Closing the mass-balance of pyroprobe research regarding biomass fast pyrolysis

by

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to obtain the degree of Bachelor of Science
at the Delft University of Technology and Leiden University,
to be defended publicly on Wednesday Februari 5, 2020 at 11:00 AM.

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Project duration:	August 19, 2019 – Februari 5, 2020	
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Abstract

Presently, the majority of the worlds energy supply is dependent on fossil fuels. As these fuels are a limited resource and have significant negative side effects, the way humanity uses these is unsustainable and other sources of energy have to be found. One of these sustainable energy sources is plant-derived biomass. However, biomass cannot be efficiently used in its natural form and needs to be converted to other products through processes such as pyrolysis and gasification. Pyrolysis will be the focus of this thesis, as fast pyrolysis of Miscanthus is studied for the BRISK 2 project at Process & Energy (TU Delft). However, the current setup used for pyrolysis research does not provide a complete mass-closure of the experiments, with only 80% of the total mass accounted for in the char, tar and gaseous yields. In order to improve this closure, four different methods were developed and investigated during this thesis.

All of the pyrolysis experiments were performed in a Pyroprobe 5200. The pyrolysis parameters were comparable to fast pyrolysis, with a high heating rate of 600°C/s, a low residence time of 10 s and a Final Pyrolysis Temperature between 600°C and 1000°C. The objective of the first adjustment was to improve the purge flow stability, reduce the amount of blockages in the system and increase the accuracy of the experiments. The flow meter, controlling the purge flow, was replaced with a mass-flow controller and a tube in the setup was simplified and shortened. No further blockages were observed and the total mass-closure improved on average by 7.85 wt% over the temperature range of 600-1000°C, with an increase at every temperature. The second considered element was the homogeneity of the biomass. Two biomass feedstocks were investigated, the first feedstock consisted of inhomogeneous pellets grinded down to a size less than 80 μm, while the second type was homogenized biomass of a size of less than 200 μm. Both biomass types performed comparably to each other and better than the previous data collected with the setup. At 600°C the inhomogeneous biomass performed better, while at 700°C the homogeneous biomass gave a higher yield.

The last two experimental series both focused on gravimetrically measuring the tars collected in the condenser of the setup, which was not gravimetrically measured before. The first of these methods removed the condenser in favour of a direct capture in a quartz trap. This gave a maximum yield increase of 1.14 wt% at 700°C. However, concerns of contaminating the gas mixture with tars arose, therefore this method was not investigated at higher temperatures. In the second technique, the 2 ml of isopropanol in the condenser was evaporated from a glass Petri dish, leaving the tars behind. This method was explored over a larger temperature range (600-1000°C), yet only provided a maximum increase of 1.5 wt% at 1000°C, while giving significant fluctuations between experiments. Thus proving that neither of these methods is a suitable way of gravimetrically measuring the condenser.

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Introduction

When people talk about turning points in history one that usually comes to mind is the ability to control fire around one million years ago. Fire gave early humans the ability to cook their food, bake pottery and protect them from dangers. However, simple wooden fires do not burn hot enough to be used for some types of pottery and most kinds of metallurgy. This all changed with the invention of charcoal for the melting of ores around 4000 BCE [1]. In order to create this charcoal, ancient humans would burn wood in an enclosed pile with a restricted availability of oxygen to limit combustion. This would remove all the volatiles in the wood, resulting in incomplete combustion and leave pure char in a process we would now call slow pyrolysis. Thus a large part of human innovation and development has depended on pyrolysis.

Fortunately, modern humans do not face the same challenges as ancient humans. The biggest challenge of the 21st century is global warming and our dependency on unsustainable resources. Currently, only a small part of our energy demand is satisfied by so called ”renewable energy sources” [2]. The two technologies that generally come to mind when discussing renewables are solar-photovoltaic (PV) cells and wind energy. One that is often forgotten is biomass, even though it contributes over half of the total current renewable energy production and has the ability to grow significantly [3].

Biomass is also more versatile when compared to other renewables. Energy sources such as solar and wind can only produce power at certain points in the day or year. This production does not necessarily overlap with the demand for power, thus requiring large storage facilities [4]. Biomass on the other hand can be used in the same way as conventional fuels, such as oil and coal. Thus, biomass energy production can fluctuate in unison with the demand for power in a similar way as conventional power generation does [5].

An additional benefit of biomass is that it can be converted to products such as methane, bio-oil and other substances. Currently, these chemicals are extracted from fossil-fuels and are not easily regenerated. Modern industries depend on these chemicals and would not be able to function without them. Hence, conversion of biomass could also provide a renewable option for industry [6].

Large-Scale Energy Storage (subdepartment of Process & Energy at the TU Delft) is one of the participants in the EU BRISK 2 project. The objective of BRISK 2 is to gather knowledge and perform research regarding biofuel production and biomass conversion [7]. The research at Large-Scale Energy Storage, regarding the BRISK 2 project, focuses on the gasification of biomass. This includes computational models of gasification and experimental work on the Novel 50 kWth Indirectly Heated Bubbling Fluidized Bed Steam Reformer. One of the steps in gasification is pyrolysis and experimental pyrolysis data can therefore be used to improve the models. However, this data needs to be accurate and precise, which has been an obstacle in the past.

This research focuses on the fast pyrolysis of Miscanthus at high temperatures with low residence times. The goal is to better understand and measure the different yield fractions. At the moment, around 80% of the mass is accounted for [8]. One part of the setup, called the condenser, is currently not gravimetrically measured and the remaining 20% is likely found there in the form of tars and water. Thus, the pyrolysis setup will be improved and optimized in order to increase the mass-closure.

1.1. Biomass

Biomass is an all encompassing term for all the organic materials within or derived from a plant or animal. This can be either in the context of a fuel for energy production or in terms of total mass in an ecosystem. Examples of biomass include plant matter, faecal waste and algae [9]. Because this research focuses on pyrolysis, this report will only focus on botanical biomass as a fuel source.

When discussing biofuels for energy production, several different generations can be stated. For the production of first generation biofuels food crops are used on arable land. This puts first generation biofuels in direct competition with food production. Due to this fact, first generation biofuels have a bad reputation, especially in parts of the world were food is scarce [10]. On the other hand, second generation biofuels are produced from the residues or waste of food crops, or are grown on marginal land where food production is not possible. This process is not in competition with food production and additionally offers the opportunity for more advanced processing, such as gasification or pyrolysis. Lastly, third generation biofuels are produced from algae, however this report will not focus on them.

1.1.1. Biomass formation

Botanical biomass is formed within plants by a process called photosynthesis. During photosynthesis carbon dioxide, water and sunlight are converted into oxygen, carbohydrates and energy. This process is called assimilation and is the basis for most life on planet earth. The water and carbon dioxide are absorbed by the plant in respectively the roots and leaves. The water is then transported to the leaves, where photosynthesis takes place. Organelles, called chloroplasts, in the cells of the leaves contain the pigment chlorophyll that is able to absorb light in order to sustain the reaction [11].

The general formula for the production of biomass can be given by:

$$6\,CO_2 + 6\,H_2O + \text{Sunlight} \xrightarrow{\text{Chlorophyll}} CH_mO_n + O_2 - 481\,\text{kJ/mol [12]}$$

Even though energy is produced during photosynthesis, this is not the main pathway for energy production. The sugars produced during photosynthesis will be metabolised by the plant into energy during a process called dissimilation or metabolism. This is a more efficient way for the plant to produce the energy it needs to survive. The plant also produces secondary products that are needed to survive. These include a wide range of molecules including polysaccharides, lipids, proteins and complex organic compounds. These secondary products are derived from intermediate products of photosynthesis or the metabolism of sugars. The exact composition of secondary products and the specific molecules produced differ between plants [11].

According to *Basu et al.*, biomass can be defined as a complex mixture of organic materials, such as carbohydrates, fats and proteins, along with small quantities of minerals, such as sodium, phosphorus, calcium and iron [12]. Botanical biomass can be split into three different component categories called extractives, cell wall components and ash. An overview has been provided in figure 1.1.

Extractives are nonstructural components that include fats, proteins, oils and sugars [13]. Solvents can be used to dissolve extractives and can thus be recovered by evaporation of the solvent. The cell wall of a plant provides the needed structural support for the cell. The cell wall consists of carbohydrates (cellulose and hemicellulose) and

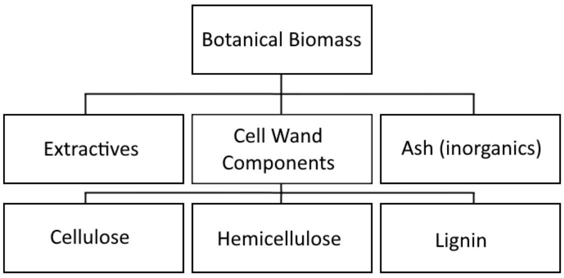


Figure 1.1: Components of botanical biomass, adapted from [12].

lignin. Cellulose and hemicellulose form fibers which the lignin holds together. The ash amounts all the inorganic particles within the cell and provide a wide range of functions.

Cellulose is a linear polysaccharide with the molecular formula $(C_6H_{10}O_5)_n$. The chain is homogeneous and consists of 7000-15000 $\beta(1\rightarrow4)$ linked D-glucose molecules, as can be seen in figure 1.2 [14]. The chains are unbranched, highly crystalline and provide a high tensile strength to the cell wall. Furthermore, cellulose is a very stable molecule and cannot be dissolved in water or most organic solvents. It is however possible to dissolve cellulose in highly concentrated mineral acids at high temperatures or by specific enzymes [15][16].

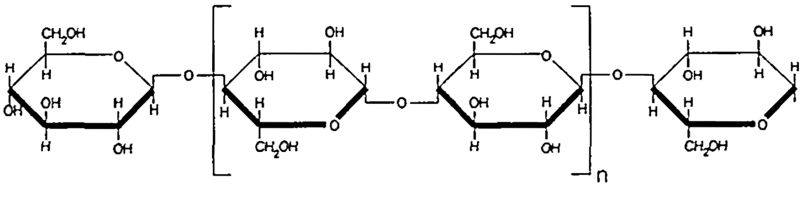


Figure 1.2: Structure of cellulose, taken from [17].

Unlike cellulose, hemicellulose is shorter, branched and heterogeneous in nature. A hemicellulose chain has a length of 500-3000 monomer units and is amorphous in shape [14]. Monomers in hemicellulose can be glucose molecules or other sugar molecules such as xylose, mannose and rhamnose. Hemicellulose can be dissolved and is also more susceptible to being hydrolyzed by acids, bases or enzymes compared to cellulose. When pyrolyzing hemicellulose more gas and less tar yields can be expected compared to cellulose [12].

Lignin is the name of a group of large, aromatic and heterogeneous organic polymers. As can be seen in figure 1.3, lignin is highly branched, cross-linked and three dimensional in shape. Three precursor monolignol monomers can be determined, which are coniferyl, sinapyl and p–coumaryl alcohols, however the exact composition will depend on the organism in question [18]. The main purpose of lignin is to act as a glue for the cell walls; it can covalently bind with hemicellulose and can create fibres by cross-linking. Due to the heterogeneity of the molecules it is hard to measure its molecular weight and only a range can be given, for example between 3000 and 8000 unified atomic mass unit [19]. During pyrolysis more phenolic products can be expected due to the aromatic nature of the molecule [20].

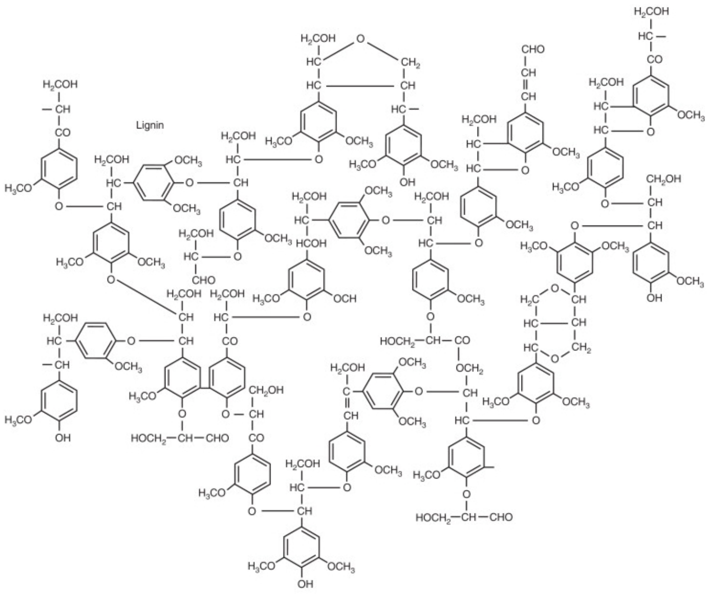


Figure 1.3: Example of a lignin structure, taken from [21].

1.2. Pyrolysis

The goal of pyrolysis is the decomposition or devolatilization of biomass into numerous smaller and simpler molecules. In order to achieve this, the biomass is heated in a non-oxidative medium to a Final Pyrolysis Temperature (FPT), which is usually between 380°C and 530°C [12]. The absence of oxygen is necessary to ensure that no gasification or combustion takes place. Furthermore, heat needs to be provided as the reactions are overal endothermic.

As a result of the pyrolysis three different fractions will form. A solid fraction (biochar), a liquid fraction (condensable gases or bio-oil) and a gaseous fraction (non-condensable gases). Additionally moisture is released from the biomass and pyrolytic water is formed which becomes part of the liquid fraction. Later these different fractions will in more detail discussed in 1.2.2.

A general overview of the pyrolysis reaction is:

$$\mathrm{C}_n\mathrm{H}_m\mathrm{O}_p \xrightarrow{\text{heat}} \sum_{Solid} \mathrm{C}_{\text{char}} + \sum_{Liquid} \mathrm{C}_a\mathrm{H}_b\mathrm{O}_c + \sum_{Gas} \mathrm{C}_x\mathrm{H}_y\mathrm{O}_z + \mathrm{H}_2\mathrm{O}\ [11]$$

One of the more influential factors on the fractions of non-condensable gases, condensable gases and solids is the FPT. At the lower temperatures primary reactions will take place. Small and light molecules within the biomass will be volatilized and polymer chains will be depolymerized. The main products of these reactions are condensable gases and biochar [22].

If the temperature is increased further, secondary reactions will start to take place. These reactions will further decompose the biomass and start to break down the condensable gases into smaller molecules, specifically non-condensable gases. In past research regarding FPT, it can moreover be seen that higher temperatures do indeed yield a significantly larger fraction of non-condensable gases and a lower fraction of condensable gases [23].

In figure 1.4, a simplified diagram of a pyrolysis process can be seen. Biomass, usually ground into small particles and sometimes already pretreated, is supplied to the fluidized bed where the reactions take place. This bed is fluidized with an unreactive medium such as nitrogen or helium. Most of the produced char will remain in the reaction vessel and will have to be removed in order to prevent accumulation. A part of the char will follow the gas stream as aerosols and needs to be separated to prevent them from poisoning the bio-oil [24]. The gases can be separated into bio-oil (condensable gases) and the non-condensable gases. Then, the non-condensable gases and char can be used to heat the new feedstock or used in other applications. The carrier gas can also be recycled since this is not being used in the reaction.

1.2.1. Types of pyrolysis

In general three different types of pyrolysis can be stated. These are slow, fast and flash pyrolysis. As can be seen in table 1.1, these types have different characteristics. The main characteristics are residence time, heating rate and final temperature. Consecutively, these parameters will change the yields of the reaction. However, the ranges of these parameters are not always clear and can differ, with some definitions giving a broader or smaller range.

Table 1.1: Typical characteristics of the three different pyrolysis types [25][26].

Pyrolysis Process	Solid Residence Time (s)	Heating Rate (K/s)	Particle Size (mm)	Temp (K)	Product Yield (%)		
					Oil	Char	Gas
Slow	450-550	0.1-1	5-50	550-950	30	35	35
Fast	0.5-10	10-200	<1	850-1250	50	20	30
Flash	<0.5	>1000	<0.2	1050-1300	75	12	13

These three types of pyrolysis will now be further discussed.

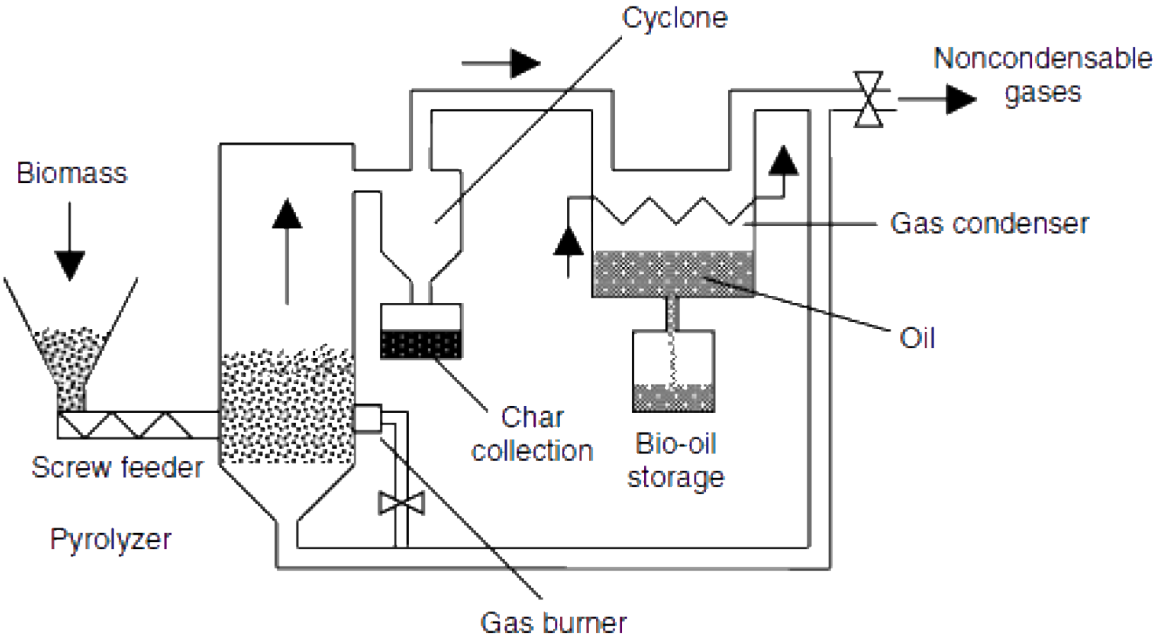


Figure 1.4: A simplified diagram of a pyrolysis process, taken from [12].

Slow pyrolysis

As said before, slow pyrolysis, also known as carbonization, is the oldest pyrolysis process used by humans. The main characteristics of slow pyrolysis are (comparably) large particle size, low heating rates, long residence times (5-10 minutes) and a low final temperature (around 400°C). Due to the large particle size (5-50 mm) the heat transfer is limiting the heating rate around 100 K/min [27].

Even though all three phases (solid, liquid and gas) are produced, the slow pyrolysis process favours the production of biochar and non-condensable gases [25]. Due to the long residence time secondary reactions can take place even though the final temperature is low. The produced condensable gases still have time to react further into more biochar and non-condensable gases, hence explaining the name carbonization. This increases the biochar and gas yield, while decreasing the oil yield.

Fast pyrolysis

Fast pyrolysis is the intermediate between slow and flash pyrolysis. Heating rates are between 100 and 1000 K/s, while residence times can reach several seconds. Depending on the parameters chosen, the process can be optimized for solid, liquid or gas production. In order to reach the optimal temperature, heat transfer plays an important role. This is necessary to avoid undesired side-reactions such as low-temperature charcoal forming reactions. Therefore, the particle size is in the order of micrometers [28].

Fast pyrolysis is the chosen method during this research.

Flash pyrolysis

The main characteristics of flash pyrolysis are the short residence times (30-1500 ms) and the very high heating rate (1000 K/s). Due to the short residence time secondary reactions do not take place. Bio-oil yields can reach up to 70-75 wt% while minimizing the amount of non-condensable gases. Thus making this process very attractive for the production of bio-oil [29].

Flash pyrolysis does have some drawbacks. As flash pyrolysis takes place over a short time period with very high heating rates and temperatures, most of the produced molecules are not yet in a stable form. Therefore, the produced bio-oil is of lower quality in regards to poor thermal stability, higher corrosivity and an increase of viscosity over time. Dissolved char in the oil will act as an catalyst further degrading volatiles, which will increase the viscosity [29].

1.2.2. Pyrolysis products

Solid products

The first fraction that will be discussed are the solids. This fraction consists of biochar, ash and aerosols.

Biochar consists mostly of pure carbon, up to 85 wt%, and only has a small fraction of hydrogen and oxygen [12]. The precise composition will depend on the parameters chosen in the pyrolysis process and the original feedstock. A typical value for the lower heating value (LHV) of biochar is between 30 and 35 MJ/kg, which is significantly higher than the original biomass or the bio-oil products [12].

The ash in the solid fraction consists mostly of inorganics, such as potassium and calcium. These inorganics can influence the reaction kinetics of the pyrolysis as catalysts [24]. The amount of ash in biomass pyrolysis is significantly lower compared to conventional fossil fuels. As ash will not decompose during pyrolysis, the amount of ash will depend on the chosen feedstock. In softwoods it is around 1 wt%, while in herbaceous biomass and agricultural residue it can be as high as 15 wt% [24]. *Mos et al.* show that the moment of harvest also influences the amount and composition of the ash [30].

During the pyrolysis process small aerosol particles will also form. These will not stay with the biochar but follow the gases to either the bio-oil or the non-condensable gases. In the bio-oil these aerosols might later cause problems during downstream processing or combustion [24]. Furthermore, they can facilitate catalysis of secondary reactions.

Liquid products

The liquid products, also known as bio-oil, is usually the desired pyrolysis product. This is due to the high versatility of the oil and easier ability to convert to other products, unlike the char and gas fractions. Because of the high pyrolysis temperatures, the bio-oil will not be in the liquid phase during the reaction and will be a vapour. Therefore they are also known as the condensable gases and will have to be cooled down and condensed in order to create the bio-oil [12].

Compared to conventional oil, bio-oil has several benefits and drawbacks. First of all, the sulfuric content of bio-oil is significantly lower than crude oils. According to *Sipila et al.* the sulfuric content of bio-oil is 0.05 wt% [31]. Crude oil on the other hand is 0.94 wt% and rising [32]. Bio-oil is also carbon neutral and can even be carbon negative if combined with Carbon Capture and Storage in contrast to fossil fuels.

However, due to the release of moisture, the production of pyrolytic water and the abundance of oxygen the heating value is decreased [33]. The LHV of bio-oil is 16-19 MJ/kg compared to crude oil at 44 MJ/kg [13]. This in turn can cause problems during the ignition of engines. In order to decrease the water content the biomass can be pretreated by torrefaction. The abundance of acids in the bio-oil can also damage the engines by corrosion. In order to avoid this corrosiveness special treatments need to be used. However, *Wang et al.* showed that the addition of a catalyst (calcium hydroxide and potassium carbonate were used) could significantly decrease the production of acids in the bio-oil [34].

Bio-oil also suffers from ageing due to the instability in the molecules as a results of the high oxygen content. This results in lower heating values and an increase in viscosity over time. These oxygen containing groups can be removed by post-processing the oil with HDO or zeolite cracking [35]. As with conventional fossil-fuels, bio-oil has other uses than fuel. An overview is provided in figure 1.5.

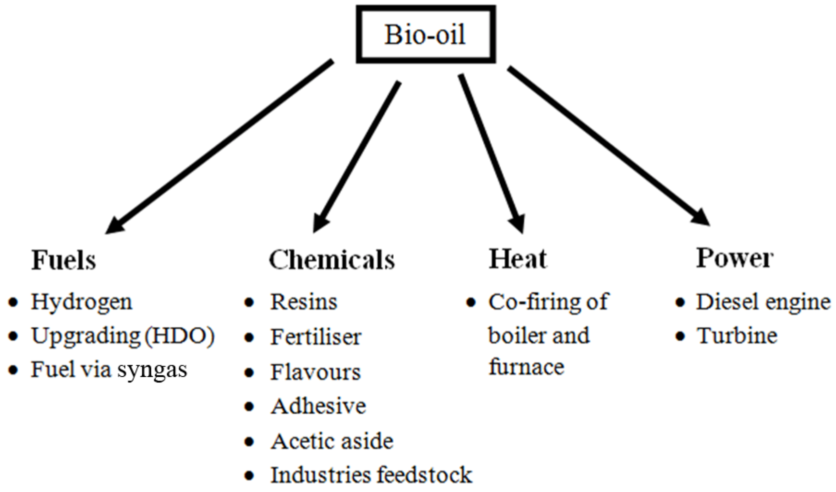


Figure 1.5: An overview of applications of bio-oil, taken from [29].

Gaseous products

As mentioned before, the gases are a mixture of condensable gases (vapour) and non-condensable gases. Due to the high temperatures in the reaction vessel, the condensable gases are still vapours. After the gases leave the pyrolyser the condensable gases will condense into liquids as bio-oil. The non-condensable gases will continue and be captured for analysis/use [12].

The non-condensable gases mostly consist of low-molecular weight gases. These include hydrogen, methane, carbon monoxide, carbon dioxide and more. Due to the fact that these gases are mostly formed by secondary reactions there is an inverse relation between the liquid and the gas fraction. This also means that the gas yield at low temperatures is insignificant, due to the lack of secondary reactions. Previous research has shown that it is possible to catalyse the production of gases, but this is not the focus of this report [36].

Earlier research done by *Basu et al.* shows that the LHV differs for gases formed by primary and secondary reactions [12]. The LHV for primary gases is around 11 MJ/Nm^3 and around 20 MJ/Nm ^{3} for secondary gases. This is still lower than the LHV of natural gas, which is around 36 MJ/m^3 [37]. This difference is due to the fact that the gases produced by pyrolysis are mostly composed of carbon monoxide and carbon dioxide, which have a low or no caloric value.

1.2.3. Parameters in pyrolysis

As mentioned before the pyrolysis conditions play an important role in the process. Therefore it is of the utmost importance that these are chosen correctly and are kept constant during the experiments. These parameters will now be further discussed.

Particle size

The particle size distribution of the feedstock can have a significant influence on the pyrolysis process. As mentioned in section 1.2.1 heat transfer plays an important role in fast pyrolysis. In order to reach high levels of heat (500°C/s) and mass transfer, particles need to around a diameter of 1-2mm, which is significantly higher than the size used in these experiments (80-200 µm) [38]. At this size the thermal conductivity of biomass is 0.1 W m^{-1} K^{-1} along the grain and 0.5 W m^{-1} K^{-1} across the grain [39]. *Shen et al.* also showed that the size of the feedstock does indeed play a role and larger particles will increase char and gas yields while decreasing tar yields [40]. The particles used during this research have been grounded to a size of less than 80 µm and thus should not be internally heat transfer limited.

Pressure

According to literature the influence of pressure on pyrolysis does not have a consensus. For instance, *Basile et al.* showed that an increase of pressure (up to 40 bar) has a significant influence on the char yields [41]. However, *Melligan et al.* show that during slow pyrolysis of Miscanthus an increase in pressure does not result in changes in yields [42]. However, Melligan does state that the characteristics of the products do change. The surface area of the char decreases, while the carbon content increases. Another interesting fact that Basile shows is that the heat requirements for pyrolysis changes due to pressure changes. The needed heat is lower at higher pressures and can even be exothermic. Nonetheless most pyrolysis research is performed at atmospheric pressure, as is this research [34], [43].

Pre-treatment

Depending on the desired outcome of the pyrolysis, pretreatment of the biomass can be necessary. Examples of methods include torrefaction (a form of mild pyrolysis), washing the biomass and hot water extraction of hemicellulose [44]. These can for instance reduce moisture content or change the bio-oil composition. One of the biomasses used during this research was homogenized, but no other specialized pretreatment methods were employed.

Medium and flow rate

As mentioned before, in order to perform pyrolysis an inert atmosphere is necessary. If oxygen is present, reactions such as combustion can take place and the biomass will not be properly pyrolyzed. Therefore a purge flow of pure nitrogen gas is usually used, however other inert gases such as helium or argon are also possible. Because these gases do not participate in the pyrolysis process it is possible to separate and recycle them in order to save cost [12].

The purge flow rate is an interesting variable in the pyrolysis process. The influence it can have differs greatly, due to the effect it has on the residence time. In general a higher flow rate will increase tar yields, while decreasing char yields, yet not very significantly [45], [46], [47], [48]. However, if the flow rate is significantly low, tar yields will drop considerably due to conversion of the condensable gases to non-condensable gases by secondary reactions [49].

Heating rate

Due to the complexity of pyrolysis the influence of a variable such as heating rate is hard to isolate. In most research the heating rate is not independent of residence time and final temperature. However, some research does exist that specifically focuses on the heating rate. For instance *Agnin et al.* show that biochar yields are dependent on the heating rate, as shown in figure 1.6 [50]. It can be seen that at higher heating rates the char yields decrease. This is expected due to the fact that at higher heating rates, secondary reactions are limited as the machine requires less time to get up to temperature [51]. Thus a high heating rate results in a lower char yield and a higher tar yield.

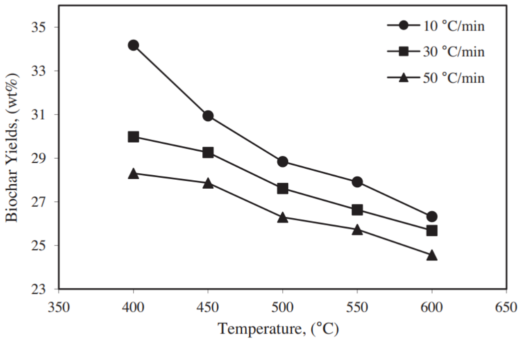


Figure 1.6: The influence of heating rate on biochar yields, taken from [50].

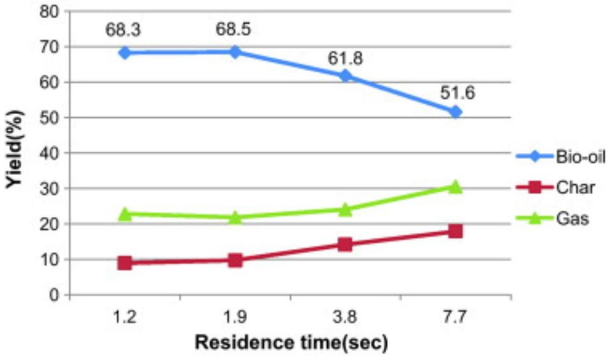


Figure 1.7: The influence of residence rate on yield composition, taken from [52].

Residence time

Vapour residence time has a large influence on the yield composition of the pyrolysis products. As mentioned before, the residence time will depend on the chosen purge flow rate. At higher residence times the condensable gases will experience more secondary reactions. This in turn will decrease tar yields while increasing char and gas yields, as can be seen in figure 1.7 [52], [53]. The produced char particles during secondary reactions can also pose other problems as mentioned in 1.2.2.

Final Pyrolysis Temperature (FPT)

The last and perhaps most important parameter in pyrolysis is the FPT. The FPT is the temperature at which the pyrolysis takes place and therefore has a major influence on the produced products. Hence, it is no surprise that research regarding the influence of the FPT is quite extensive. However, most of these studies were performed between 300°C and 600°C which lies outside the temperature range used in this project (600-1000°C) [55], [52], [53], [23]. Yet, *Park et al.* and *Tsai et al.* did investigate higher temperatures up to 800°C [48], [56].

Typically, an increase in temperature leads to a decrease in char yield, while increasing gas yields. Tar yields usually show a hyperbolic behavior where at first an increase in yield is expected, but at higher temperatures the yield will decrease as can be seen in figure 1.8. This behavior is due to an increase in secondary cracking at higher temperatures producing lighter tar species and non-condensable gases [54]. Therefore an optimal temperature can be found for bio-oil production. This temperature does however depend on the chosen biomass. For instance, *Kim et al.* showed an optimal temperature for Miscanthus sacchariflorus at 350°C, while *Demiral et al.* showed 550°C for grape bagasse [53], [57]. Previous research performed in Process & Energy at the TU Delft showed a potential optimal temperature for Miscanthus giganteus at 600°C [8].

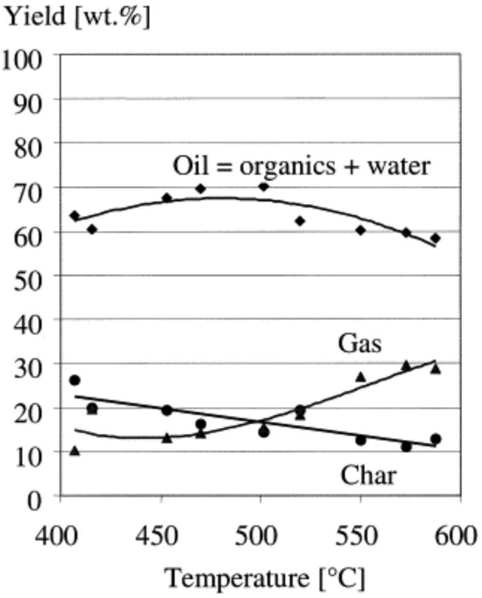


Figure 1.8: Typical influence of the temperature on the yield composition, taken from [54].

1.3. Feedstock

The feedstock chosen for this research is Miscanthus x giganteus, also known as elephant grass. This plant is a hybrid between the wild plants Miscanthus sinensis and Miscanthus sacchariflorus [58]. Miscanthus giganteus is an example of a second generation biomass and its popularity has been increasing the last couple of years. This is mostly due to its ability to grow on marginal land and its efficiency regarding water and nutrient use [59].

Miscanthus agricultural yields in Europe and the USA is around 15-30 tonne per hectare, yet yields are highly dependent on soil quality, weather conditions and moment of harvest [60]. For instance, *Stavridou et al.* showed that in areas of Europe with a soil salinity of 0.5-0.99 dS m^{-1} or lower a decrease of 11% dry mass yield can be expected [61].

Miscanthus can either be harvested early during the autumn or later during winter or even early spring. If left in the field and harvested later the biomass will dry over time. This will decrease the dry mass yield of the harvested crop [62]. A benefit of a later harvest is the increased combustion characteristics and increased oil production during fast pyrolysis [30].

One tonne of Miscanthus can generate up to 4 MWh when combusted and produces only 5.4 g CO_2 per kWh. This gives a significantly lower carbon footprint compared to LPG at 323 g, oil at 350 g and coal at 484 g CO_2 per kWh [63]. According to *Tolbert et al.*, the composition of Miscanthus Giganteus is 37 wt% cellulose, 36 wt% hemicellulose and 25 wt% (Klason)lignin [19]. According to earlier research at Process & Energy (TU Delft) the moisture content of Miscantus is 6.7 wt% and 8.7 $\pm$ 1.47 wt% [64], while an other source provides 8.76 wt% [65].

1.4. Research questions

This report will focus on the optimization of the mass-balance closure of fast pyrolysis research. This optimization specifically regards the fast pyrolysis of Miscanthus x giganteus in the Pyroprobe 5200 used at the Process & Energy department of the TU Delft. This goal results in the following main research question.

How can the conduction of the experiments and the sampling techniques be optimized in the Pyroprobe in order to achieve higher mass balance closure values?

Due to the complex nature of this research it will be necessary to first state and answer a number of sub questions. These will provide a more detailed description of the research.

- *How does the purge flow stability influence the yield composition of Miscanthus pyrolysis?*
- *What is the influence of homogeneity of the biomass on the yield composition during Miscanthus pyrolysis?*
- *How can the tars and moisture collected in the condenser be gravimetrically quantified and how does this impact the total pyrolysis yield composition?*

2

Materials and Experimental Methodology

Due to the fact that this research is focused on setup optimization, it is of the utmost importance that the setup is properly understood. Therefore, the base setup and a general description of an experiment will first be described. Then the chosen methods of answering the research questions will be explained.

2.1. Setup description

All the experimental runs during this research were performed with a modified Pyroprobe 5200 from CDS Analytical. The modifications on the machine were made during previous research by Christos Tsekos and others in order to simplify the machine. The Pyroprobe 5200 can be used for micro-scale pyrolysis research under a high temperature environment [66]. This machine is part of the sub-department Large-Scale Energy Storage at Process & Energy (TU Delft). The traps, holders and quartz wool were also all produced by CDS Analytical.

2.1.1. Biomass and sample preparation

During the experiments, two types of Miscanthus biomass were used. The first type of Miscanthus (now called Non-homogenized biomass) was harvested in 2017 by the company Comgoed in The Netherlands and are provided in pellets. These pellets were grinded down and sieved to a size of less than 80 µm. This size was required to minimize the effects of heat transfer limitations and homogenize the biomass. Figure 2.1 shows the freshly grinded Miscanthus on the left and 6 months old Miscanthus on the right. Both are the same particle size, however the older Miscanthus shows a slight discoloration compared to the fresh biomass, likely due to ageing.

A second type of Miscanthus (now called Homogeneous biomass) was also used during the experiments. This Miscanthus was homogenized by the Centre for Research & Technology, Hellas (CERTH) in Greece for the Brisk 2 project. As can be seen in figure 2.1 (middle), this Miscanthus is of a rougher grind (less than 200 µm) compared to the other type. The particles possess a thinner and elongated shape compared to the powder form of the Miscanthus produced from the pellets.

Samples are prepared in a 2.1 mm quartz holder. These are hollow tubes with no blockages at both exits. In order to create a bed to keep the biomass in place, roughly 15-25 mg of quartz wool is seared and pressed down at one end of the holder. Subsequently, 30 ± 0.2 mg Miscanthus is added and careful attention is spent to create a solid and level bed with no particles sticking to the walls of the

Figure 2.1: Freshly ground (left), homogenized (middle) and old Miscanthus biomass (right).

holder. In order to properly seal the biomass in the holder, a cap is created from seared quartz wool. After each step the holder is weighed and cleaned with compressed air to get rid of any particles that settled on the outside of the holder. When an experiment is completed the holder is emptied of its residues and seared with a torch to clean the surface of left over char and soot.

2.1.2. Detailed description of specific components

The base setup has the following main components: mass-flow controller, probe/interface, oven, first trap, condenser and gas syringe. A schematic overview is provided in figure 2.2 and a picture of the completed setup can be seen in figure 2.3.

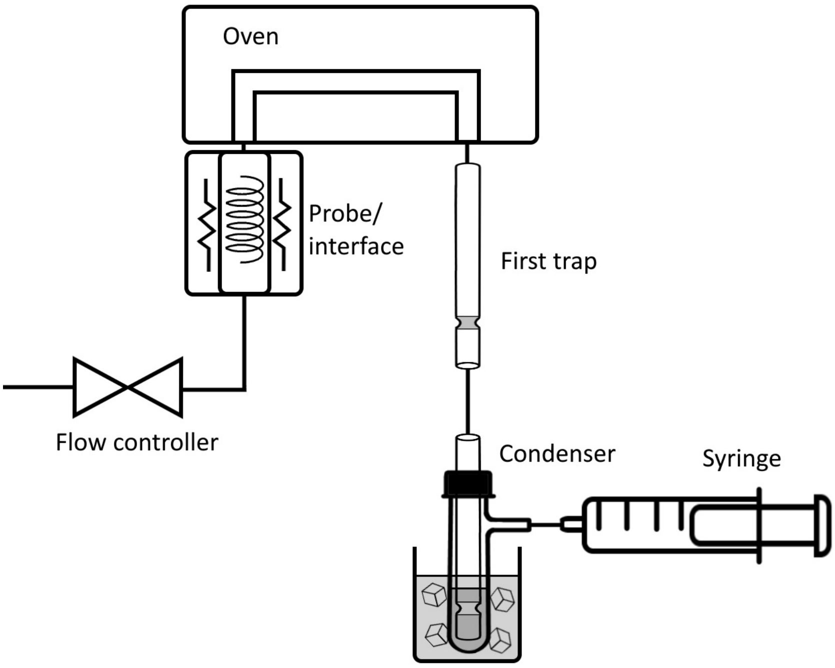


Figure 2.2: Schematic of the base setup.

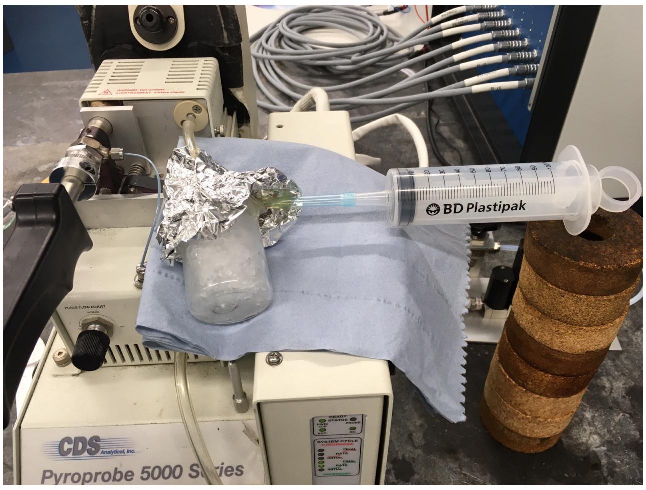


Figure 2.3: A picture of the completed base setup.

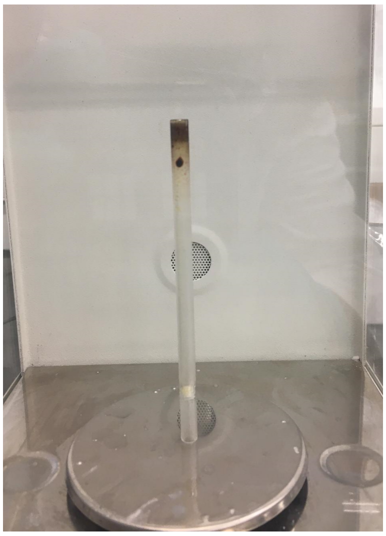


Figure 2.4: A picture of weighing the first trap.

Flow controller

During previous research, a flow meter from TA Instruments was used to check and control the nitrogen purge flow through the system. Observations during experiments showed that the purge flow through the machine would change over time due to pressure changes in the supply system. An integrated gas system is installed in the lab at Process & Energy and the pressure would depend on the amount of active users. In order to mitigate this problem and improve accuracy, the flow meter was replaced with a mass-flow controller (Alicat Scientific). During all experimental runs this mass-flow controller was set to 10 ml/min and no significant deviations were noted.

Probe and interface

The probe/interface is where the quartz holder is positioned and the pyrolysis takes place. The interface had a resting temperature of 50°C and would increase to 300°C at a heating rate of 100°C/min at the start of an experiment. When the interface reaches 300°C the platinum probe coil surrounding the holder will activate and start heating at a rate of 600°C/s to the final temperature. However, as *Pecha et al.* had shown, a discrepancy between the nominal FPT of the platinum coil and actual temperature of the biomass exists [67]. Therefore, adjustments in the nominal FPT and holding time had to be made, which can be seen in table 2.1. These corrections were determined by measuring the temperature in the centre of the platinum coil with a thermometer, thus showing the actual temperature that to the nominal FPT provided.

Table 2.1: Adjustments in temperature and holding time

Final Pyrolysis Temperature (°C)	Nominal pyroprobe temperature (°C)	Pyrolysis time (s)	Holding time (s)
600	744.32	10	11.50
700	878.37	10	11.90
800	1008.42	10	12.50
900	1140.47	10	12.90
1000	1272.52	10	13.50

Oven

The purpose of the oven is to heat a small metal tube that acts as a connection between the probe and the first trap. In order to minimize the potential for gases and tars to get trapped, the oven is heated at a temperature of 325°C and the tube was shortened compared to previous research.

First trap

One end of the first trap was inserted into the oven while the other end was outside the machine at 50°C. The function of the first trap is to cool down and capture the majority of condensable gases/tars. With this goal in mind the trap was thoroughly cleaned with isopropanol, dried in an oven around 100°C and gravimetrically weighed before each experiment. After the experiment it was weighed again in order to calculate the tar yield as can be seen in figure 2.4. This step had to be performed as quickly as possible, due to the fact that volatile tars would evaporate from the trap if waited too long.

Condenser

The end of the first trap is connected with a plastic tube to the second trap, also known as the condenser. The goal of the condenser is to capture any remaining condensable gases. This is done by bubbling the purge flow through the second trap and isopropanol while the whole condenser is put in an ice bath.

The condenser consists of five parts: the second trap, a cap, an O ring, a test tube with secondary exit and an ice bath. Just like the first trap, the second trap is cleaned with isopropanol, dried but not weighed. The test tube, cap, tubing and O ring are cleaned as well. The end of the trap is inserted into the test tube and submerged in 2 ml of isopropanol (IPA), while the O ring and cap create an airtight seal at the top. A picture of the completed condenser can be seen in figure 2.5.

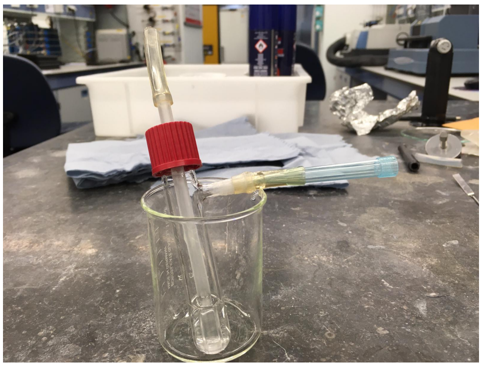


Figure 2.5: A picture of the completed condenser without the ice bath.

After the experiment the first trap is placed in 3 ml of isopropanol and the second trap in the previously used 2 ml. They will be allowed so soak for at least 45 minutes in order to dissolve any captured tars sticking to the traps. When the 45 minutes have passed the 2 and 3 ml will be combined, filtered, bottled in a HPLC bottle and placed in a fridge. This is done so the tars can later be analyzed in a HPLC analyzer or by other means.

Syringe

In order to be certain that all the gases are collected, a syringe is connected to the condenser when the interface reaches 270°C. These gases will consist of the nitrogen purge flow and the non-condensable gases produced during pyrolysis. Before each experiment a timed test is performed to determine if the setup leaks. Without starting the experiment the syringe is attached to the system and a timer is started. After 5 minutes the syringe should be at 50 ml, if this is not the case a leak in the system is present and has to be fixed. In order to be certain all the gases are collected the syringe stays connected for an additional five minutes after pyrolysis. Later the collected gases are analyzed with a micro-GC.

2.2. Gas Chromatography Analysis

During the experiment gas is collected in the syringe. This gas consists of the nitrogen purge flow and the non-condensable gases produced during pyrolysis. The main gases that are produced and measured by the micro-GC are H_2, CO, CH_4 and CO_2. A Gas Chromatography Analysis is performed in order to quantify the specific gases and calculate the gas fraction.

Gas Chromatography (GC) is similar to other types of chromatography. It consists of a mobile and a stationary phase. The mobile phase is a carrier gas (usually nitrogen), while the stationary phase is a tube. The analyzed molecules will be carried by the mobile phase through the tube. Different molecules will have distinct interactions with both phases. Some will prefer the mobile phase and exit the tube quite quickly, while others will prefer the stationary phase and take longer to exit. The time it takes to exit (also known as retention time) can be measured and thus provides an indication of the molecules in the gas.

A Varian CP-4900 Micro Gas Chromatograph was used with Galaxie as its software package. A template specifically designed for pyrolysis research was used, which could indicate and volumetrically quantify hydrogen, nitrogen, carbon monoxide, methane and carbon dioxide. It is not possible to detect air from the atmosphere that has entered the system as the GC is not able to measure oxygen and the nitrogen is mixed with the nitrogen from the purge flow. The software calculates a volumetrical percentage of each compound, which together with the total volumetric gas yield can be converted into weight percentages for H_2, CO, CH_4, CO_2 and normalized in regards to nitrogen.

One GC analysis takes roughly 2-3 ml of gas and needs to be repeated to a total of four runs. This is done in order to negate errors in the machine and improve accuracy. Of the four runs, one is usually an outlier and is discarded while the other three are averaged. Frequently, the first run is the outlier likely due to the fact that the tube connecting the syringe to the GC is able to slightly fill with air, thus contaminating and diluting the collected gas.

2.3. Experimental parameters

In order to be able to properly compare the different experiments to each other, several experimental parameters were kept constant. These include the pyrolysis time, heating rate, nitrogen purge flow rate and biomass weight. However, the FPT and the biomass type were changed during the experiments. As mentioned in 2.1.2, the temperatures and holding times had to be corrected by the values in the table 2.1. In order to create accurate results the experiments at each temperature were duplicated with a difference in char yields of less than 2 wt%. An overview of all parameters can be seen in table 2.2.

Table 2.2: All of the parameters for all experimental series

Series name	**FPT (°C)**	**Pyrolysis time (s)**	**Heating rate (°C/s)**	**Purge flow rate (ml/min)**	**Biomass weight (mg)**	**Biomass type**
Non-homogenized biomass	600, 700	10	600	10	30 ± 0.2	Non-homogenized biomass
Setup without condenser	600, 700	10	600	10	30 ± 0.2	Non-homogenized biomass
Evaporation method	600, 700, 800, 900, 1000	10	600	10	30 ± 0.2	Homogeneous biomass

2.4. Purge flow stability

The first factor that was examined was the influence of the purge flow on the yield compositions. As stated in 1.2.3, the purge flow rate will influence the residence time and can have a quite significant effect on the resulting tar and gas yields. Therefore two changes were made in the setup compared to previous experiments.

As mentioned in 2.1.2, previously the Pyroprobe setup used a flow meter instead of a mass-flow controller. This resulted in differences in purge flow between and during experiments. This was due to the fact that the nitrogen is supplied through an integrated system in the lab. At moments of high nitrogen demand (e.g. when many machines were running) the flow rate would drop beneath 10 ml/min and thus create inconsistencies in the experiments.

Figure 2.6: A picture of the previously used tube.

The second change compared to the previous setup was the tube in the oven. The old tube consisted of two separate metal tubes connected to each other, as can be seen in figure 2.6. The connecting part in the middle would be able to get blocked by tars condensing. These blockages would significantly decrease the flow rate, resulting in a lower mass-balance and fail the experiment [8]. The new tube on the other hand consisted of a single metal tube with a direct connection between the probe and first trap.

These experiments were performed with the implementation of both the mass-flow controller and the shorter oven tube. Furthermore, the chosen FPTs were 600°C and 700°C, with the Homogeneous biomass as the chosen biomass. The other parameters were kept constant with other experiments and can be found in 2.3.

As can be read in 3.2, these changes significantly improved the total yield composition and were therefore kept during the later experiments.

2.5. Homogeneous biomass

The second series of experimental runs had the goal of investigating the influence of homogeneity of the biomass on the mass yield composition. Previous experiments had used two types of biomass, a heavily grinded inhomogeneous biomass (Non-homogenized biomass) and a Homogeneous biomass. During these experiments suspicions arose that the difference of the biomass might influence the yield compositions of the pyrolysis. Therefore it was decided that a comparison of the yield compositions of the biomasses should be made.

These experiments had the same experimental parameters as mentioned in 2.3. A FPT of 600°C and 700°C, a pyrolysis time of 10s, the heating rate set to 600°C/s and the purge flow controlled at 10 ml/min. Once again, all the experiments were duplicated in order to get precise results. Both the Non-homogenized biomass and Homogeneous biomass were used.

2.6. Gravimetrically measuring the tars from the condenser

As stated in 1.4, one of the goals in this research was to gravimetrically measure the tars and moisture that are collected in the condenser. Previously, tars collected in the condenser have been examined with HPLC analysis, but not gravimetrically weighed. Therefore two different methods were developed to achieve this objective.

Removal of the condenser

The first method developed was a modification on the condenser. In this method, from now referred to as ”Setup without condenser”, the condenser is dismantled and only the second trap is used. As one might expect; no condenser, ice bath or isopropanol is used as can be seen in figure 2.7. This makes it possible to, like the first trap, gravimetrically measure the trap before and after the experiment. This allows precise measurements of all the tars and moisture collected in the second trap.

However, this method does have its limitations. First of all, the time a molecule stays in the second trap is lower compared to the condenser, due to the shorter travel distance. Secondly, the second trap is not cooled and is at room temperature.

Figure 2.7: A picture of the Setup without the condenser.

Thirdly, some compounds will dissolve well in isopropanol and might not condense with its removal. These complications combined means that the lighter tar species are less likely to condense and will instead enter the syringe. This will decrease the gravimetrical tar yield and contaminate the gas, which will influence the GC results.

Because of the issues with this method, only a small amount of experiments were performed. Two temperatures were investigated, 600°C and 700°C, with the other pyrolysis parameters as mentioned in 2.3. The Non-homogenized biomass was used during these experimental runs.

Evaporation method

The second method that was developed hoped to solve the aforementioned issues. In this setup the condenser is used once again and no changes to the experimental setup are made compared to the base setup. The adjustment in the approach is after the experiment. As mentioned in 2.1.2, the tars collected in the first and second trap will soak in IPA after which they will be filtered and bottled. In the evaporation method this last part was changed.

Before the experiment a glass Petri dish was cleaned, dried and weighed. After the experiment the 2 ml IPA that resided in the condenser was placed in the Petri dish and allowed to rest in the fume hood. This allowed all the IPA to evaporate from the Petri dish only leaving tars behind. After all the IPA was evaporated (after roughly 2 hours) the Petri dish would be weighed once again in order to determine the weight of the tars. Glass Petri dishes were chosen for this method due to the big surface area, which allowed for fast evaporation, and its resistance against IPA. A lab weighing cup was also tested, but not used as the IPA could be absorbed into the cup, thus hindering its evaporation, or dissolve the cup itself.

Because an increased yield in the condenser was expected at higher temperatures, due to lighter tar species being produced, a larger series of temperatures was investigated. The temperatures of 600°C, 700°C, 800°C, 900°C and 1000°C were chosen as the FPT. During these experiments the Homogeneous biomass was chosen, as it was certain that this biomass would perform optimal as it was homogenized. The other parameters were the same as in other experiments and can be found in 2.3.

3

Results and Discussion

3.1. Problems during experiments

A total of 47 experiments were performed. Of these 47 experiments, 13 could be classified as complete failures, 14 experiments yielded good results, 4 were performed for later analysis and the other 16 were neither complete failures or yielded the best results. Most of the failures were either due to leakages or incomplete pyrolysis.

Examples include:

- Holder with biomass falling out of the probe in the interface.
- Significant leakages causing the syringe not to fill up.
- Coil not heating up properly and failing to reach FPT.

Incomplete pyrolysis

If the pyrolysis was not successful, several observations would usually be made. Immediately upon weighing the first trap the tar yield would be very low and noticed. When the holder was removed from the probe its colour would either be light or dark brown instead of black, signifying that the biomass did not reach the proper temperature and was only lightly scorched instead of pyrolyized. The weight of the holder would also be higher compared to normal and the char yield would be between 40-75 wt%. In contrast, the volumetric gas yield would be normal, as this was mostly filled by the nitrogen purge flow. It can be assumed that the actual gas yields were lower, however no GC analyses were performed since the experiments were deemed a failure.

Leakages at the condenser

Leakages during the experiments were usually easy to notice. First of all, a distinct and significant odor could be detected around the machine. This was due to tars and non-condensable gases escaping from the machine. It could be compared to the smell of badly burning wood and would quickly spread through the lab. Frequently, but not always, the syringe would also fail to properly fill. Lastly, the tar and gas yields were lower compared to the expected values, while the char yields were not affected.

At the beginning of the experiments these leakages would most of the time occur in the condenser. This was noticed due to the fact that no leakages occurred

Figure 3.1: A picture of the soap flow meter.

after the condenser was removed during the series with the Setup without the condenser. The most likely explanation is that the cap of the condenser was not tightened enough, thus creating a leakages at the O-ring.

However, this leakage was hard to identify as an open soap flow meter was used to measure the flow at different locations in the setup (see figure 3.1). Since the top of the soap flow meter was open to the environment, the gas flow would be able to easily escape and no pressure would build up in the setup. This is not the case in the actual setup, where the system closed as the gas is captured in a syringe. However, in order to fill the syringe, the friction of the syringe needs to be overcome and thus a pressure difference will be created. This overpressure creates a leakage at the O-ring, while none would be found if the pressure is equal to the atmospheric pressure when the soap flow meter is used.

Leakages at the seal between the first trap and oven

In later experiments leakages started to occur at a different part of the machine. In order to create a proper seal between the first trap and the oven, a big screw with the trap in the middle needs to be aligned and tightened. As can be seen in figure 3.2, this screw consists of a metal screw and a plastic shroud. The metal screw creates the actual seal but due to its connection to the oven would be to hot to touch. The plastic shroud allows the user to properly tighten the screw. These two parts are connected to each other by three smaller screws equally spaced out so the screw perfectly rotates around the first trap (see figure 3.3). One of the small screws fell out at an earlier moment leaving only two screws to keep the metal and plastic shroud together.

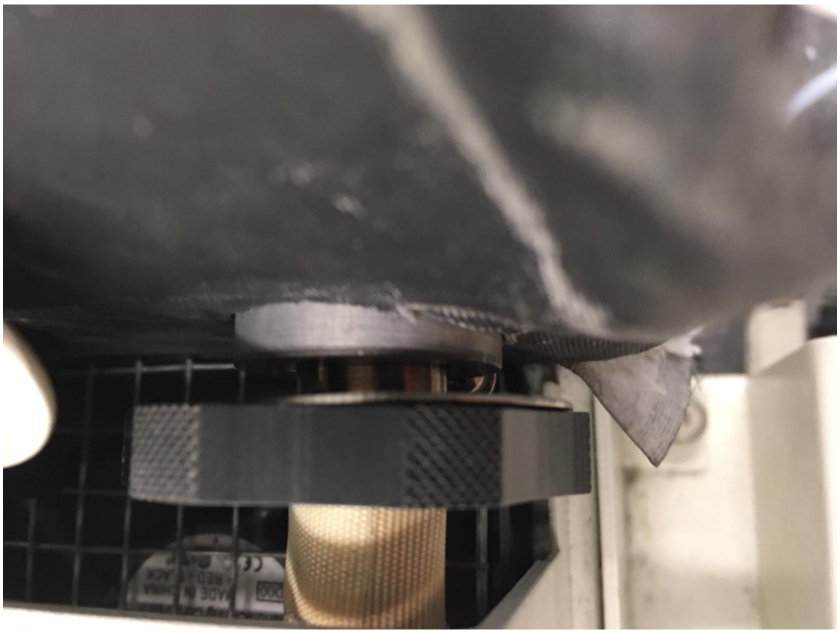


Figure 3.2: A picture of the connection between the first trap and oven.

During the later experiments one of the two remaining small screws loosened and fell out as well. This proved to create a significant complication. Due to the fact that only one screw remained, all force used to turn the seal would be exerted on this one screw. A secondary effect (and perhaps more significant) of only having one screw is that when turning the seal the plastic shroud would pivot around the screw instead of the first trap (see figure 3.3). This would make it almost impossible to create a tight seal, because tightening the seal would take it out of alignment, resulting in a significant leakage. As mentioned in 2.1.2, a leakage test would be performed with the syringe before each experiment and if a leakage was found this was fixed. Normally this would take five to ten minutes, yet after the screw fell out this would take up to a hour with roughly half of the experiments still failing. This significantly slowed down experiments and caused a lot of frustration. After a week and a half this problem was fixed by creating a brace for the other holes.

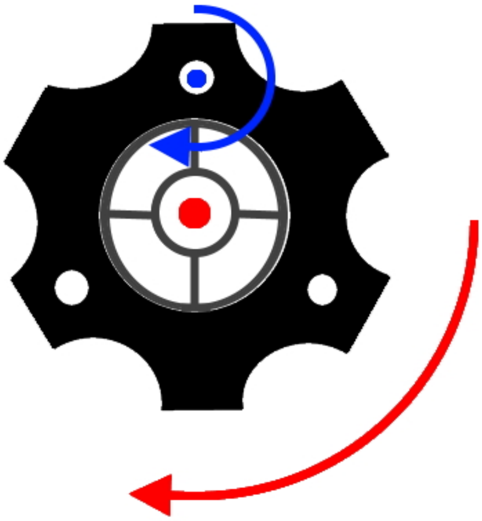


Figure 3.3: A drawing of the pivot problem with only one screw. The red arrow shows the turning with 2 or 3 screws in place, pivoting around the centre, while the blue arrow shows the pivot around the singular screw.

3.2. Purge flow stability

In order to single out the influence of both changes, the first experiments were run with the implementation of the mass-flow controller, yet with the old tube still in place. However, the data gathered with this setup cannot be used due to very significant leakages. Therefore, only the influence of both changes with be compared to the old setup with the flow meter and old tube. The data from the old setup (with the flow meter and old tube in the oven) has previously been gathered by Christos Tsekos (not yet published) and will from now on be called ”Previous data”. The new data has been taken from the experimental series of the Evaporation Method and will be called ”New data”. Therefore the specific parameters can be found in 2.3 and 2.6.

As can be seen in figure 3.4, overall the total mass-closure of the pyrolysis of Miscanthus has significantly been increased. At every temperature an improvement was measured. On average the total yield increased with 7.85 wt%, with greater improvements at higher temperatures. The lowest gain was measured at 600°C with 5.04 wt%, while the greatest was at 1000°C with 10.24 wt%. These increases were mostly due to an increase in tar yields. At lower temperatures a small increase in the char yield was found, while at higher FPTs a slight increase was measured in the gas yield. Furthermore, the trends found during this research are similar to previous Miscanthus research performed at Process & Energy [8] and similar pyrolysis research on other feedstocks by different institutions [68], [69], [70].

3.2.1. Char yields

The first of the products that will be discussed in detail is the char fraction. As can be seen in figure 3.5, the char yields of the New data are very similar compared to the Previous data. Only at the lower temperature of 600°C a significant difference can be found between the yields. As all the experiments at 600°C during this research had this increase (see 3.3 and 3.4.1), it is likely that the Previous data is incorrect due to inhomogeneity of the used sample and having a higher degree of volatiles.

3.2.2. Tar yields

A far more significant improvement could be found in the yields collected from the first trap. As figure 3.6 shows, the yields from the New data were significantly higher compared to the Previous data. On

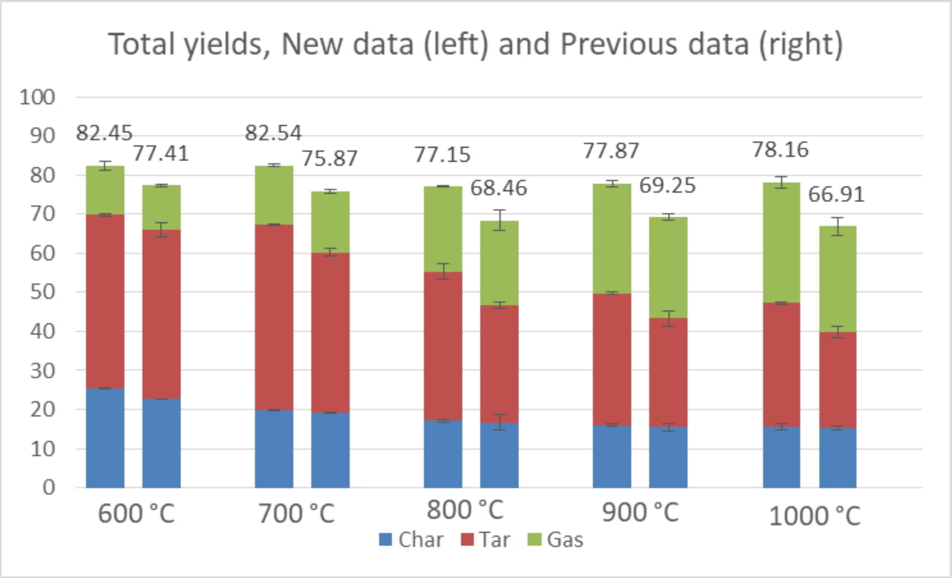


Figure 3.4: The total mass yields over the temperature range (600-1000°C) with the new data on the left and old data on the right.

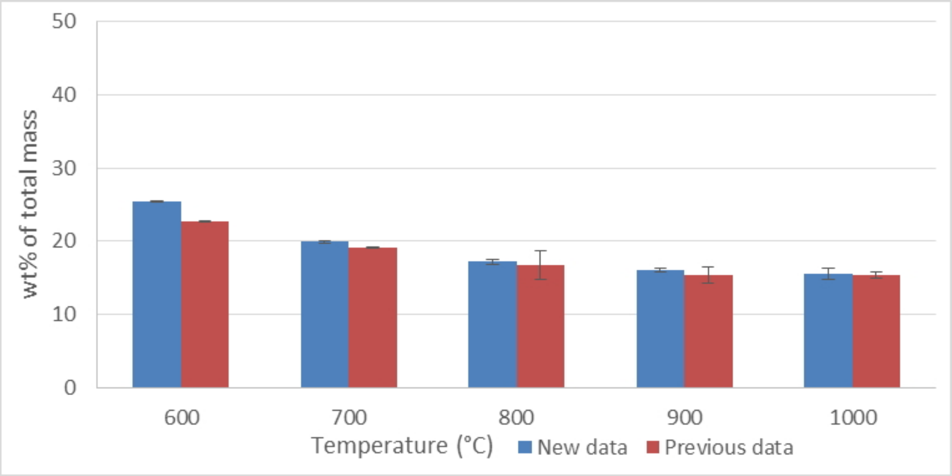


Figure 3.5: The char yields over the larger temperature range (600-1000°C).

average an increase of 5.75 wt% could be found over the whole temperature range. The smallest increase could be found at 600°C with 1.16 wt% and the biggest at 800°C with 8.20 wt%.

An improvement in the precision of the results can also be seen in the graph. The error bars of the New data are significantly smaller in size compared to the Previous data. This decrease in standard deviation shows a great improvement of the precision of the experiments. The origin of both improvements is likely the replacement of the flow meter with a mass-flow controller, which provided a more stable purge flow.

3.2.3. Gas yields

The last fraction that will be discussed is the gas fraction. As previously mentioned, the micro-GC is able to measure the production of hydrogen, carbon monoxide, methane and carbon dioxide. Therefore, these will also be the four gases that are discussed in detail. The GC is also able to measure nitrogen but as the purge flow is also nitrogen, this was only used to normalize the gas fractions. A bar chart of

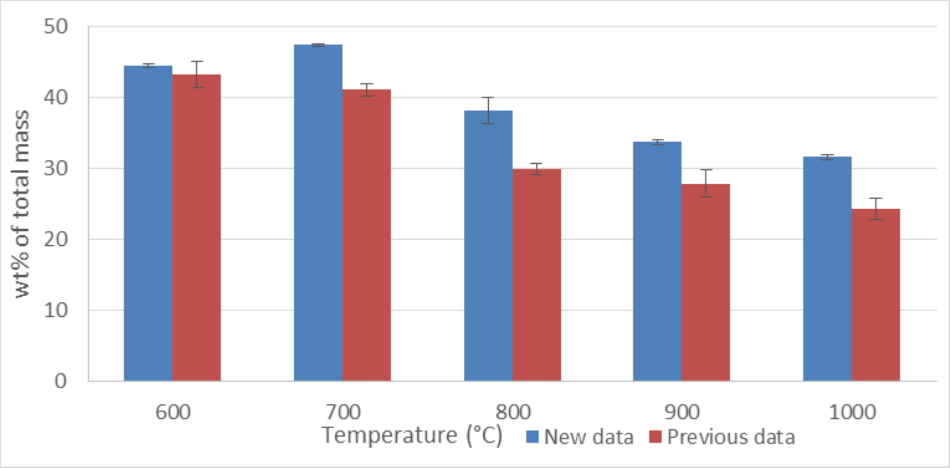


Figure 3.6: The tar yields over the larger temperature range (600-1000°C).

the gas yield can be seen in figure 3.7. The general observation that can be made is a slight increase of total gas yield at higher temperatures.

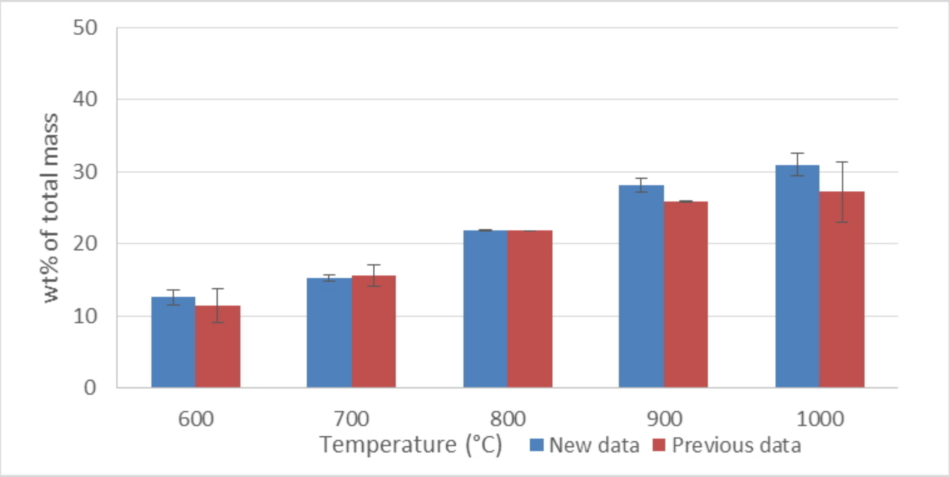


Figure 3.7: The gas yields over the larger temperature range (600-1000°C).

Hydrogen gas yield

Hydrogen is the lightest and least produced gas by the pyrolysis process of the four gases. As figure 3.8 shows, the mass-yield of hydrogen is very low (less than 1wt%) and is barely produced at 600°C and 700°C. Around 800°C the production rate increases, yet is still very small even at 1000°C. It can also be seen that the error bars on the New data are significantly smaller than in the Previous data, once again indicating a higher precision in the experiments.

Carbon monoxide gas yield

The carbon monoxide production rates show a similar behavior as the hydrogen yields. They also increase at higher FPTs and are products of secondary reactions. Once again, it is not possible to state that the Previous or New data is superior, due to the similarity of the yields and sizes of the error bars.

Methane gas yield

As was the case with the carbon monoxide, the methane yields of the Previous and New data are very similar in size and increase with the FPT. As methane is also a product of secondary reactions, this was expected. It can once again not be stated that either of the data sets provides a better yield.

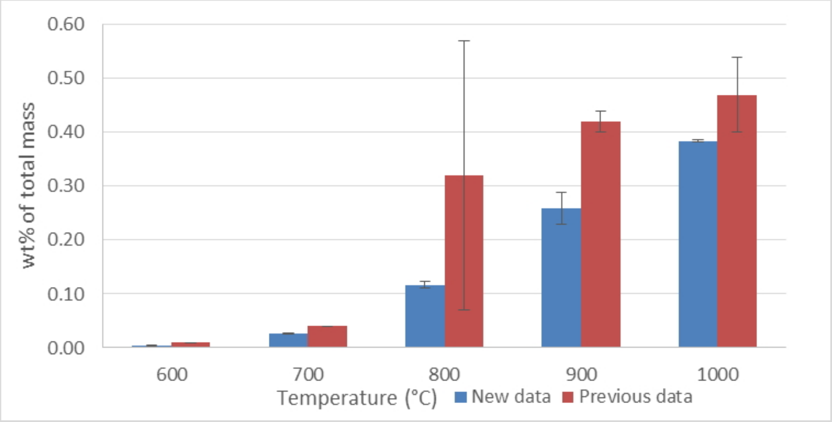


Figure 3.8: The hydrogen yields over the larger temperature range (600-1000°C).

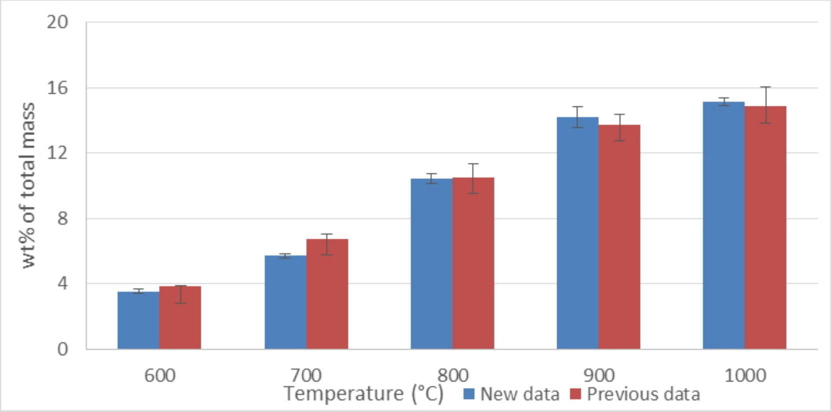


Figure 3.9: The carbon monoxide yields over the larger temperature range (600-1000°C).

Carbon dioxide yield

Lastly, we shall discuss the carbon dioxide fraction. Unlike the previous gases, carbon dioxide provides significant differences between the data sets, as can be seen in figure 3.11. On average a difference of 1.66 wt% can be found. As CO_2 is mainly a product of primary reactions, a slight increase with FPT should be expected until 800°C, after which it should plateau as no extra primary reactions take place. This was the case in the Previous data, yet not in the New data. However, at 1000°C the error bar is quite large and thus no conclusions can be made with certainty.

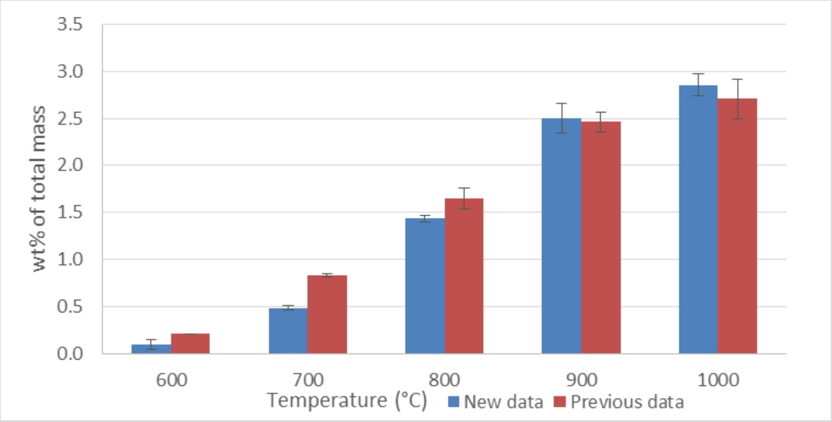


Figure 3.10: The methane yields over the larger temperature range (600-1000°C).

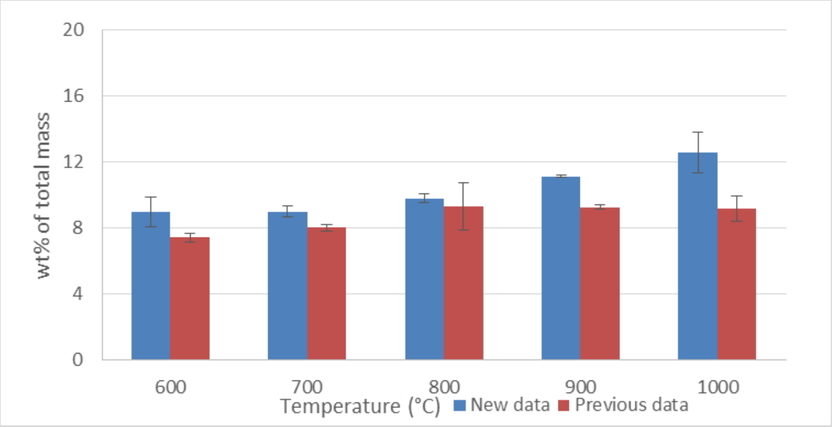


Figure 3.11: The carbon dioxide yields over the larger temperature range (600-1000°C).

3.3. Homogeneity of biomass

The second factor that will be discussed is the homogeneity of the biomass. Once again, the data gathered by Christos Tsekos will be used as a reference to previous results, named ”Previous data”. The data showing the homogeneous biomass is taken from the Evaporation Method experimental series and is called ”Homogeneous biomass”. A new experimental series that used the inhomogeneous biomass will also be used and is called ”Non-homogenized biomass”. The chosen temperatures are 600°C and 700°C and the results can be seen in figure 3.12.

Char yield

Under the conditions used during the experiments, no significant differences in char yield between the two types of biomass can be found. The difference at 600°C was 1.2 wt% and at 700°C 0.34 wt% both in favour of the Non-homogenized biomass. Yet these changes are so small that they are likely due to fluctuations between experiments instead of a difference in biomass. However, as already mentioned in 3.2 the char yields at 600°C are both significantly higher than the Previous data (3.9 wt% for the Non-homogenized biomass and 2.7 wt% for the Homogeneous biomass).

Tar yield

For the tar yields, the same applies as for the char yields. The difference in tar yield at 600°C is 2.61 wt% in favour of the Non-homogenized biomass, while at 700°C the homogeneous biomass had an edge with a yield increase of 3.13 wt%. Once again, both biomasses perform better compared to the Previous data, with an average increase of 3.48 wt% for the Non-homogenized biomass and 3.74 wt% for the Homogeneous biomass.

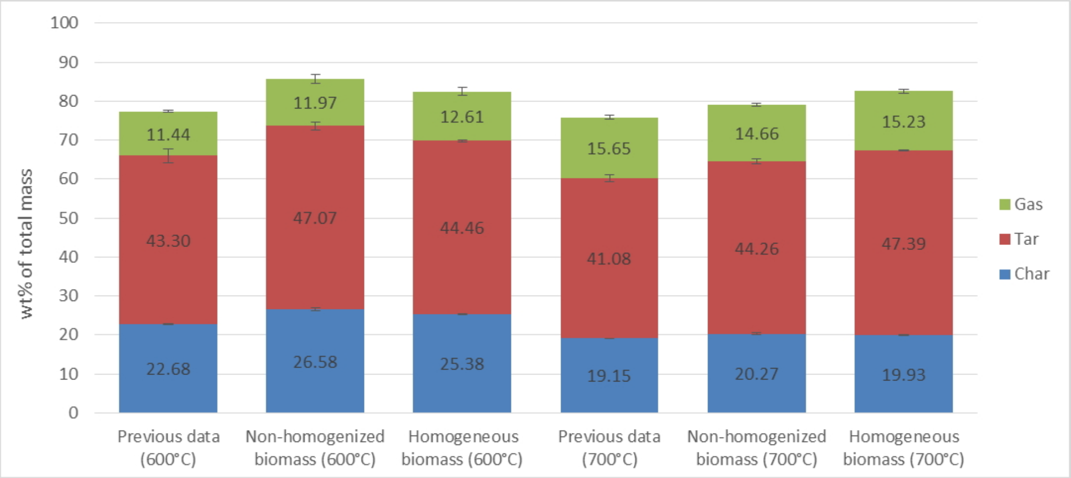


Figure 3.12: The yield compositions of Homogeneous biomass and Non-homogenized biomass at 600°C and 700°C, compared to the Previous data.

Gas yield

The differences in gas yield were small as well. At both temperatures the Homogeneous biomass provided a higher yield (0.65 wt% at 600°C and 0.57 wt% at 700°C). Both types of biomass performed similar to the Previous data. Neither did significant differences exist in the yields for the specific gases (H_2, CO, CH_4, CO_2), as can be seen in A.1. However, due to the relative size of the error bars no solid conclusions can be made.

Total mass closure

As discussed and figure 3.12 shows, a small difference can be found between the two biomasses. The total mass yield of the Non-homogenized biomass is 3.17 wt% higher compared to the Homogeneous biomass at 600°C. However, at 700°C the Homogeneous biomass is 3.36 wt% higher than the Non-homogenized biomass. This shows that none of the biomass types performs better in general. This also proves that the Non-homogenized biomass, produced from the inhomogeneous pellets, provides enough homogeneity (in regards to the mass yield) at this particle size (less than 80 μm).

3.4. Weighing second trap

As stated in 2.6, two different methods of gravimetrically weighing the second trap were explored. The first one examined was the removal of the condenser and directly weighing the second trap. Due to limitations, it was decided that a new method would be developed which was the evaporation of the solvent from the condenser. Now the results from both these methods will be further discussed.

3.4.1. Removal of the condenser

Since the Removal of the condenser was the first method tested, this will also be the first method discussed. This procedure was performed at both 600°C and 700 °C with the Non-homogenized biomass. The previously measured data from the Non-homogeneous biomass will be used as a reference. A yield composition bar chart can be seen in figure 3.13 comparing the overall results. In figure 3.14 a zoomed in view of only the tar yield collected in the second trap can be seen. Although it was mentioned in 2.6, no condensation of tars or moisture were observed in the syringe.

Char yield

Due to the fact that all changes during this series were downstream from the probe and holder, no significant changes should be found in the char yields. This is indeed the case, as the difference in char yield at 600°C and 700°C is only 0.35 wt% and 0.46 wt% respectively.

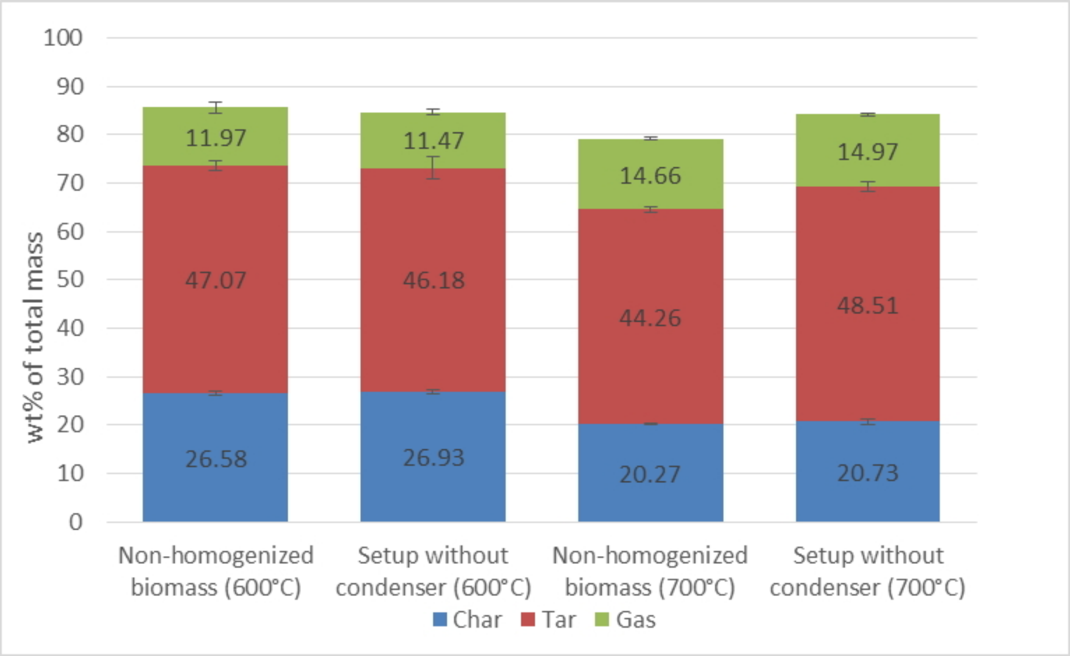


Figure 3.13: The yield composition of the Setup without the condenser compared to the Base setup with condenser (Non-homogenized biomass) at 600°C and 700°C.

Tar yield

At 600°C, the total tar yield from the Setup without condenser was 46.18 wt%, this was made up by 45.89 wt% in the first trap and 0.29 wt% in the second trap. This shows a total decrease in tar yield of 0.89 wt% compared to the Non-homogenized biomass data. At 700°C, the total was 48.51 wt%, of which 47.37 wt% was measured in the first trap and 1.14 wt% in the second trap. This shows a significant increase of tars collected in the first trap (3.11 wt%). This increase was not expected as the changes to the setup were downstream of the first trap. Furthermore, this tar yield of the first trap is similar to the tar yield collected from the Homogeneous biomass at 700°C (see 3.3).

As figure 2.6 shows in detail the extra tar yield collected in the second trap is low. This extra yield amounts to 0.29 wt% at 600°C and 1.14 wt% at 700°C. Thus showing this method does not provide a very significant improvement of the mass-closure. However, care must be taken before drawing a conclusion due to the low amount of temperatures (2) investigated.

Gas yield

For the gas yields the same holds as for the char and first trap yields. No significant changes in both the total gas yield and the specific gas yields (see A.1).

Total mass-closure

The weighing of the second trap does seem to slightly increase the total mass-closure. However, at 600°C a slight decrease is found of 1.03 wt%. If the temperature is increased to 700°C the mass-closure improves with an increase of 5.00 wt% compared to the Base setup with the condenser. Yet only a small amount of this improvement is specifically due to the second trap (1.14 wt%). Thus when disregarding the variations in the char, tar from the first trap and gas fractions only a very small increase of 1.14 wt% is found.

3.4.2. Evaporation of solvent

As the specific fraction yields from this experimental series has already been discussed in detail in 3.2, only a quick overview will be given. On average the total yield increased with 7.85 wt% over the whole temperature range (600-1000°C). The majority of this increase could be found in the tar collected in the

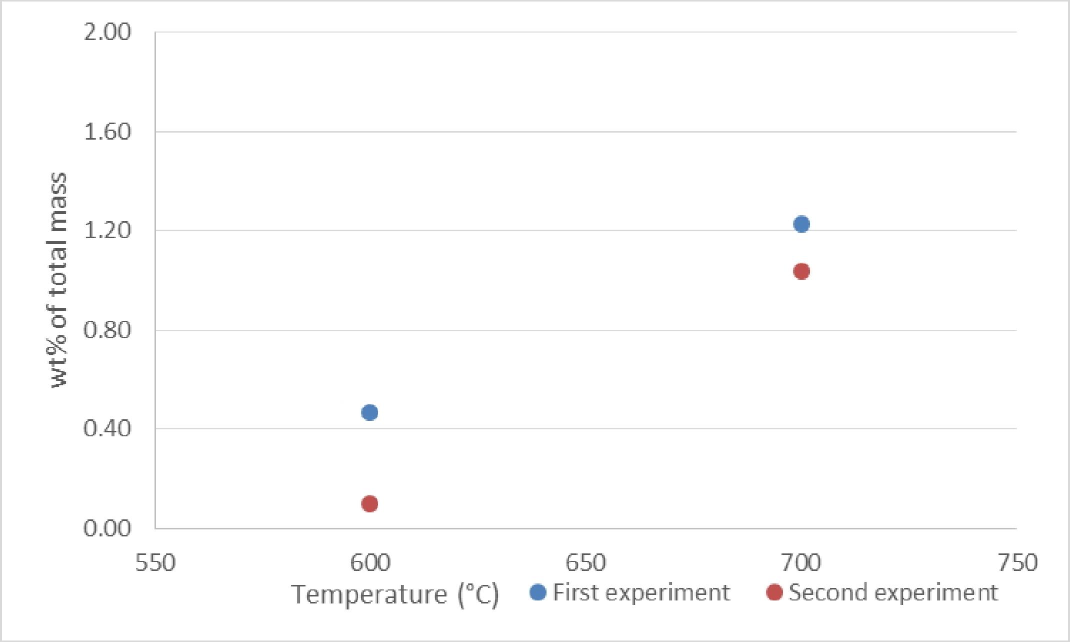


Figure 3.14: The additional tar yields with the removal of the condenser at 600°C and 700°C.

first trap. The additional yields to the tar fraction derived from the condenser (not taken into account in 3.2) can be found in figure 3.17 and will now be discussed.

From visual observations it can clearly be stated that the condenser captured tars and could be recovered with this method. Immediately after the experiment the 2 ml of IPA recovered from the condenser would be colourless. After evaporating for an hour, the remaining IPA would be not be colourless anymore and would have a yellow tint, as can be seen in figure 3.15. This discoloration could always be found in the tars collected from the first trap and indicate a high concentration of tars. Furthermore, after all of the IPA was evaporated, spots of residue tars could clearly be seen (see figure 3.16). These left over tars are likely very heavy in weight and take a long time to evaporate.

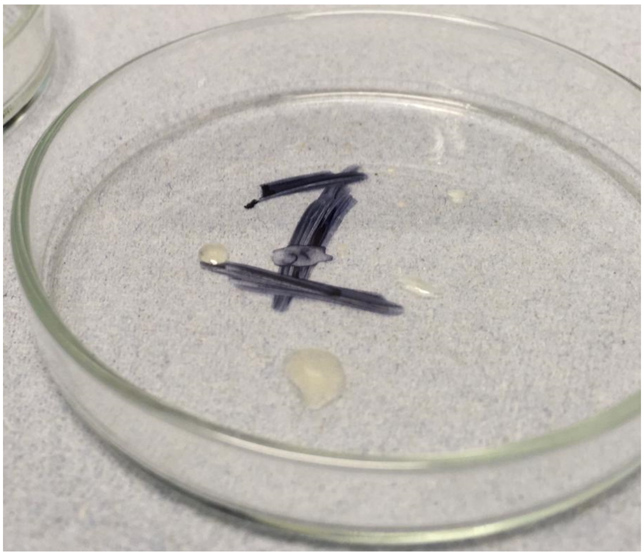


Figure 3.15: Discoloration of the IPA from the increased concentration of tars.

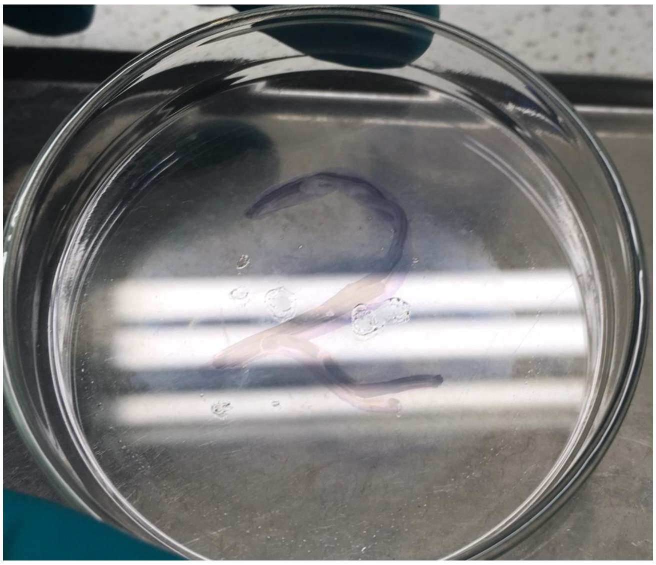


Figure 3.16: The residues left after evaporation from the Petri dish.

Figure 3.17 shows the measurements from the two separate experiments performed at each temperature. Here it can clearly be seen that an additional tar yield is indeed measured at all temperatures (0.9 3wt% on average and a maximum of 1.40 wt% at 1000°C). However, the figure also shows a signficant amount of variability in the recovered weight at each temperature between two experiments. The use of glass Petri dishes likely introduced this variability, as the dish is several orders of magnitude heavier compared to the tars. Furthermore, this method is only able to measure the heaviest tars, as the lighter tars, moisture of the biomass and pyrolytic water have already been evaporated. Because of the severe lack of precision in the method and its limitations of measuring all the compounds, it is hard to recommend it to measure the weights collected in the second trap.

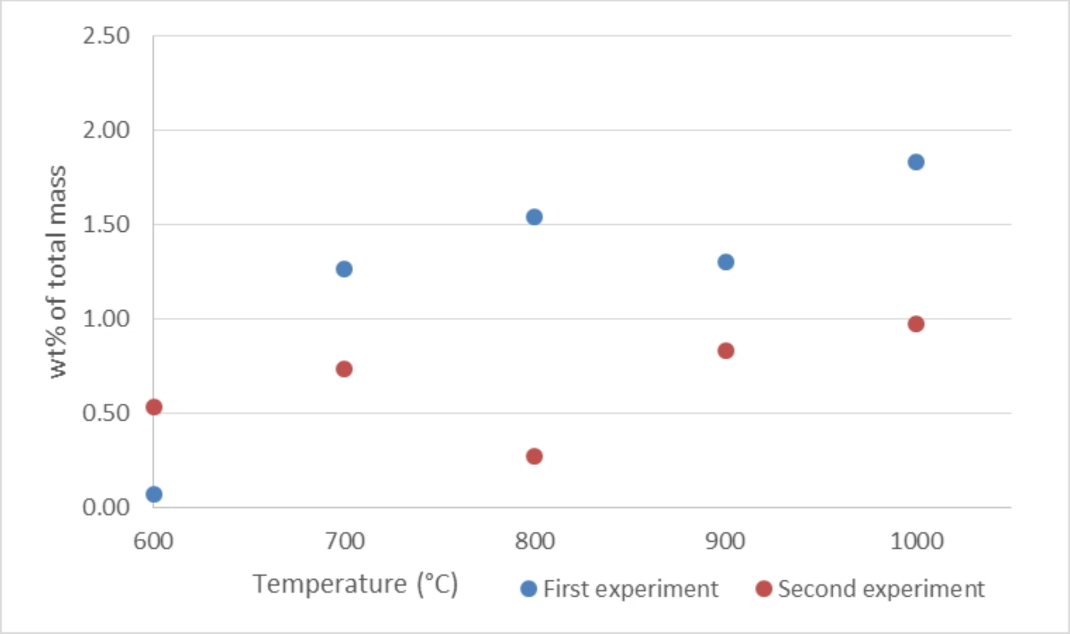


Figure 3.17: The additional tar yields with the Evaporation method over a large temperature range (600-1000°C)

4

Conclusion and Recommendations

4.1. Conclusion

As mentioned in 1.4, the goal of this thesis was to improve and optimize the techniques used in the Pyroprobe setup to increase mass-closure of the experiments. With the specific goal of fast pyrolysis of Miscanthus. This objective was further subdivided into improving the purge flow stability, the influence of homogeneity of the biomass and gravimetrically measuring the tars collected in the second trap. In order to provide an answer to all these subquestions, several experimental series were performed.

The first question was stated as: ”How does the purge flow stability influence the yield composition of Miscanthus pyrolysis?”. Two changes were made to the setup in order to improve the stability. The first was replacing the flow-meter with a mass-flow controller to keep the purge flow at a steady rate of 10 ml/min. The second improvement was shortening the tube in the oven, which significantly decreased the chance trapping tars and creating blockages in the tube. On average an increased yield of 7.85 wt% over the whole temperature range (600-1000°C) was measured, with an increase at every temperature compared to the Previous data. This increase was mostly due to higher tar yields measured in the first trap. Furthermore, a small increase in char yield at 600°C was measured.

The second factor that was investigated was the influence of the homogeneity of the biomass on the mass-balance. To find an answer, a second series of experiments were run with Non-homogenized Miscanthus biomass (heavily grinded inhomogeneous, less than 80 µm). At 600°C, the Non-homogenized biomass provided a 3.17 wt% higher yield, while at 700°C the Homogeneous biomass (less than 200 µm) gave a 3.36 wt% higher yield. Thus showing that none of the types performed significantly better at these temperatures, while both performing better than the Previous data, and that the Non-homogenized biomass biomass was sufficient for pyroprobe research.

Lastly, two methods were developed to gravimetrically measure the condensable gases collected in the condenser/second trap. In the first method the condenser was removed and the second trap was directly weighed. This gave a slight increase (maximum of 1.14 wt% at 700°C) in tar yield, yet had significant problems. As it was not cooled or submerged, suspicions arose that not all tars would be collected in the trap and would end up in the gas syringe. This would contaminate the gas mixture and influence the gas yields in the GC. Thus only two experiments were run at 600°C and 700°C.

The second approach tried, used the condenser once again. The 2 ml of isopropanol (IPA) from the condenser would be put in a Petri dish after the experiment in order to evaporate the IPA. This would allow the tars to stick to the dish and to gravimetrically weigh their complete weights. This method once again gave very low yields (average of 0.93wt% and maximum of 1.40 wt% at 1000°C), while showing significant variability in yields between experiments. A second issue that arose was that the light tars and moisture captured in the condenser would evaporate before the IPA and were thus not measured.

4.2. Recommendations

Now some recommendations for further research will be provided in order to further improve the mass-closure.

- Due to time constraints, it was not possible to perform Karl Fisher moisture analysis on the IPA in the condenser. It is likely that moisture from the biomass and pyrolytic water is present in the 2 ml of IPA.
- At the moment the gas is collected with a syringe. This syringe needs a slight overpressure in the system in order to overcome friction and fill. At the moment, it is not known what the pressure in the system after the mass-flow controller is and this pressure could play a role in the pyrolysis. Instead of a syringe, a tedler bag could be used to decrease the required friction.
- At the moment only H_2, CO, CH_4, CO_2 are measured in the gas analysis. This range could be expanded to higher hydrocarbons, such as C_2H_6 and C_3H_8.

A

A.1. Specific gas yields for the Non-homogenized biomass, Homogeneous biomass and Setup without condenser

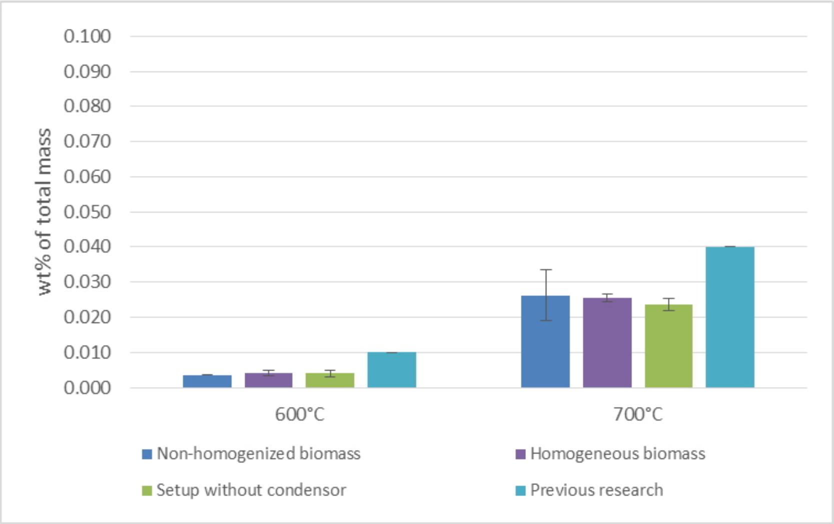


Figure A.1: The hydrogen yields for three of the setups at 600°C and 700°C.

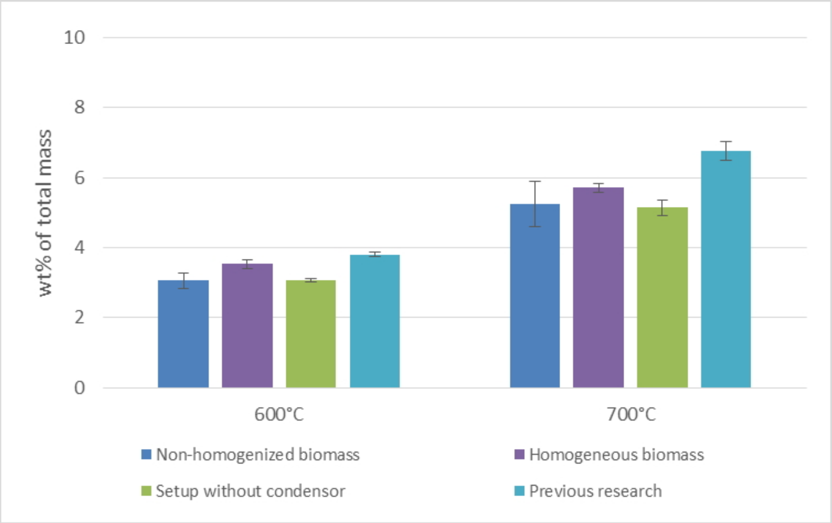


Figure A.2: The carbon monoxide yields for three of the setups at 600°C and 700°C.

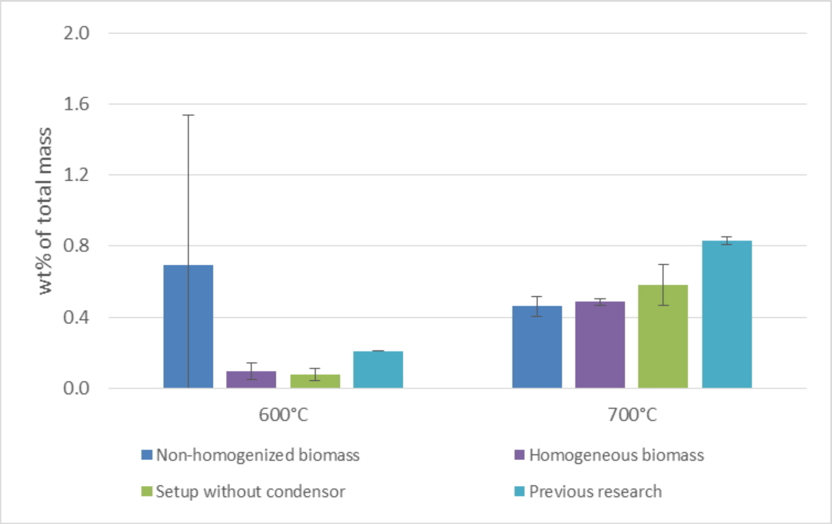


Figure A.3: The methane yields for three of the setups at 600°C and 700°C.

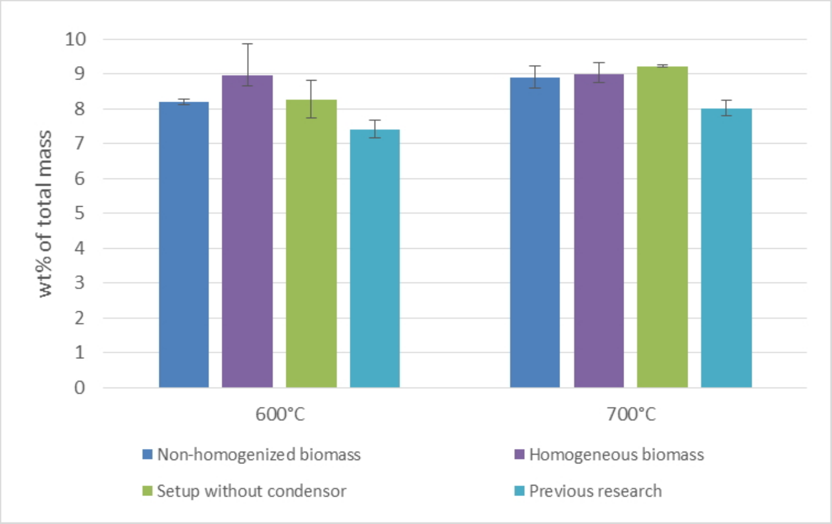
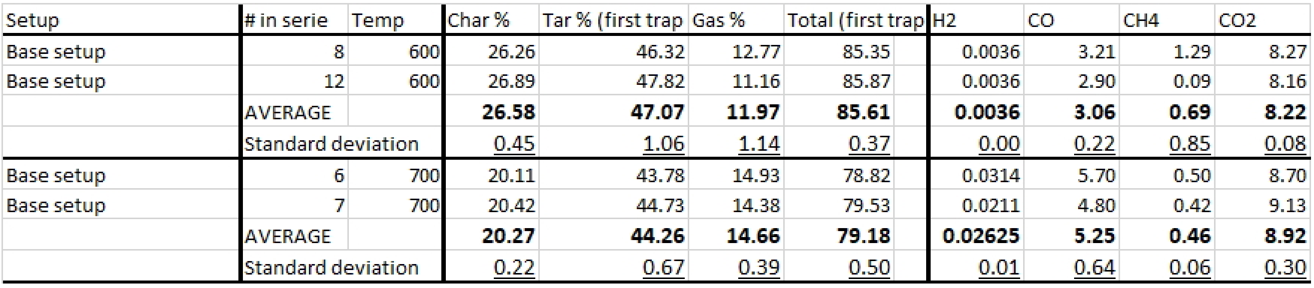


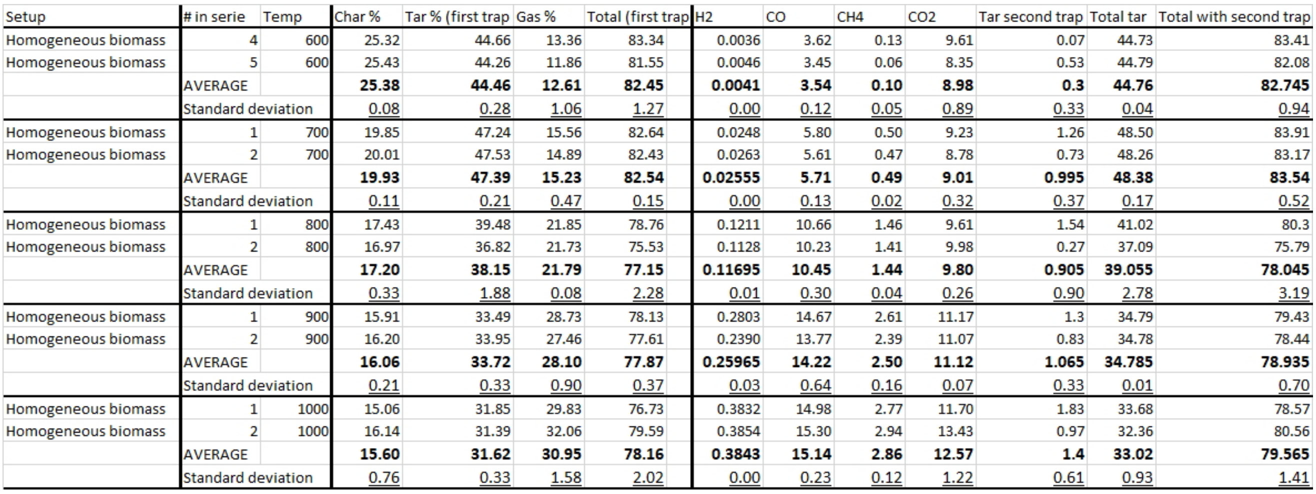
Figure A.4: The carbon dioxide yields for three of the setups at 600°C and 700°C.

A.2. Tables with all the yields



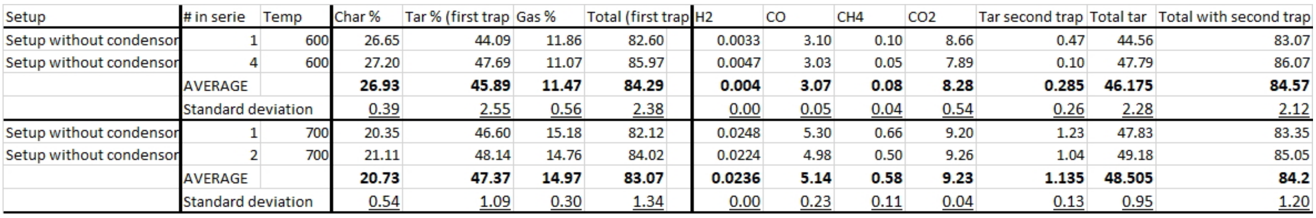
Setup	# in serie	Temp	Char %	Tar % (first trap	Gas %	Total (first trap	H2	CO	CH4	CO2
Base setup	8	600	26.26	46.32	12.77	85.35	0.0036	3.21	1.29	8.27
Base setup	12	600	26.89	47.82	11.16	85.87	0.0036	2.90	0.09	8.16
	AVERAGE		**26.58**	**47.07**	**11.97**	**85.61**	**0.0036**	**3.06**	**0.69**	**8.22**
	Standard deviation		0.45	1.06	1.14	0.37	0.00	0.22	0.85	0.08
Base setup	6	700	20.11	43.78	14.93	78.82	0.0314	5.70	0.50	8.70
Base setup	7	700	20.42	44.73	14.38	79.53	0.0211	4.80	0.42	9.13
	AVERAGE		**20.27**	**44.26**	**14.66**	**79.18**	**0.02625**	**5.25**	**0.46**	**8.92**
	Standard deviation		0.22	0.67	0.39	0.50	0.01	0.64	0.06	0.30

Figure A.5: A table with the yields gathered from Non-homogenized biomass.



Setup	# in serie	Temp	Char %	Tar % (first trap	Gas %	Total (first trap	H2	CO	CH4	CO2	Tar second trap	Total tar	Total with second trap
Homogeneous biomass	4	600	25.32	44.66	13.36	83.34	0.0036	3.62	0.13	9.61	0.07	44.73	83.41
Homogeneous biomass	5	600	25.43	44.26	11.86	81.55	0.0046	3.45	0.06	8.35	0.53	44.79	82.08
	AVERAGE		**25.38**	**44.46**	**12.61**	**82.45**	**0.0041**	**3.54**	**0.10**	**8.98**	**0.3**	**44.76**	**82.745**
	Standard deviation		0.08	0.28	1.06	1.27	0.00	0.12	0.05	0.89	0.33	0.04	0.94
Homogeneous biomass	1	700	19.85	47.24	15.56	82.64	0.0248	5.80	0.50	9.23	1.26	48.50	83.91
Homogeneous biomass	2	700	20.01	47.53	14.89	82.43	0.0263	5.61	0.47	8.78	0.73	48.26	83.17
	AVERAGE		**19.93**	**47.39**	**15.23**	**82.54**	**0.02555**	**5.71**	**0.49**	**9.01**	**0.995**	**48.38**	**83.54**
	Standard deviation		0.11	0.21	0.47	0.15	0.00	0.13	0.02	0.32	0.37	0.17	0.52
Homogeneous biomass	1	800	17.43	39.48	21.85	78.76	0.1211	10.66	1.46	9.61	1.54	41.02	80.3
Homogeneous biomass	2	800	16.97	36.82	21.73	75.53	0.1128	10.23	1.41	9.98	0.27	37.09	75.79
	AVERAGE		**17.20**	**38.15**	**21.79**	**77.15**	**0.11695**	**10.45**	**1.44**	**9.80**	**0.905**	**39.055**	**78.045**
	Standard deviation		0.33	1.88	0.08	2.28	0.01	0.30	0.04	0.26	0.90	2.78	3.19
Homogeneous biomass	1	900	15.91	33.49	28.73	78.13	0.2803	14.67	2.61	11.17	1.3	34.79	79.43
Homogeneous biomass	2	900	16.20	33.95	27.46	77.61	0.2390	13.77	2.39	11.07	0.83	34.78	78.44
	AVERAGE		**16.06**	**33.72**	**28.10**	**77.87**	**0.25965**	**14.22**	**2.50**	**11.12**	**1.065**	**34.785**	**78.935**
	Standard deviation		0.21	0.33	0.90	0.37	0.03	0.64	0.16	0.07	0.33	0.01	0.70
Homogeneous biomass	1	1000	15.06	31.85	29.83	76.73	0.3832	14.98	2.77	11.70	1.83	33.68	78.57
Homogeneous biomass	2	1000	16.14	31.39	32.06	79.59	0.3854	15.30	2.94	13.43	0.97	32.36	80.56
	AVERAGE		**15.60**	**31.62**	**30.95**	**78.16**	**0.3843**	**15.14**	**2.86**	**12.57**	**1.4**	**33.02**	**79.565**
	Standard deviation		0.76	0.33	1.58	2.02	0.00	0.23	0.12	1.22	0.61	0.93	1.41

Figure A.6: A table with the yields gathered from the Homogeneous biomass.



Setup	# in serie	Temp	Char %	Tar % (first trap	Gas %	Total (first trap	H2	CO	CH4	CO2	Tar second trap	Total tar	Total with second trap
Setup without condensor	1	600	26.65	44.09	11.86	82.60	0.0033	3.10	0.10	8.66	0.47	44.56	83.07
Setup without condensor	4	600	27.20	47.69	11.07	85.97	0.0047	3.03	0.05	7.89	0.10	47.79	86.07
	AVERAGE		**26.93**	**45.89**	**11.47**	**84.29**	**0.004**	**3.07**	**0.08**	**8.28**	**0.285**	**46.175**	**84.57**
	Standard deviation		0.39	2.55	0.56	2.38	0.00	0.05	0.04	0.54	0.26	2.28	2.12
Setup without condensor	1	700	20.35	46.60	15.18	82.12	0.0248	5.30	0.66	9.20	1.23	47.83	83.35
Setup without condensor	2	700	21.11	48.14	14.76	84.02	0.0224	4.98	0.50	9.26	1.04	49.18	85.05
	AVERAGE		**20.73**	**47.37**	**14.97**	**83.07**	**0.0236**	**5.14**	**0.58**	**9.23**	**1.135**	**48.505**	**84.2**
	Standard deviation		0.54	1.09	0.30	1.34	0.00	0.23	0.11	0.04	0.13	0.95	1.20

Figure A.7: A table with the yields gathered from the Setup without condenser with the Non-homogenized biomass.

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