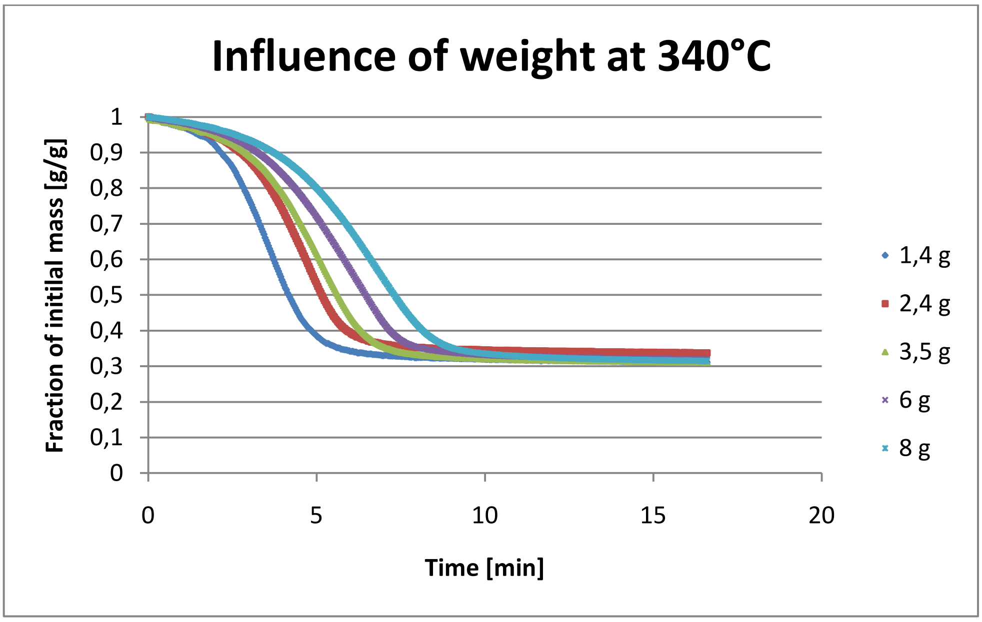


Figure 9: Graph of the influence of the weight at 340°C

Therefore, Figure 10 shows the time for 95% of conversion of the different weight wood chips in order to see how for lighter pieces it is converted in less time.

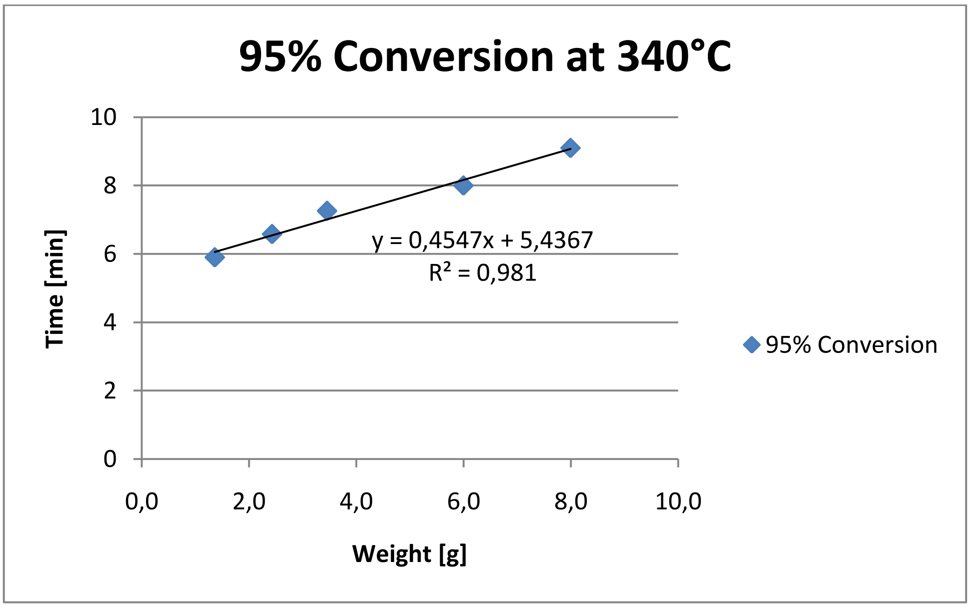


Figure 10: Graph of 95% conversion at 340°C

To sum up all the previously graphs, it can be easily observed that the as long as the temperature is increasing, the char yield and the time conversion are decreasing, hence it is obtain less amount of char in less time with more temperature, see Figure 11.

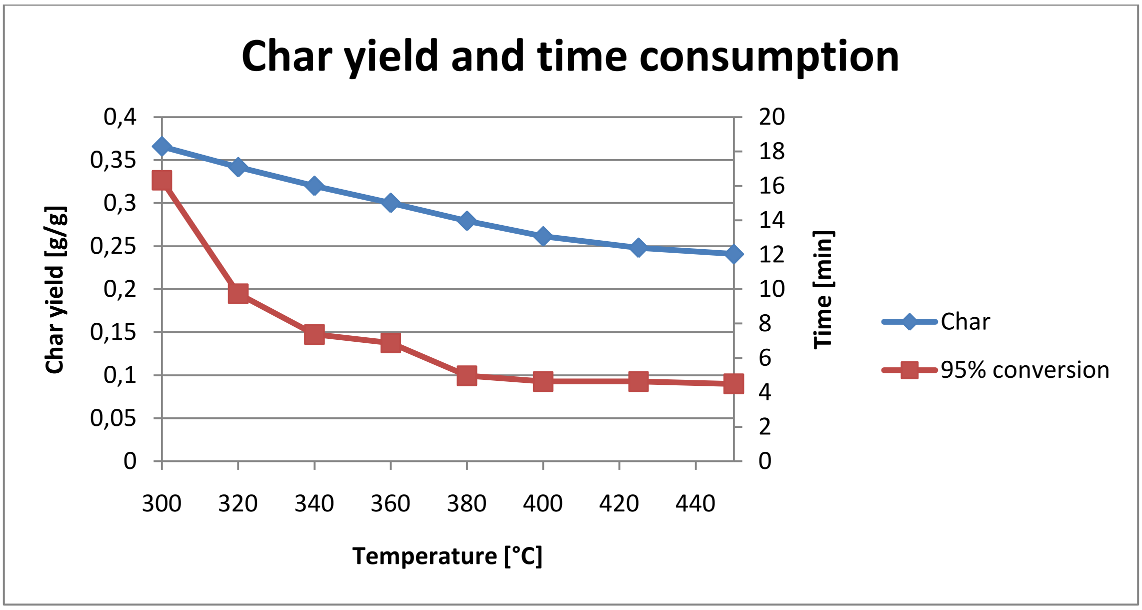


Figure 11: Graph of char yield and time consumption of wood chips

4.2 Bio-oil

Then it was done some experiments with bio-oil (from a plant in Finland): from a liquid state it was obtained a porous sponge state, really breakable into little pieces almost only touching as it is shown in Figure 12.

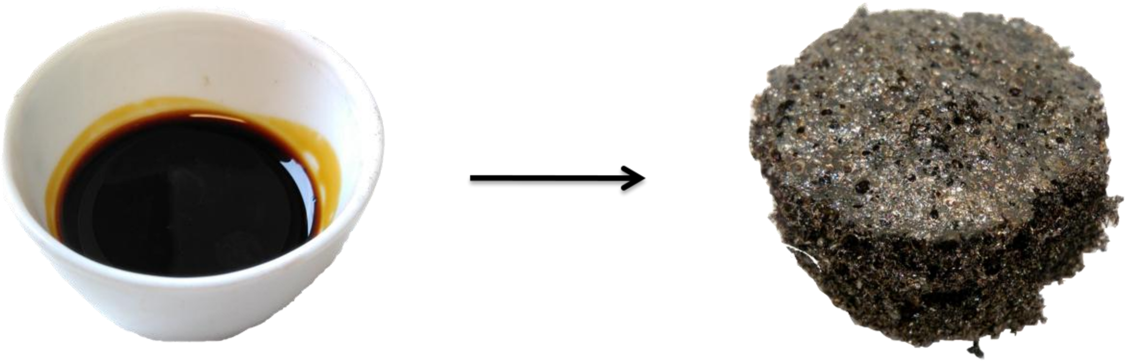


Figure 12: Picture of bio-oil before and after pyrolysis

4.3 Wood + tar

Once it was done pure wood, it was started with the impregnation process; with the help of a paint brush the wood chip pieces were impregnated of oil at different percentages. It was impossible to impregnate more than 40%. Figure 13 shows a piece of wood impregnated with oil and the same piece after pyrolysis.

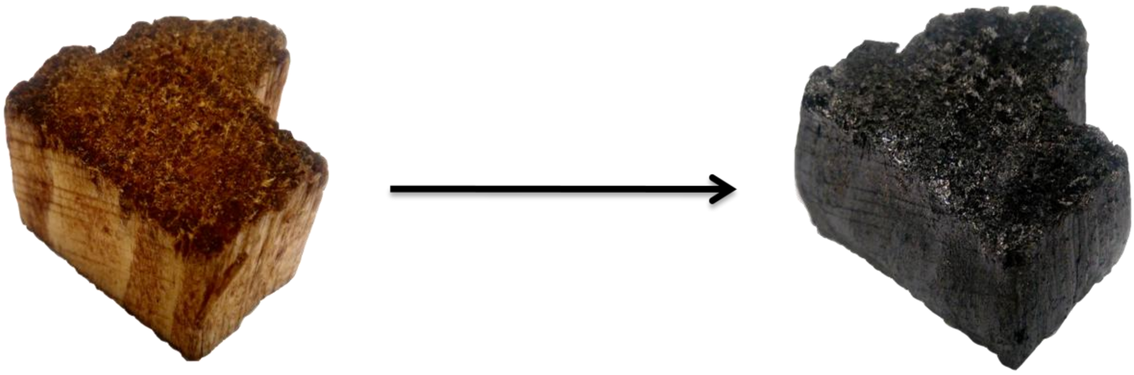


Figure 13: Picture from a woodchip impregnated of oil to char of it

In this graph (Figure 14) we can noticed that the decomposition is slower with oil but it takes almost the same time to reach the final weight, it is decomposed the same amount.

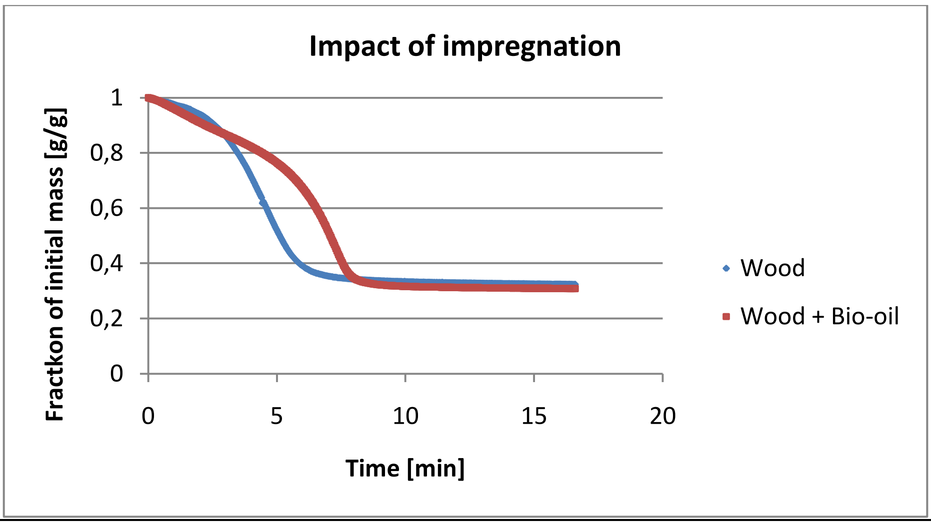


Figure 14: Graph showing the impact of the impregnation

4.4 Char + tar

The final experiments were with impregnated char from the optimal temperature (340°C). The optimal temperature was decided to be 340 because the good relation between the amount of char and the time that was taken to obtain them, see Figure 15:

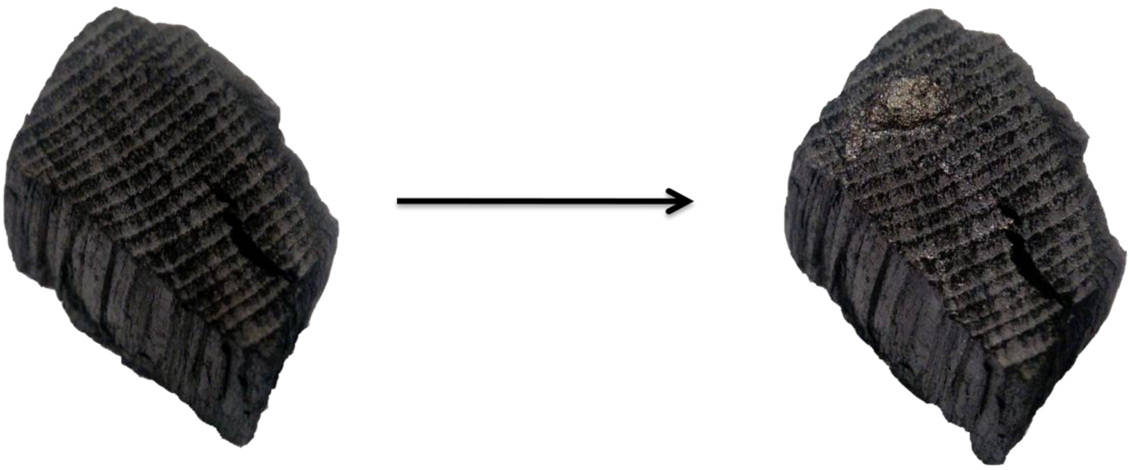


Figure 15: Picture of char impregnated of oil before and after pyrolysis

In this picture, we can notice how the char was impregnated and what happened with this oil after pyrolysis.

Therefore, with all this kind of data, we can make compare different variables: The following graph (Figure 16) shows the total mass yield of the various samples at different temperatures, how it is decreasing when the temperature is increasing but it is almost constant when char is again pyrolysed.

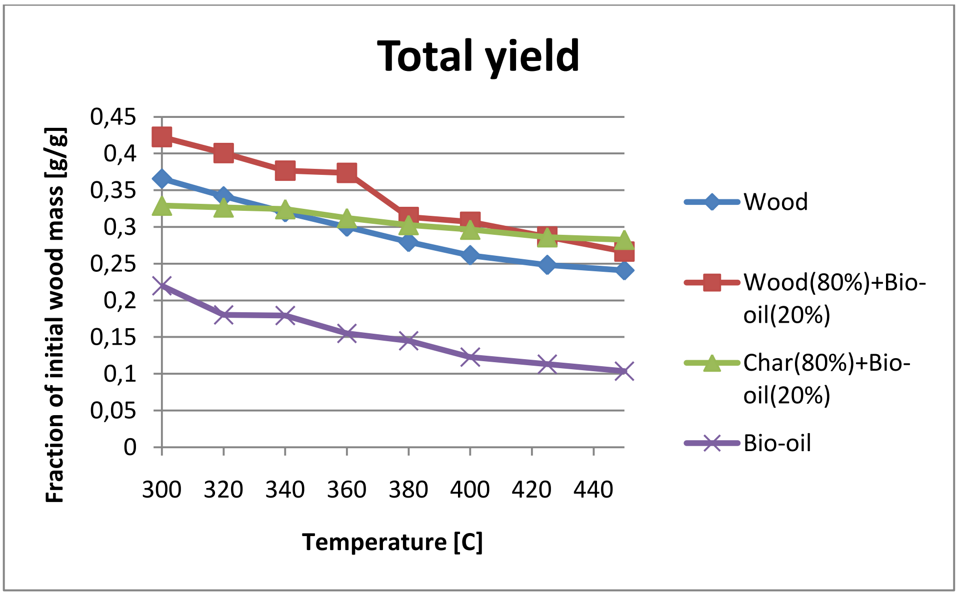


Figure 16: Graph of the total yield of different samples at different temperatures

If we make all the samples start at 1 (100% of the piece at the beginning), we can see clearly how from pure wood, oil and wood with oil it is reduced almost the same amount, while once it is char when it is pyrolysised again with oil, it barely changes the amount of mass(all the samples at 340°C), see Figure 17.

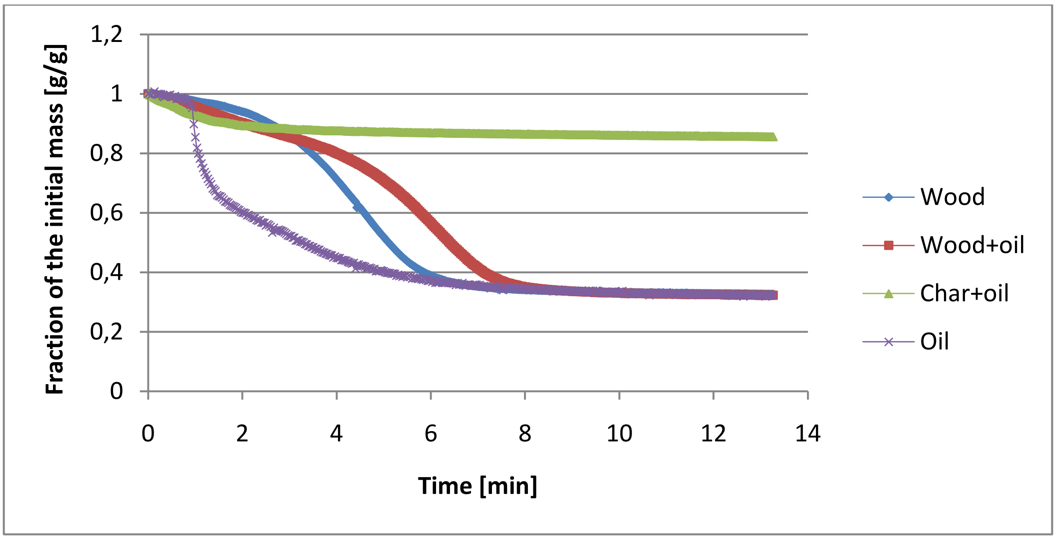


Figure 17: Graph about the comparison mass yield for the different samples (all at 340°C)

At the moment that it is compared wood-oil with only oil, it is noticed that with more percentage of oil, it is obtained more mass yield.
As long as it was not possible to impregnate more than 40% of oil in the wood chip, it was made an experiment mixing oil with wood powder, see Figure 18.

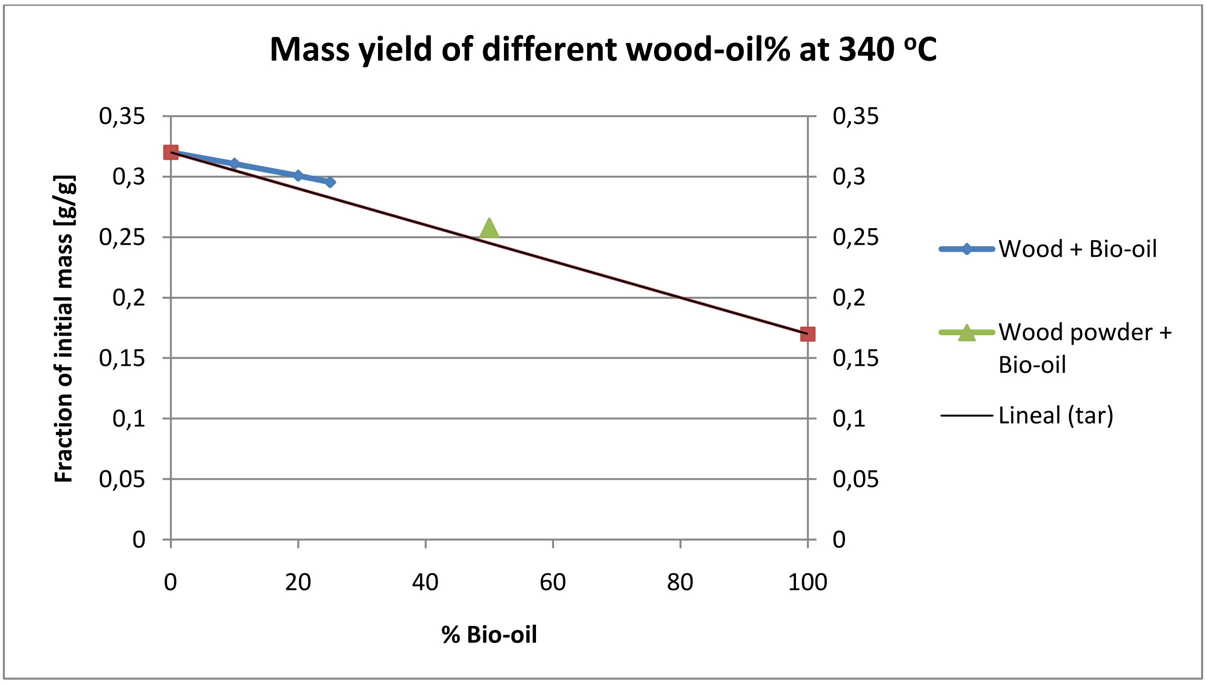


Figure 18: Graph of mass yield of different wood-oil% at 340°C

Meanwhile, for char-wood, it is almost the same mass yield for it in compare with tar, see Figure 19.

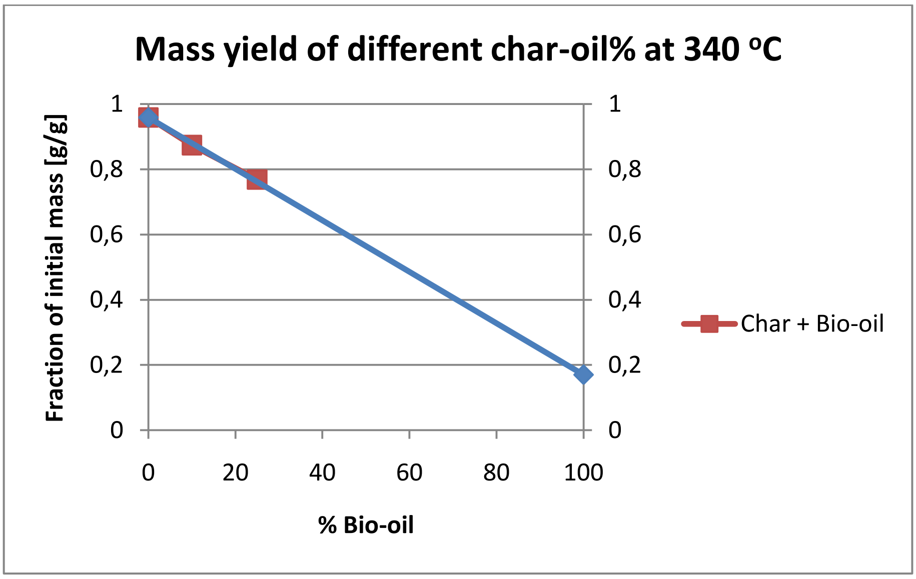


Figure 19: Graph of mass yield of different char-oil% at 340°C

4.5 <u>Elemental Analysis</u>

Some samples at 300, 340, 400 ºC of wood, wood and oil, char and oil and oil were sent to the Faculty of Chemistry in the University of Vienna to determine the content of Carbon (C), Hydrogen (H), Nitrogen (N) and Sulfur (S). In the Table 2 we can see the results:

Table 1: Content of CNHSO in the different samples

	%C	%H	%N	%S	% O
Wood (300°C)	73,05	4,56	0,09	<0,02	22,31
Wood (340°C)	74,98	4,03	0,10	<0,02	20,89
Wood (400°C)	76,96	3,62	0,17	<0,02	19,26
Tar (300°C)	71,88	4,86	0,28	<0,02	22,98
Tar (340°C)	74,45	4,59	0,31	<0,02	20,64
Tar (400°C)	78,12	3,89	0,35	<0,02	17,64
Wood-oil (300°C)	73,23	4,63	0,14	<0,02	22,00
Wood-oil (340°C)	74,63	4,39	0,12	<0,02	20,86
Wood-oil (400°C)	76,73	3,77	0,16	<0,02	19,34
Char-oil (300°C)	75,52	4,00	0,15	<0,02	20,33
Char-oil (340°C)	75,15	4,27	0,12	<0,02	20,47
Char-oil (400°C)	77,83	3,58	0,13	<0,02	18,46

The richest the sample in carbon, the better for steel production. In Figure 20, it is shown that with more temperature, it is obtained more content of Carbon.

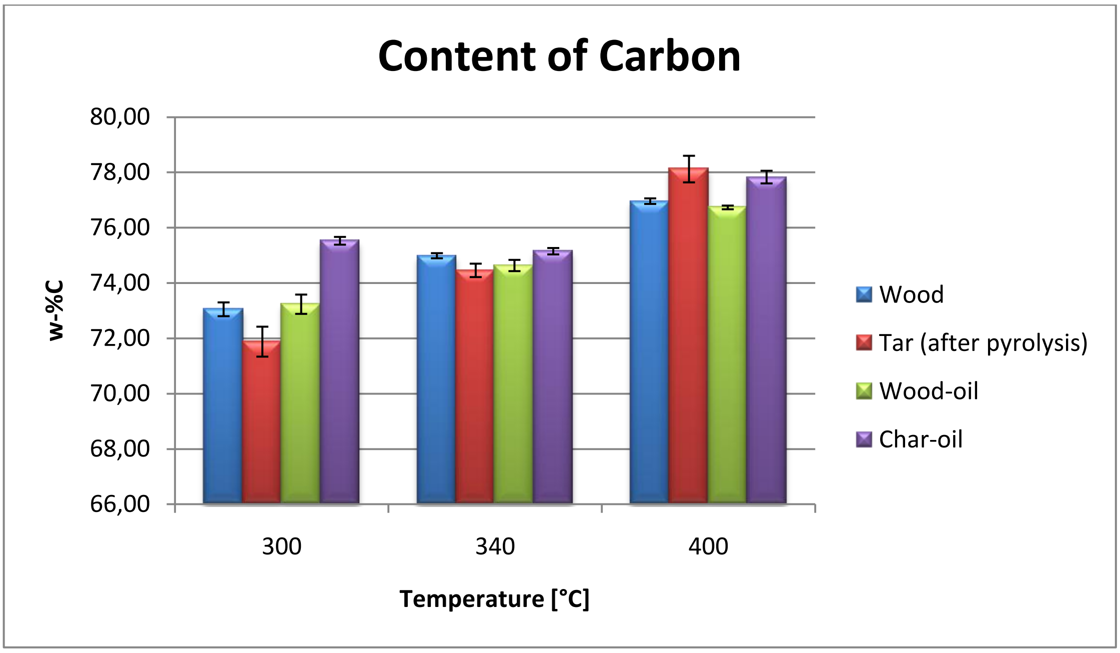


Figure 20: Graph of the content of Carbon of the different samples

Figure 21 shows the content of Hydrogen in each sample; contrary to Carbon, with more temperature it is obtained less Hydrogen.

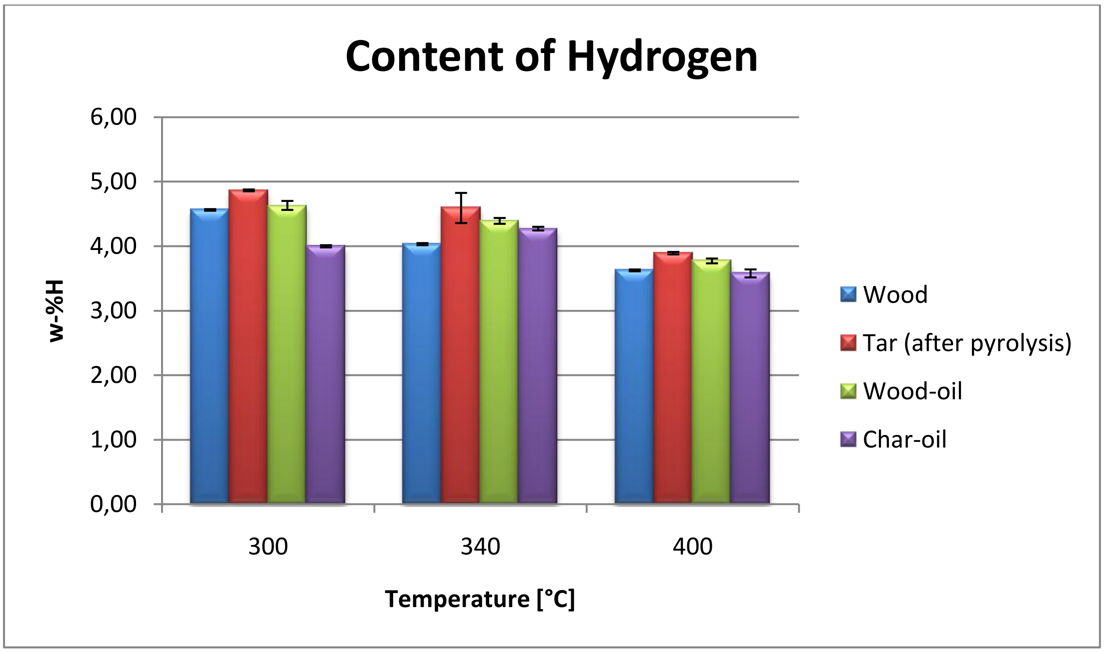


Figure 21: Graph of the content of Hydrogen of the different samples

Figure 22 shows the content of Oxygen in the different samples; as Hydrogen, with more temperature, it is obtained less content.

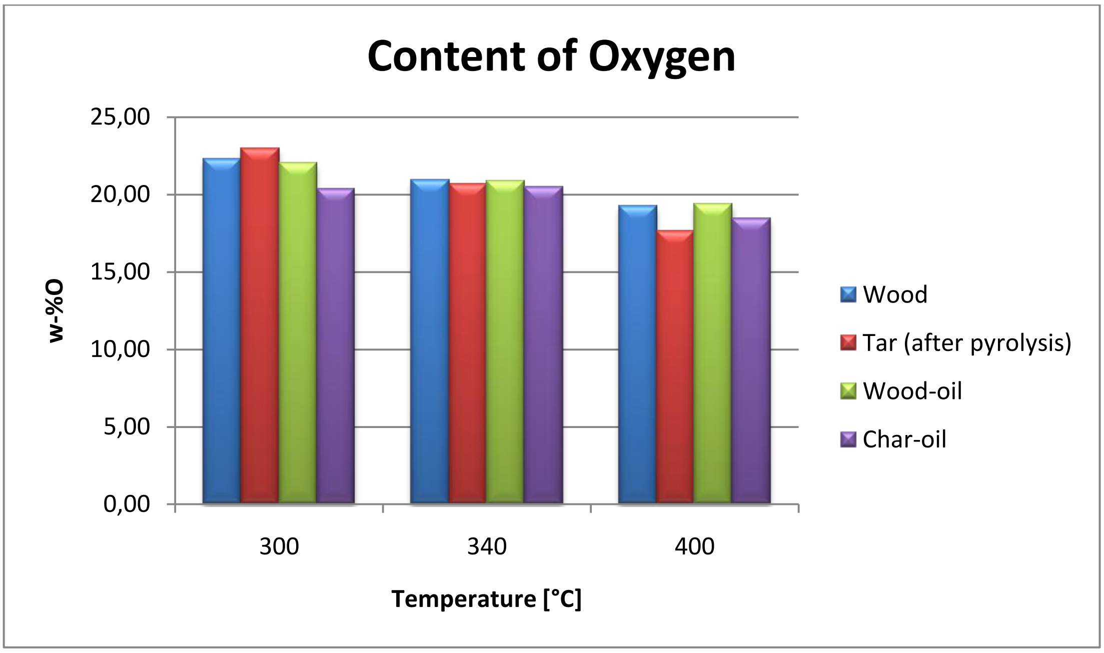


Figure 22: Graph of the content of Oxygen of the different samples

4.6 <u>HHV</u>

The High Heating Value is the amount of energy released as heat in the combustion process of a specific element.

The calorimetric bomb (Figure 23) determines the High Heating Value of a given sample knowing the weight of it by heating up the water that surrounds the combustion chamber in the combust. The ignition is made by an electric spark which ignites a cotton thread that will propagate the flame to the sample.

Figure 23: Picture of calorimetric bomb

Looking at the results (Figure 24), we can conclude that the char, pyrolysied wood, has that highest HHV of all the samples taken at 340ºC.

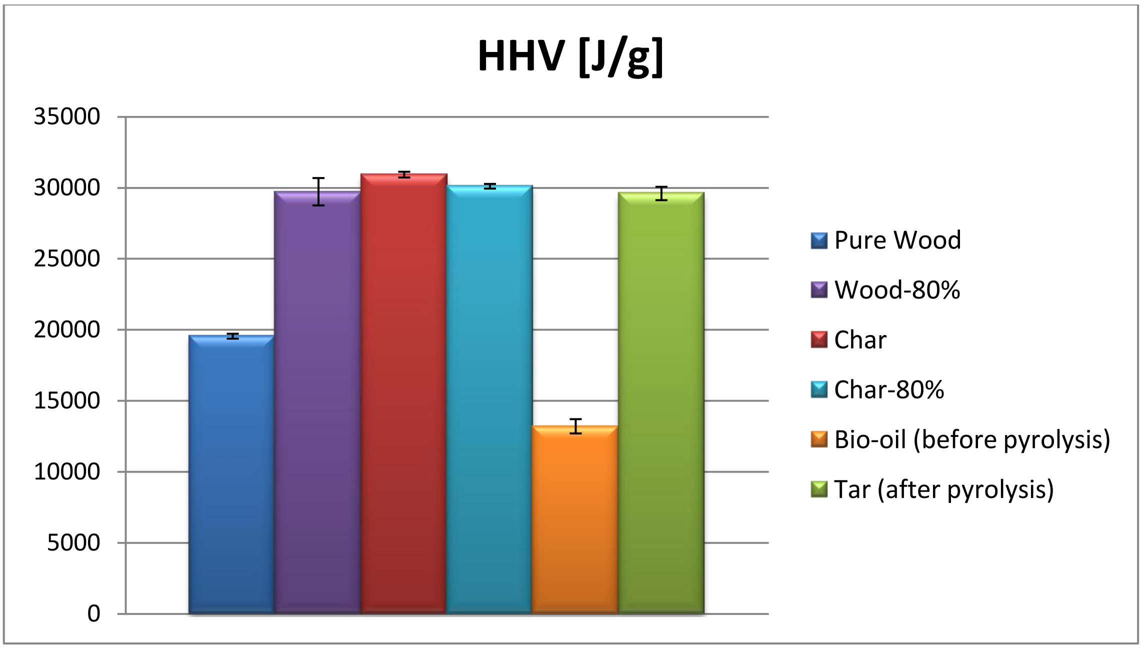


Figure 24: Graph of different HHV of various samples

Is was also done some experiments to see how the pyrolysis temperature affects to the High Heating Value in this case to pure wood (Figure 25):

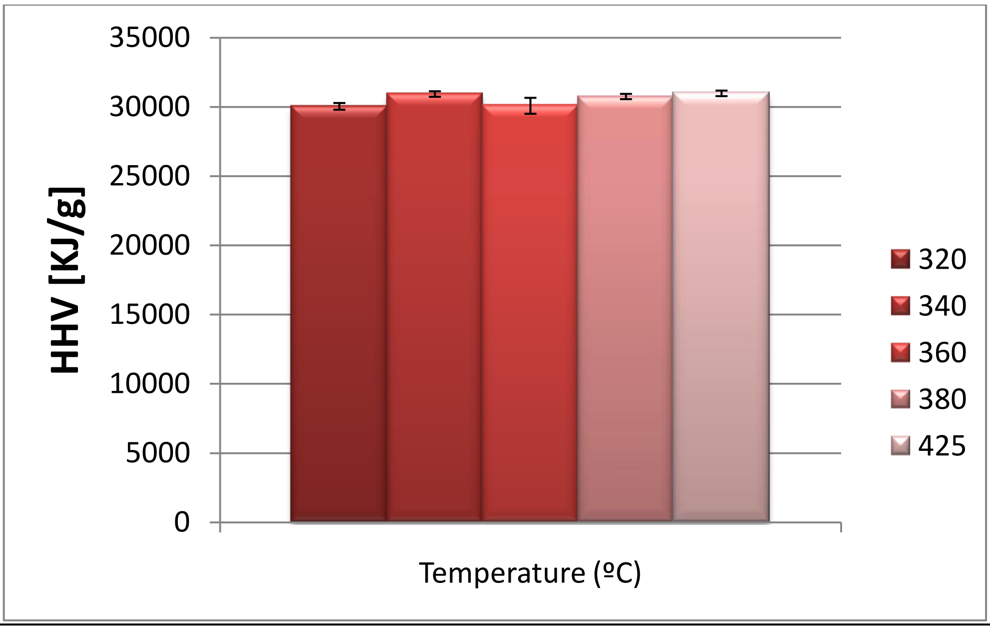


Figure 25: Graph of different HHV depending on the temperature

4.7 Mass and energy balance

It was also done some calculations in order to know the mass and energy yield.

The mass yield can be defined as the ratio between the actual mass after pyrolysis and the mass before it.

$$y_c = \frac{m_c}{m_w} \, [g/g]$$

The energy yield can be defined as the ratio of the amount of usable energy delivered from a particular energy resource to the amount of energy used to obtain that energy resource.

$$y_E = \frac{m_c * HHV_c}{m_{w,i} * HHV_w} \, [KJ/KJ]$$

Table 2: Values of the mass and energy field

		y_c	y_E
Wood	char	0,31995	0,50617644
	w-80%	0,37671	0,572742339
	c-80%	0,3243	0,499469343
Oil	Tar	0,179416	0,080059979

With this data, it can be compared the mass and energy yield between the pure wood with the char, the wood impregnated with oil and the char impregnated with oil; and also it is compared the bio-oil with tar, see Figure 26:

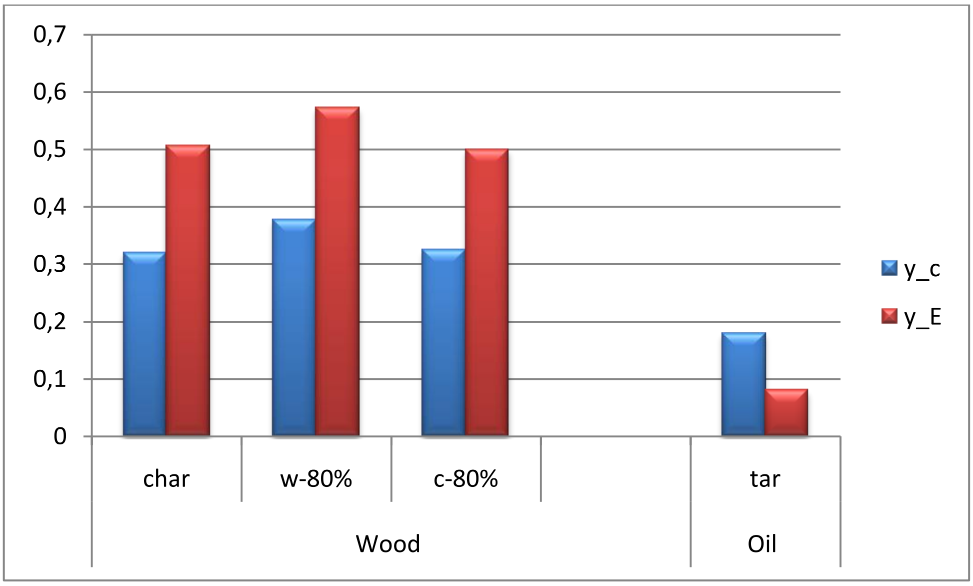


Figure 26: Graph of mass and energy yield in comparison with the raw materials

From the graph, it can be concluded that wood with 20% of oil has the best mass and energy yield in compare with the pure wood. On the other hand, tar in relation with bio-oil has the worst mass and energy yield.

5 Conclusions

After all the experiments, some conclusion can be recovered:

- At lower temperatures pyrolysis takes more time.
- Weight is a clearly factor of how the piece get the final weight.
- At a fixed temperature, it is going to decompose the same amount of weight of the pieces.
- Increasing the temperature gives less mass yield for every sample.
- Impregnation gives the same mass yield than pure chips.
- Doing twice pyrolysis you obtain almost the same piece at the second stage.
- It is only possible to impregnated 40% (40-oil/60-wood).
- Impregnated char with oil and char have almost the same mass and energy yields.
- Pyrolysis at more temperature gives biochar with more HHV.
- With more temperature, it is obtained more content of Carbon and less of Hydrogen and Oxygen.
- A good final option can be Wood+Bio-oil at 340°C.

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