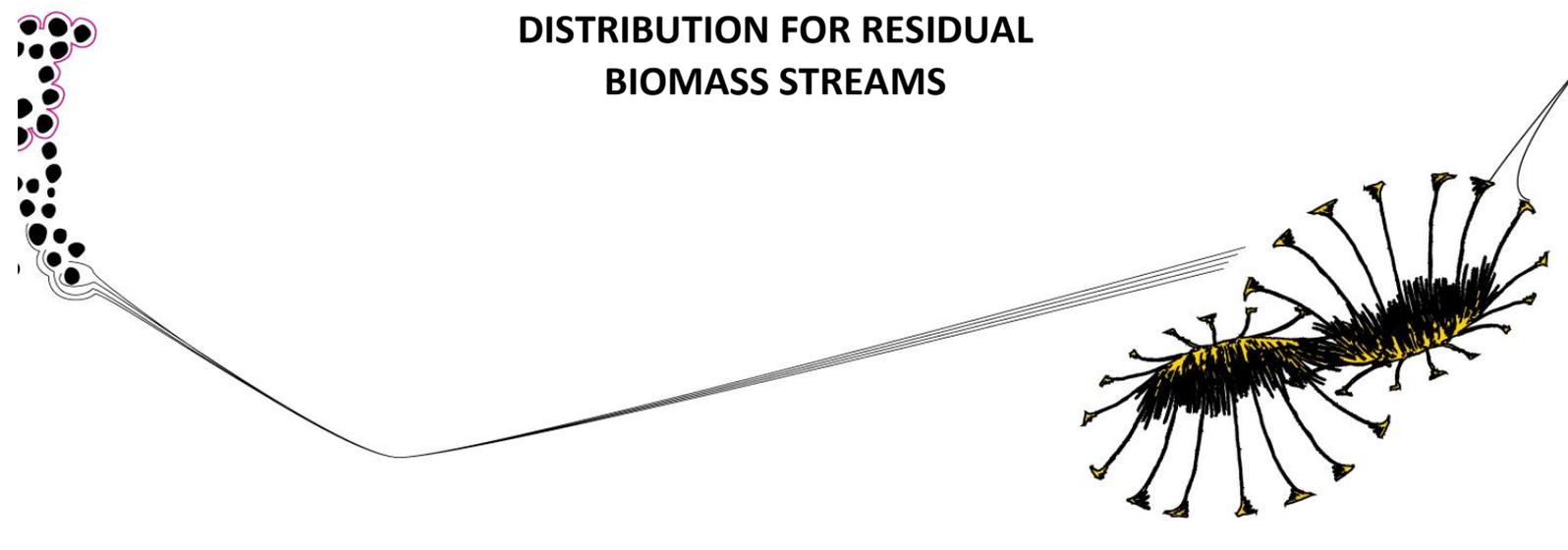




**FAST PYROLYSIS PRODUCT  
DISTRIBUTION FOR RESIDUAL  
BIOMASS STREAMS**



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## Abstract

Fast pyrolysis is a well established thermochemical process for converting ligno-cellulosic biomass into bio-oil, gases and bio-char. The bio-oil can be further upgraded and refined for the production of renewable liquid fuels or high value chemicals. Raw bio-oil can be used directly for electricity generation. The distribution between solid, liquid and non-condensable gases depends on the type of biomass and on the pyrolysis conditions. The objective of this report is to evaluate the product distribution from the process of fast pyrolysis using different biomass feedstocks. A series of experiments were performed on a newly built experimental setup consisted of a screw fast pyrolysis reactor along with two condensers and char vessel for collecting the bio-oil and the char respectively. The setup was validated by performing experiments using pine wood chips, to determine mass balance closure and reproducibility. In order to improve the operability of the setup a number of operational problems were solved. Four types of biomass were studied in this work: Dried Distilled Biomass (DDB), pine wood chips, soft wood pellets and wheat straw. The pyrolysis behavior of the selected feedstocks were determined via thermogravimetric analysis (TGA). With the wheat straw feedstock, the influence of the pyrolysis temperature on the product distribution has been determined as well. Additional analysis and characterization of the produced pyrolysis oil, char and gases has been performed in BTG's laboratory. The maximum oil yield achieved from the pine wood chips was 72% whereas for the soft wood pellets, wheat straw and DDB the oil yield was lower to 63%, 60% and 19% respectively. The mass balance closure in experiments with pine wood ranged between 85 - 102%, with wood pellets between 72 - 85 % and with wheat straw between 61 - 95% while in DDB experiments the closure was insufficient. Considering the energetic yield in the case of DDB, a 60% of the initial feedstock energy is being recovered.

*Keywords: Fast pyrolysis, bio-oil, DDB, biomass, screw reactor, BTG*

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## 1. Introduction

The growing concern for the global warming, resulting from the emission of greenhouse gases (GHG), along with the abatement of fossil fuel reserves have increased the world's interest towards sustainable energy sources. Until recently, the global energy demand was 515 EJ/year [1], major part (80%) of which is covered by fossil energy sources like coal, petroleum and gas and there is estimation that these sources might be drastically reduced by 2050 [2]. Therefore, it is desirable to alter our dependence on fossil fuels by covering our energy demand mainly from renewable energy sources.

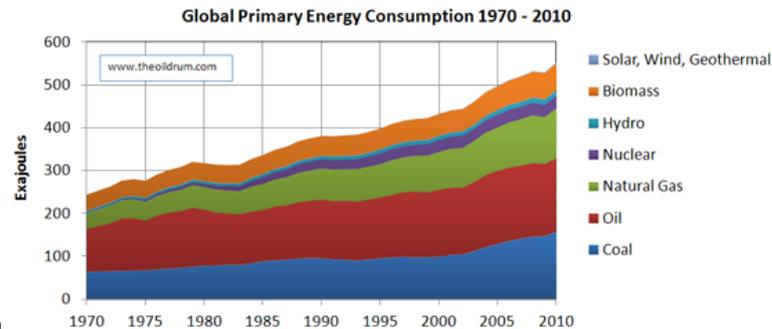


Figure 1: Global primary energy consumption (1970-2010) [1]

Energy produced from biomass has recently gained a lot of attention due to the wide availability and environmental-friendly nature [3]. Since early years it was used as the substantial energy source and nowadays it is estimated that biomass can contribute to 10-14% of the global energy supply [4]. Compared to other renewable sources it is advantageous as it produces liquid, solid and gaseous fuels whereas the rest give only heat and power. It is also a source of carbon and therefore the only renewable alternative which is currently available to replace fossil fuels in the petrochemical industry and in the production of transportation fuels [5]. All the carbon that is being released during combustion was originally captured by the biomass from the atmosphere via photosynthesis in which carbon dioxide and oxygen are converted into energy. The renewable nature of biomass is shown in Figure 2.

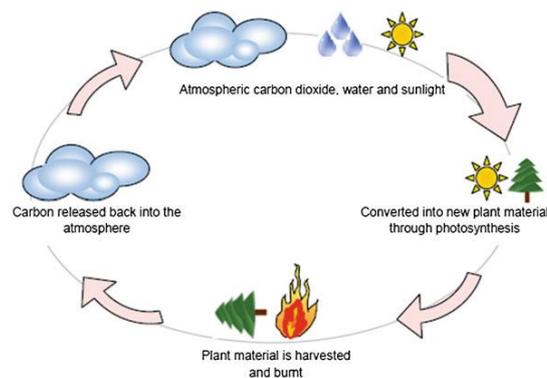


Figure 2: Renewable nature of biomass conversion into energy [6]

The transition towards a bio-based economy comprises of biomass as the main material for energy production. The transformation of biomass into value-added fuels and chemicals will diversify the energy resources. Biofuels produced from plant biomass would help mitigate carbon dioxide emissions and hence global warming. Until recently the majority of produced biofuels were based on sugar, starch and vegetable oils. These are termed as "first generation" biofuels and can be easily extracted using conventional technology. However, despite the benefits, they create some ethical concerns which aroused from competition with food production and biodiversity [7].

Due to these concerns the interest has shifted to the "second generation" biofuels. Within this concept, the food chain is not affected as the edible parts of biomass are used for consumption from humans and animals. The non-edible parts, second and third generation biomass, are used for the production of green

chemicals and transportation fuels. The remaining part can be used for the production of heat and power. Until now, the production of these fuels is not cost-effective due to a number of technical barriers that need to be overcome.

### 1.1 Biomass composition

Biomass is the organic material of living or recently living organisms. It is composed by a mixture of organic molecules containing carbon hydrogen, oxygen, nitrogen and in smaller quantities alkali, alkaline earths and heavy metals. It is derived from the reaction between CO<sub>2</sub>, water and sunlight via photosynthesis that converts solar into chemical energy to produce carbohydrates as can be seen in Figure 3.

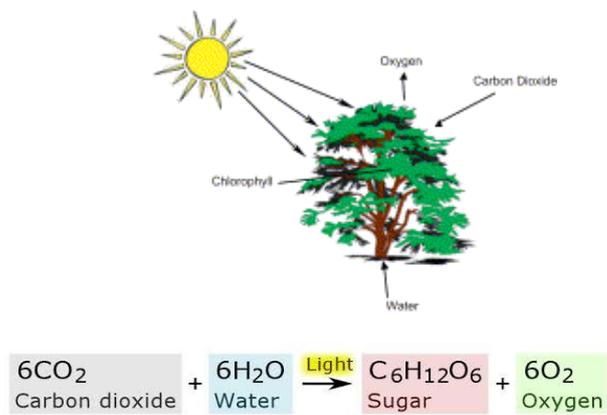


Figure 3: Biomass production through photosynthesis process

There are four main types of biomass which are the woody plants, herbaceous plants/grasses, aquatic plants and manure. Woody biomass has been extensively studied and mainly consists out of three types of polymers namely cellulose, hemicellulose and lignin.

Cellulose is glucose polymer with linear chains of (1-4)-D-glucopyranose, in which the units are linked 1-4 in the β-configuration, with an average molecular weight of 100.000 gram/mole and represents the largest fraction of biomass about 40-50%.

Hemicellulose is a mixture of polysaccharides with an average molecular weight less than 30.000 gram/mole. In contrast to cellulose which contains only anhydrous glucose, hemicellulose contains sugar monomers such as glucose, manose, xylose and arabinose and represents a portion of around 25-35% of the total woody biomass.

Lignin, from Latin meaning wood, is a complex amorphous polymer of aromatic alcohols known as monolignols, based on phenyl propane units. It has three dimensional structure and a molecular weight of greater than 10.000 gram/mole. Lignin represents typically 15-20% in dry wood biomass. In Figure 4 the structure of the tree main compounds of woody biomass can be seen [8].

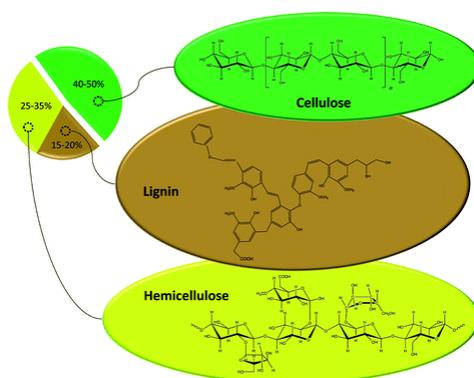


Figure 4: Lignocellulose composition: cellulose, hemicellulose and lignin [9]

Lignocellulosic biomass can be converted via different conversion techniques, which are explained in more detail in the next paragraph.

## 1.2 Biomass conversion technologies

There are two primary group of conversion technologies to transform biomass into energy: thermochemical and biochemical conversion. The thermochemical technology comprises of four different pathways to convert biomass to useful products as it is shown in Figure 5. Direct combustion of biomass provides heat for steam production in a boiler which generates electricity. Gasification creates a fuel gas that can be used either in a turbine or in internal combustion engine to generate electricity as well. Fast pyrolysis creates a liquid fuel (bio-oil), which can be a promising substitute of fuel oil or diesel in the near future.

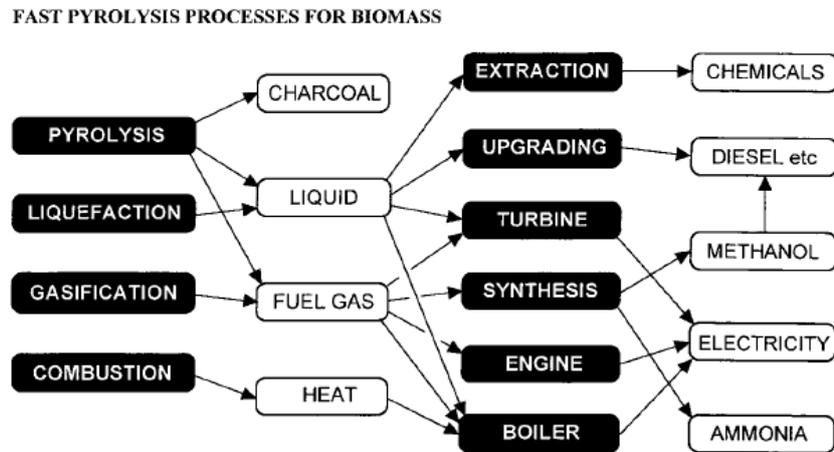


Figure 5: Thermochemical biomass processes and products [5]

Gasification is the conversion of biomass to a gaseous fuel is partially oxidized at high temperatures, between 500-1300°C and at pressures that vary from atmospheric to 33 bar [5]. The advantages of this process is that the product gas consists of a mixture of hydrogen and carbon monoxide (sygas) and can be used as a feedstock in the production of chemicals or transportation fuels via the Fischer-Tropsch process [10, 11]. However, the complexity of this technology and the fact that it is not yet mature compared to other technologies, makes gasification not a good alternative for generating electricity.

In the combustion process the biomass is burned in the presence of air and the chemical energy within the biomass is converted into heat, mechanical power and electricity with various equipment such as furnaces, stoves, steam turbines etc. The temperature for this process ranges between 800-1000°C and the feedstock should contain less than 50% moisture otherwise pre-drying is needed. The high moisture content of biomass is favorable only to biological conversion processes.

Another way of converting biomass into useful products is through liquefaction process. During liquefaction, the biomass is converted into a variety of liquid hydrocarbons like bio-crude or bio-oil at low temperatures (<400°C) and high pressures. Liquefaction usually produces high viscosity oils and usually solvents, reducing gases and catalysts are needed to be present in addition to biomass. Compared to pyrolysis, liquefaction has some drawbacks as it needs more complex and more expensive reactors and feeding systems and thus the interest for this technology is low [7, 10]. The pyrolysis process is analyzed in the following chapter.

### 1.3 Fast pyrolysis

Pyrolysis is the thermal degradation of biomass by applying heat in an oxygen-free environment. This process can be divided in three categories depending upon the operating conditions: a) slow pyrolysis, b) flash pyrolysis and c) fast pyrolysis. In slow pyrolysis we have slow heating rates (0,1-1°C/s), long residence times of 45-550 seconds and large biomass particles whereas flash pyrolysis occurs in high temperature range (777-1027°C) with extremely high heating rates (700°C/s) and with very fine biomass particles [7]. Fast pyrolysis is the process where thermal decomposition of organic material (biomass) occurs at elevated temperatures, around 450-600°C, in an oxygen depleted environment at pressures varying from atmospheric up to 3 MPa [6]. This process yields mainly to three products:

- Pyrolysis oil (aqueous and oil phase) [60-75 wt.%]
- Pyrolysis gas (non-condensable vapors) [12-20 wt.%]
- Char [13-20 wt.%]

Within fast pyrolysis the feedstock is rapidly heated with high heating rates, vaporized and condensed to dark brown oil which is termed as pyrolysis oil or bio-oil. The typical conversion of the feedstock to bio-oil is around 60-75 wt.%. The fast pyrolysis of biomass has already been accepted as a feasible and viable route to renewable liquid fuels, chemicals and derived products. Typically, a lower process temperature and longer vapor residence times favor the charcoal production. Higher temperature and longer residence times will increase the biomass conversion to gas and moderate temperature and short vapor residence time are optimum for producing liquids. It is a more advanced process that can be carefully controlled to give high yields of liquid.

Essential aspects of a fast pyrolysis reactor are:

- Very high heating and heat transfer rates (around 100°C/s)
- Moderate and carefully controlled temperature of around 500°C
- Rapid cooling of the pyrolysis vapours

There are several ways to utilize the produced bio-oil from fast pyrolysis. It can substitute diesel in internal combustion engines, boilers and furnaces. Furthermore, a variety of value-added chemicals can be extracted or derived such as fertilizers, food flavorings and emission control agents [5]. The Biomass Technology Group (**BTG**) has an experience over 20 years on fast pyrolysis of biomass. The reactor technology is based on the rotating cone reactor which was developed in 1989 during a PhD research project at the University of Twente [12]. The rotating cone reactor employs ablative pyrolysis with hot sand particles for enhancing the heat transfer and is shown in Figure 6.

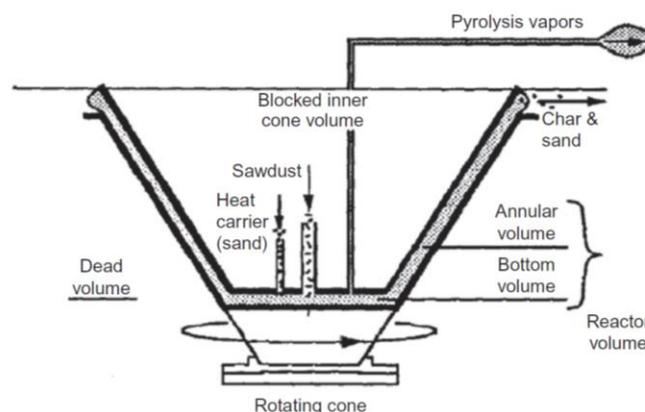


Figure 6: Rotating cone reactor [13]

In this concept biomass particles (up to 10 mm) at room temperature and hot sand particles are introduced near the bottom of the cone where the solids are mixed and transported upwards by the driving force of the rotating cone. A characteristic in this reactor concept is the rapid heating along with the short residence time of the gas phase [5, 14]. Below a schematic representation of the BTG-BTL fast pyrolysis process can be seen.



Figure 7: The BTG-BTL pyrolysis process [15]

The BTG-BTL process is commercialized in an ongoing project called the "EMPYRO project", which involves the construction of a commercial large scale fast pyrolysis plant (5t/h) in Hengelo, The Netherlands. This project is a consortium of eight partners from three countries subsidized by the European Union and is coordinated by BTG. The main goal of this project is to demonstrate a 25 MWth polygeneration plant by using woody biomass as starting material to produce electricity, process steam and pyrolysis oil [16].

#### 1.4 Biomass feedstocks

The various biomass feedstocks contain different amount of cellulose, lignin and hemicelluloses. The varying polymer structure and length along with the cross-linkage result in different thermal decomposition behavior and products during gasification and pyrolysis process [17]. The selected feedstocks were: pine wood chips, wheat straw pellets which is an agricultural waste, soft wood chips (feedstock of the EMPYRO plant) and Dried Distilled Biomass (DDB), which is a byproduct from 2<sup>nd</sup> generation bio-ethanol process with sticky nature and foul smell. The DDB was obtained from the company BioGasol, which convert wheat straw in a second generation bioethanol plant in Denmark. Table 1 presents the ultimate analysis of the different feedstocks. The raw feedstocks used in the experimental work are shown in Figure 1.

Feedstocks	C [wt%]	H [wt%]	N [wt%]	O [wt%]	Moisture [wt%]	Ash [wt%]
DDB 2013	33,405	5,699	1,251	16,825	0	28,2
Straw pellets	43,697	5,749	0,886	43,298	8,76	6,37
EMPYRO wood pellets	51,445	6,303	0	41,912	0	0,34
Pine wood	80,321	3,645	0	14,284	0	1,75

Table 1: Ultimate and proximate analysis of the biomass feedstocks



Figure 8: Raw feedstock materials: a) DDB b) EMPYRO wood pellets c) Pine wood d) Wheat straw

## 2. Experimental & methods

### 2.1 Ash content determination of solid residue

The chemical breakdown of biomass with thermo-chemical process produces a solid residue. After the combustion of biomass with air, this residue is called ash and is comprised of mostly oxides and sulphates. The determination of mineral ash in biomass is usually being done by heating an accurately weighed biomass sample in an adequately muffle furnace at temperatures in the range 200 to 750°C for 4 hours as described in American Society for Testing Materials (ASTM D-3174) [4, 18]. The purpose of the ash content test was to investigate the temperature region where the vapor production is maximized and consequently the oil production in the fast pyrolysis process. In order to estimate the amount of biomass feedstock that is being vaporized in different temperatures, the ash content of DDB samples was determined. The temperature range for this procedure varied from 200°C to 750°C with a step of 50°C. The procedure starts by placing the biomass samples in the drying oven at 110°C overnight to remove any potential moisture content. After drying, biomass samples were placed into three crucibles which have been previously cleaned up with soap and alcohol. Three crucibles were used for a more accurate ash estimation. Subsequently, the crucibles were filled with 2 spoons of biomass and were weighed on a precision scale. Meanwhile, the oven was being heated up to the desired temperature and when the temperature was established we place the samples in the oven and we. After leaving the samples for 4 hours, we turn the oven off and we wait for the samples to cool down. Subsequently, we weigh the crucibles and we calculate the amount of ash that has been created. Hence, by subtracting this amount we determine how much material has been evaporated at a certain temperature. We followed the same procedure in the reducing atmosphere test. The samples were placed in the oven where nitrogen was flowing through in order to create an inert atmosphere. The temperature ranged again from 200 to 750°C in order to compare with the oxidizing atmosphere test.

## 2.2 Screw pyrolysis procedure

A series of fast pyrolysis experiments to determine the yields of products and especially the yield of bio-oil was performed. A screw reactor was selected for these experiments wherein the biomass is transported through the reactor by means of a screw conveyor. By adjusting the frequency of the conveyor, the residence time of the biomass inside the reactor could be changed. The biomass feeding to the reactor was performed manually using a sluice system based on two ball valves which operate automatically in a certain sequence. Typically, around 5 grams per 30 seconds of biomass were introduced to the system from the biomass hopper (X-2). Additionally, an argon gas purge flow was placed in-between the two valves to prevent the backflow of pyrolysis vapours.

The characteristic of this process is the rapid heating of the material and this is achieved upon entering the reactor by the use of specifically designed copper heating system. Three different heating zones inside the reactor were employed. The first zone is very close to the feeding section (1,5 cm), where the fast pyrolysis reaction takes places. The other two heating zones, heating zone 2 and 3, keep the biomass in the process temperature before it leaves from the reactor. The latter heating zones are made of conductive wire (kanthal) surrounded by ceramic beads.

During the pyrolysis of biomass vapor and gases are being produced that leave the reactor through the heated line (HE-04) and travel to the condensation part of the setup. Firstly, the vapours enter the condenser (C-1) which has a double wall of stainless steel and cooling water flows through the annular space between these walls. Once the vapours were being condensed to liquid, the latter flows to vessel X-6 by gravity where it was collected. The uncondensed vapors and gasses leave from the top of the condenser C-1 and were entered to the condenser C-2 which was equipped with a laboratory glass cooler. Part of this vapors and gasses are condensed into liquid, which flows down to the collection vessel X-7, and the rest uncondensed gas and vapor leave from the bottom and travel to the condenser C-3 which is also connected to vessel X-7. The temperature of the cooling water circulation was set for all the experiments to -5°C. The gasses that were leaving from the last condenser before exiting to the ventilation system were passing through a parallel cotton wool filter section (X-8 and X-9) in order to remove most of the impurities that they would contain. In this way, the contamination of the gas analysis equipment was prevented. A GC sample point is constructed before the gasses leaving from the cotton wool filters transported to the ventilation system. The char that was produced during the process was conveyed via the screw to the char collection vessel X-4. Continuously purge of nitrogen in this vessel was provided in order to prevent any self-ignition of the char. With a MFC the exact amount of nitrogen was controlled which was useful in the calculation of the total gas production. In Figure 9 the scheme of the experimental setup can be seen.

# Experimental setup

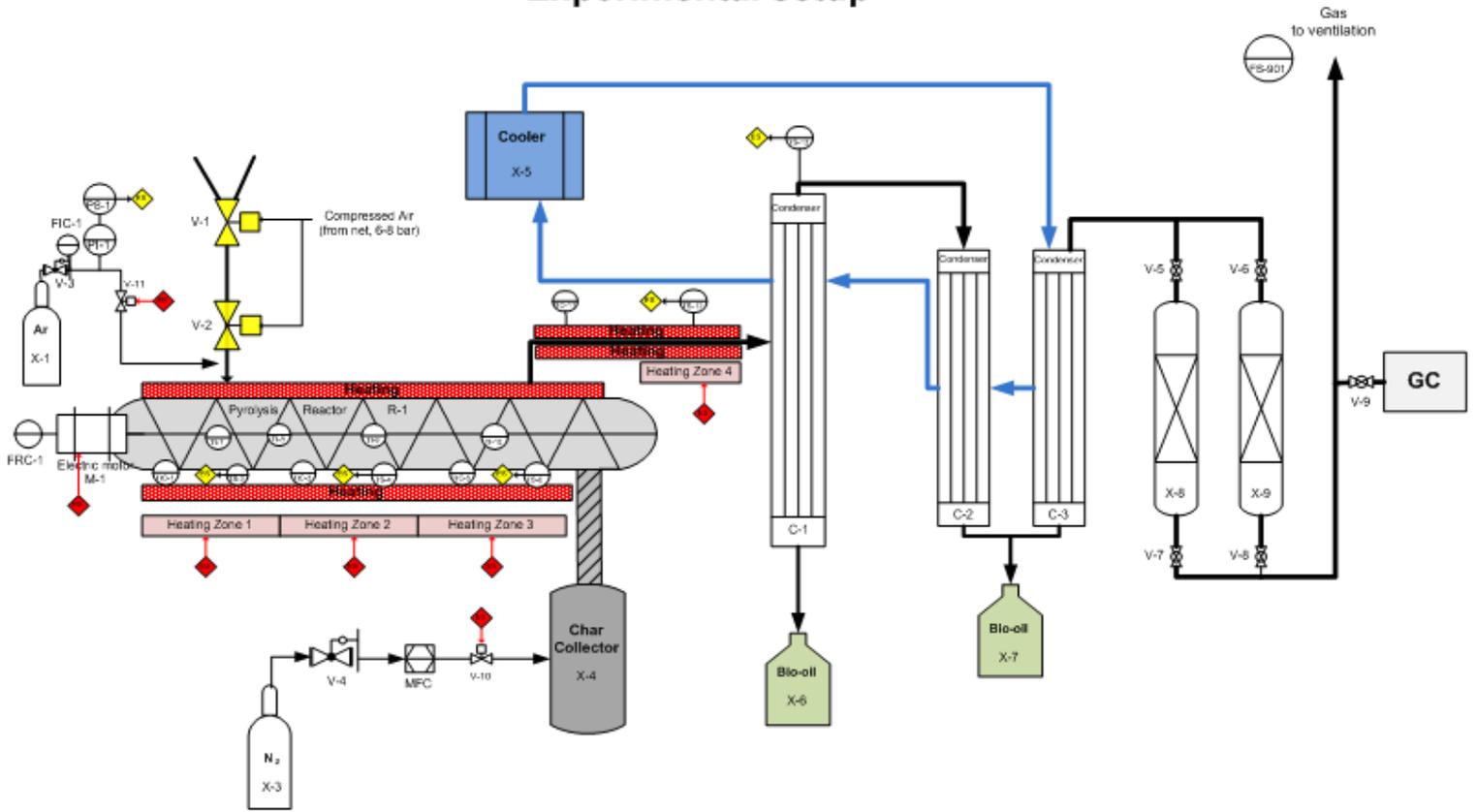


Figure 9: Experimental setup scheme of screw pyrolysis

Figure 10 shows the newly built experimental setup placed in BTG's experimental hall.



Figure 10: Experimental setup

In total, twenty six experiments have been conducted using four different feedstocks. After completion of each experiment, the products were being collected in separate storage vessels. The main oil production was taking place in the first condenser vessel whereas the oil production in the second vessel was lower deriving from the condensation of vapors leaving the first condenser. Acetone was used to collect the remaining (extra) oil in the condenser tubes and the condensation vessels. After collection, the bottle was placed in an ultrasonic cleaning bath to evaporate acetone and receive the remaining oil. During the experiments, gas samples were taken via a syringe and were injected in the gas chromatograph. The objective of this technique is to separate the gas mixture into its constituents. The analysis of the permanent gas composition was performed using a Synspec GC type 955, equipped with a Molesieve 80/100 5A column with internal diameter of 1/8" and length of 80 cm and a Porapak R80/100 column with internal diameter of 1/8" and length of 80 cm. This system is capable of detecting and measuring the following gases: H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>.

### 2.3 Mass balance and yield calculation

The yields of the products are reported on dry basis (kg product/kg dry biomass). The calculation of the product yields were based on both as-received basis (ar) and dry basis (dry). The amount of water (f<sub>w</sub>) that existed in the raw material was subtracted by initial biomass to calculate the weight of the dry biomass [19]. The formulas are described below:

$$Y_{dry} = \frac{Y_{ar}}{(1 - f_{w,biomass})}$$

$$Y_{dry} = \frac{\text{kg of product formed}}{\text{kg of biomass(ar) consumed} (1 - f_{w,biomass})}$$

Before each experiment the bucket with biomass that was going to be used during an experimental test was placed on precision scale and thus the total amount of biomass that was consumed during an experimental test was known. After each experiment, the char inside the vessel was collected and weighed. The char yield was calculated by:

$$Y_{char,dry} = \frac{\text{kg of char collected}}{\text{kg of biomass(ar) consumed} (1 - f_{w,biomass})}$$

The amount of produced gas was measured according to the molar fractions we got from GC measurements. The average gas density was determined as the summation of the molar fractions of the pyrolysis gases times their respective density. The equation is shown below:

$$\rho_{average} = \sum x_i \cdot \rho_i$$

Before the start of each experiment we were measuring the purge of helium with a gas meter. The purge gas was flowing for 3 minutes through the system and we were able to calculate the exact flow by subtracting the final from the initial indication of the gas meter. The gas yield was calculated according to the following equation:

$$Y_{gas,dry} = \frac{\int_{t_o}^{t_{end}} \left( \left( \Phi_g \frac{P}{RT} \right)_{out} - \left( \Phi_g \frac{P}{RT} \right)_{in} \times \sum_{\text{gas components}} \frac{x_i RT}{P} \rho_{average} \right) dt}{\text{kg of biomass(ar) consumed} (1 - f_{w,biomass})}$$

where  $\Phi_g$  is the helium flow rate,  $x_i$  is the molar fraction of the  $i$  gas,  $P$  is the pressure during the experiment equals to 101300 Pa,  $T$  is the temperature equals to 293 K and  $R$  is the universal gas constant equals to 8,314 m<sup>3</sup> Pa / (mol\*K). Furthermore, the yield of the pyrolysis oil was calculated as follows:

$$Y_{\text{pyrolysis oil,dry}} = \frac{\sum_{\text{vessels, condensers}} \text{kg of liquid collected}}{\text{kg of biomass(ar) consumed} (1 - f_{\text{w,biomass}})}$$

The mass balance was defined as the summation of  $Y_{\text{char,dry}}$ ,  $Y_{\text{gas,dry}}$  and  $Y_{\text{pyrolysis oil,dry}}$ . The mass balance closure of all the experiments can be seen in Figure 11. In pine wood experiments the closure ranged between 85 - 102%, in wood pellets experiments ranged from 72 - 85 % and in wheat straw experiments from 61 - 95% whereas in DDB experiments the mass balance closure was inadequate. A possible explanation for this could be the loss of gases while taking samples via a syringe. Another reason for the insufficient closure could be the loss of oil during collection from the condensation vessels.

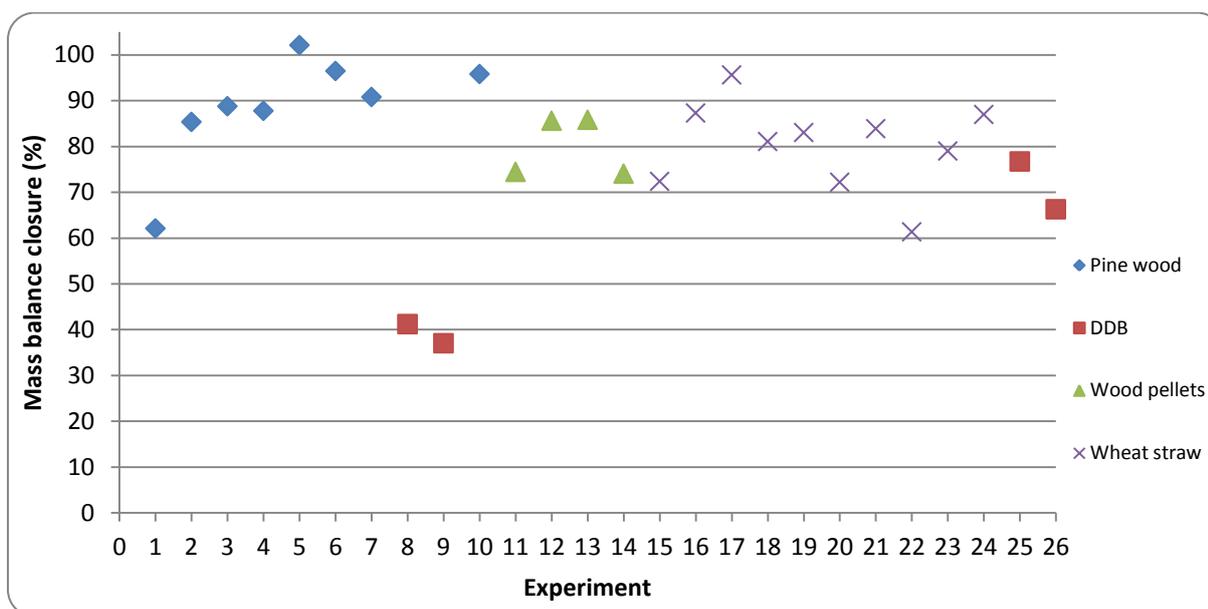


Figure 11: Mass balance closure of each experiment

## 2.4 Calorific value and energetic yield calculation

The calorific value is a measure of the energy available from per unit volume or mass of any fuel when it is combusted. It is very critical in determining the energy balance which is the ratio between the energy which is required to produce the fuel and the energy which the produced fuel has. The higher the calorific value of the fuel, the higher the possible energy output. It is expressed as Higher Heating Value (HHV) and Lower Heating Value (LHV). The difference between these two terms is the heat of evaporation of the water formed from the hydrogen in the material and the moisture [20]. The HHV indicates the suitability of the material as a fuel. The heating values of biomass feedstocks and products can be determined by the ultimate analysis [13, 21]. For the calculation of the HHV, we followed the method provided by Phyllis, the Energy research Center of Netherlands (ECN) database, using the Milne formula.

$$HHV_{\text{Milne}} = 0.341 * C + 1.322 * H - 0.12 * O - 0.12 * N + 0.0686 * S - 0.0153 * ash$$

where C, H, O, N, S are the mass and the ash fractions in wt% of dry material and HHV the heating value in MJ/kg. Then we consider the moisture that exists in the feedstock to calculate the  $HHV_{ar}^1$  from the following equation:

$$HHV_{ar} = HHV_{dry} * \left( \frac{1 - w}{100} \right)$$

Subsequently, follows the calculation of the lower heating value, also termed as net calorific value (NCV), which is more useful in comparing fuels where condensation of the combustion products is impractical.

$$LHV_{ar} = HHV_{ar} - 2.442 \left\{ \left( 8.936 * \frac{H}{100} \right) * \left( 1 - \frac{w}{100} \right) + \frac{w}{100} \right\}$$

The overall energetic yield of the oil produced has been determined as the summation of the oil produced of different phases (i.e. water phase and organic phase) times the LHV divided by the LHV of the original feedstock and it is shown below:

$$n = \frac{[(Y_{organic} \times LHV_{organic}) + (Y_{water} \times LHV_{water})]}{LHV_{Original\ Feedstock}}$$

## 2.5 Oxygen content calculation

The oxygen content of the DDB after the oven test was calculated according to the elemental analysis of the original feedstock. The analysis of the original DDB is shown in Table 1 and the ash content was determined at 800°C. The calculation has been done according to the following equation:

$$O\% = 100 - C\% - H\% - N\% - Ash\%$$

where

$$Ash\ of\ DDB_{ash} = \frac{100\% * 28,2\%}{x\%}$$

where x is the amount of ash that has been measured from the DDB oven test in different temperatures and 28,2% is the amount of ash in the original feedstock measured at 800°C.

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<sup>1</sup> ar = as received

### 3. Results and discussion

#### 3.1 Fast pyrolysis of different feedstocks in the screw reactor

The pine wood chips were used in the first seven experiments for validating the experimental setup. The DDB was used as biomass feedstock in the next two experiments in which we have encountered clogging and slugging problems inside the reactor and more specifically in the vapor line that connects the reactor with the first condenser. Clean wood pellets, that are going to be used as feedstock in the EMPYRO plant, and wheat straw pellets were used in the following experiments.

##### 3.1.1 Pine wood [Experiments 1-7 & 10]

In the first seven screening experiments pine wood chips was used as a biomass feedstock. An amount of 4,17 gr per 30 sec was fed to the system which means a feeding rate 0,5 kg/hr. The valve 1 (V-1) opened 2 times while the valve 2 (V-2) was closed to ensure that all the biomass has been transported to V-2 which subsequently opened 2 times with the V-1 to be closed. The sequence had a duration of approximately 15 seconds ensuring that biomass has been transferred in the reactor. The first experiment had to be terminated after an hour due to overpressure in the system. Vapor line clogging was the main problem that prevent the pyrolysis vapours from being transferred to the first condenser (C-1). Mass balance closure for the first experiment was plausible only with estimation of the gas flows as no GC measurements of produced gas were provided. For the next experiments gas sample were taken every 40 minutes and were analyzed in the gas chromatograph.

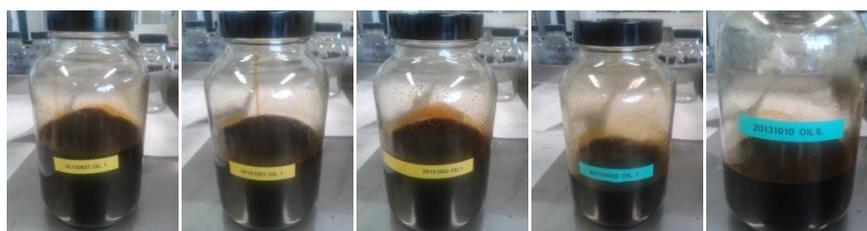


Figure 12: Bio-oil from the experiments with pine wood chips

The temperature in the screw reactor was set to 500°C (heating zones 1-4) in experiments 1 to 7 whereas in the 10th experiment the temperature in zone 1 was set up to 550°C. The temperature of the cooling water, which was flowing through the condensers, was set to -5°C. The biomass convey was enabled with the nuts addition - two at a time - in the feeding system. The first experiment had to be terminated after 35 minutes because an overpressure in the system was observed and caused by a blockage in the vapor line. The runtime in the next pine wood experiments ranged between 60 - 120 minutes. In the 6<sup>th</sup> experiment, the feeding interval was changed to 1 minute aiming to increasing the oil production.

##### 3.1.2 DDB [Experiments 8-9 & 25-26]

The Dried Distilled Biomass was used as a feedstock in these experiments in order to investigate the characteristics of this novel type of biomass. For the first two experiments the feeding rate was kept the same as in previous experiments. The runtime of the 8<sup>th</sup> and 9<sup>th</sup> experiment was 55 and 44 minutes respectively due to operational problems. The main problem was the clogging in the feeding section and in the vapor line caused by the sticky nature of DDB. To address this problem, 3 nuts were added in the feeding hopper, facilitating the biomass transport along the system. The nuts travelled from the feeding section through the screw to the char vessel. Additionally, hammering on the feeding valves facilitated the removal of biomass material that was stacked in the space between the valves. Figure 13 shows the poor quality of produced bio-oil, containing mostly water.



Figure 13: Bio-oil from the experiments with DDB

### 3.1.3 EMPYRO wood pellet [Experiments [11-14]

The clean wood pellets were examined in the next four experiments. Before the test, the inlet of the reactor and the valves of the feeding section were cleaned thoroughly. A drill was used to clean the vapor line by removing the contaminants that prevent the condensation of pyrolysis vapors. Additionally, a higher temperature (550°C) in the vapor line (zone 4) was set to prevent any potential condensation of the vapors. However, clogging problems occurred in the 11<sup>th</sup> and 12<sup>th</sup> experiment due to the contamination of the gas flow meter from previous DDB experiments. In the following experiments, the flow rate of the purge gas was measured before the start of each experiment and afterwards the gas meter was removed. Figure 14 shows the produced pyrolysis oil having a dark brown color with relatively low amount of water.



Figure 14: Bio-oil from the experiments with EMPYRO wood pellets

### 3.1.4 Wheat straw [Experiments [15-24]

In the last series of experiments, the product distribution of wheat straw as a starting material was investigated. The feeding valve sequence was changed in order to facilitate the convey of biomass inside the reactor where the pyrolysis reactions happened. Whenever the biomass feeding was inadequate, a temperature increase in the in heating zone 1 was observed, recorded by the thermocouple that was placed 1,5 cm away from the center of the reactor. Respectively, the reactor temperature was decreased due to endothermic pyrolysis reactions and the heat needed was provided by the reactor surroundings. Therefore, when no biomass was fed, the heat needed for the pyrolysis reactions increased the reactor temperature. An example of the temperature profile inside the reactor can be seen in Figure 15. T<sub>1</sub> to T<sub>4</sub> represent the heating zones inside the reactor as mentioned in section 2.2.

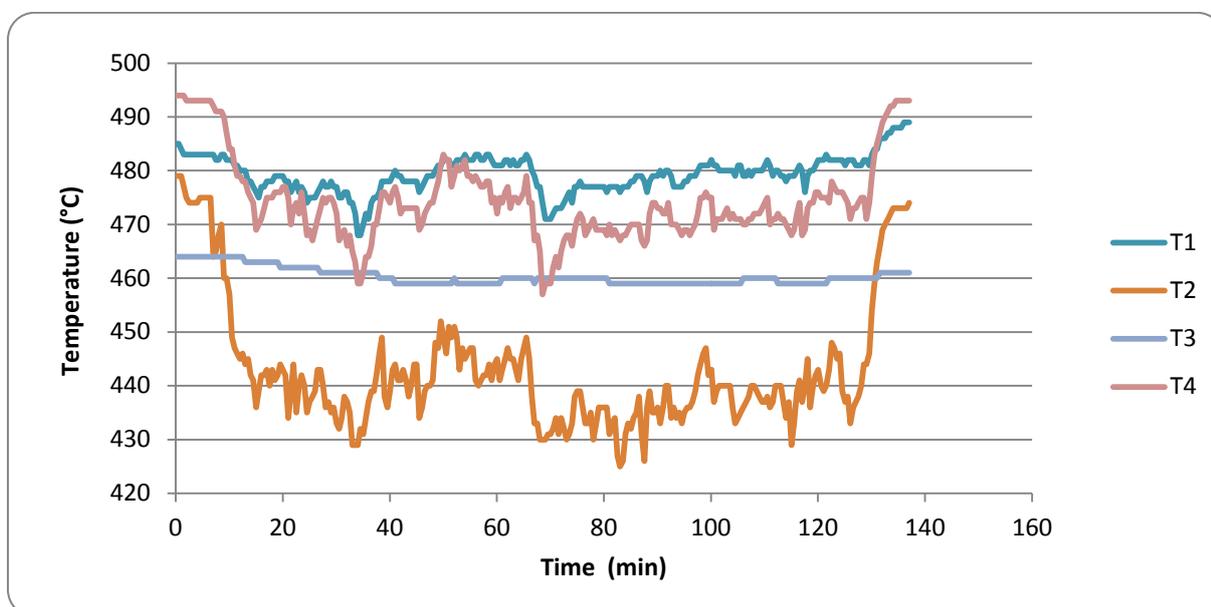


Figure 15: Temperature profile inside the reactor (from the 19<sup>th</sup> experiment)

In these experiments, two different cooling systems were used; 50°C for the first condenser and -5°C for the second and third to achieve higher condensation in the first condenser where the major oil was produced. These experiments were also performed with different operating temperatures ranging from 450 - 700°C, in order to investigate the effect of the reaction temperature on the oil and char yields. During these experiments, the vapor line was contaminated and contaminants were removed by using a drill. Figure 16 presents the collected bio-oil that after water separation.



Figure 16: Bio-oil from the experiments with wheat straw (organic and water phase)

### 3.2 Oxidizing and reducing atmosphere test

The results from the oxidizing atmosphere test are presented below. Figure 16 depicts an upward trend in the vaporized content of the DDB until the 450°C where a 60% of the initial amount was evaporated. A decrease in the amount of vaporized biomass between 450°C to 550°C is observed. This deviation in the vaporized biomass is not in line with the literature [22] as we expected the vaporized content and the temperature to increase proportionally. The same behavior in the biomass vaporized content was observed after additional measurements which were performed in the same temperatures (450, 500 and 550°C). The vaporized amount increase is attributed to the cellulose decomposition. The decrease in the evaporating biomass that occurs in the following temperatures could be ascribed to a low oxygen content inside the crucibles.

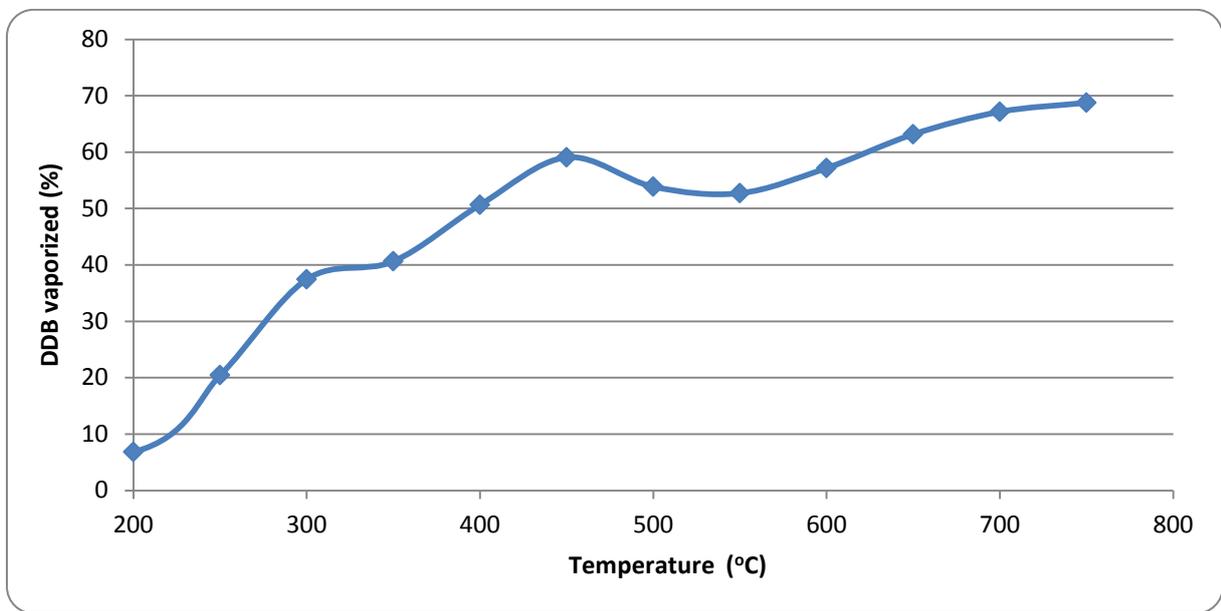


Figure 17: DDB vaporization in oxidizing condition

In reducing atmosphere test the samples were subjected to heat treatment with nitrogen flow for four hours. In these conditions, the oxidation is prevented by removing oxygen and other oxidizing gases. Figure 18 depicts a linear upward trend of the vaporized biomass at the temperature region between 200°C and 400°C. A sharp increase at 450°C is observed with a 62% of the initial biomass to be evaporated. This increase, as mentioned before, is due to the cracking of cellulose's polymer bonds during heating process.

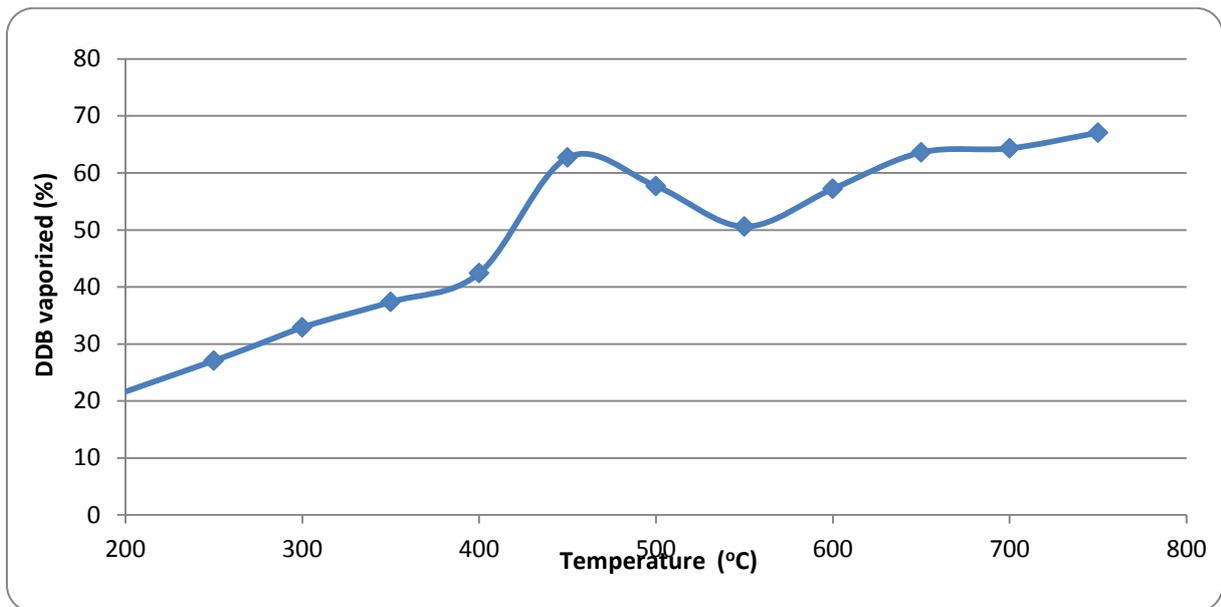


Figure 18: DDB vaporization in reducing condition

The comparison between the two atmosphere tests is shown in Figure 19. Generally under reducing conditions the temperature should be equal to or lower than the corresponding temperature under oxidizing conditions. The difference in these temperatures generally increases with increasing iron content in the ash. From 200°C to 400°C, the amount of vaporized biomass is higher in oxidizing conditions as expected. At 450°C and 500°C a higher amount of vaporized biomass in the reducing conditions is observed whereas in the remaining temperatures the vaporized biomass percentage is almost the same.

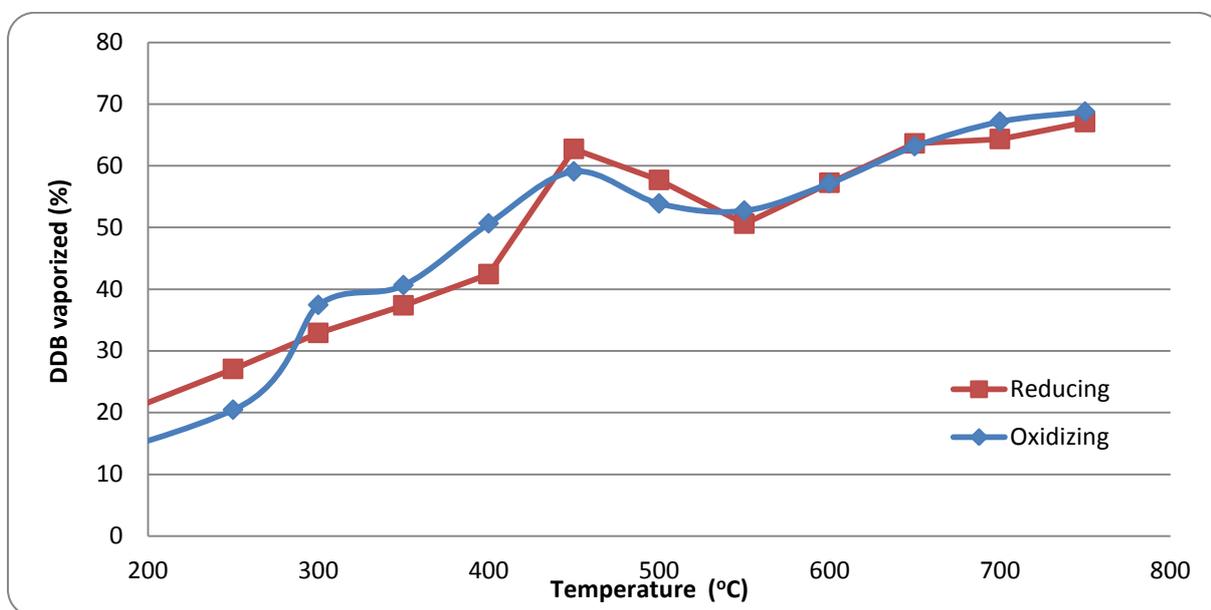


Figure 19: Comparison of the DDB vaporized in oxidizing and reducing conditions

The elemental analysis of DDB at different temperatures is shown in Figure 20. The analysis has been performed in the elemental analyzer in BTG's laboratory and the oxygen content has been calculated according to section 2.5. The carbon content decreases until 450°C, followed by a sharp increase until 550°C where it starts to decrease until the final temperature of the test. Comparing the oxidizing and reducing atmosphere test with the elemental analysis, a reciprocal dependence on the vaporized content and the carbon concentration is observed.

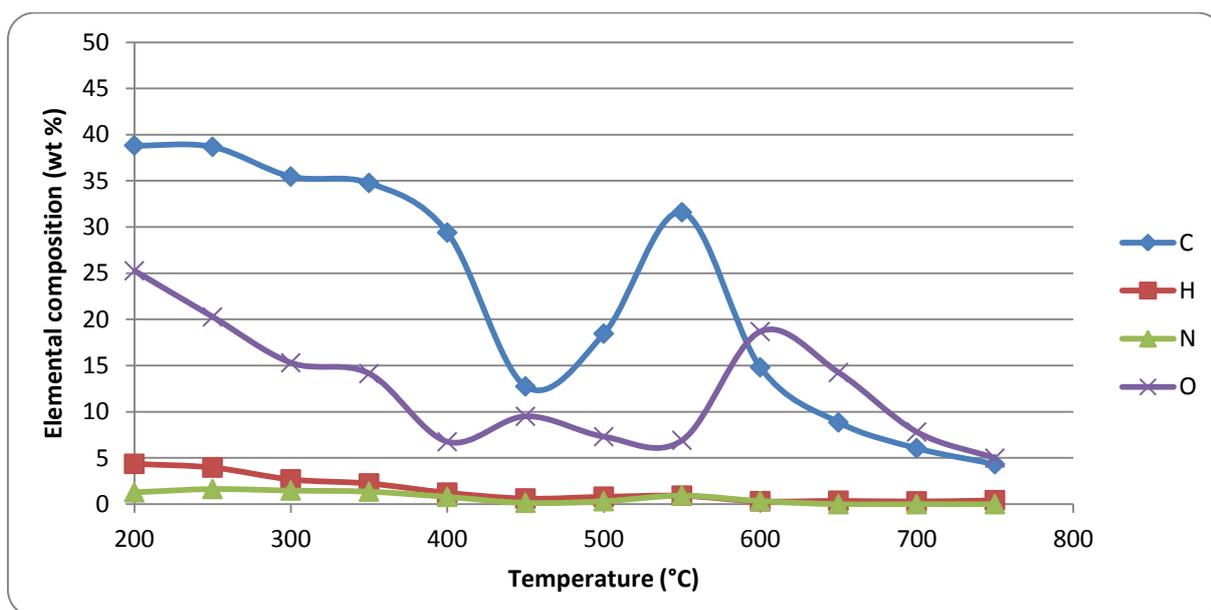


Figure 20: DDB elemental analysis of ash residue in different temperatures

### 3.3 Product yields

The oil, char and gas yield for each biomass feedstock has been determined according to section 2.4. The operating conditions in the first three experiments with pine wood were identical. The operating pressure was close to ambient while the temperature of the four heating zones of the reactor was at 500°C and of the cooling system at -5°C. Figure 21 shows the oil yield to range between 60 and 67%. The first experiment is not a good representative for the oil production due to operational problems. The following four experiments with pine wood feedstock were carried out with the temperature in heating zone 1 to be

increased to 550°C. The temperature in the remaining heating zones and in the cooling system was kept the same. It is clearly shown in Figure 22 that this temperature increase affects positive the oil production, reaching a maximum of 72,7% in the 7<sup>th</sup> experiment.

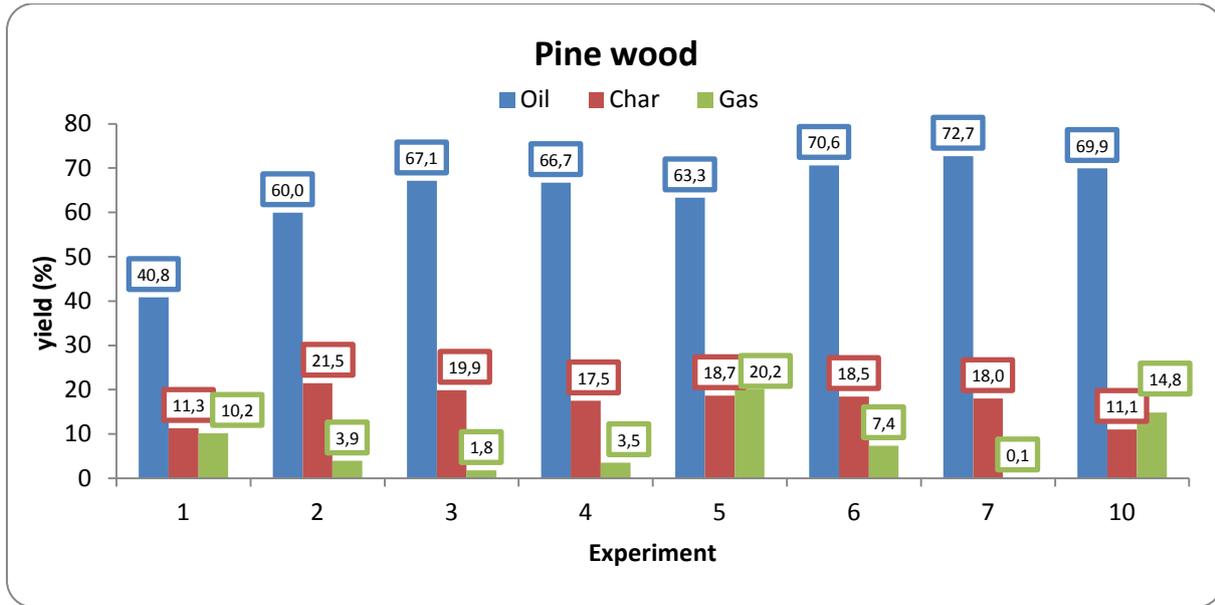


Figure 21: Oil and char yield for pine wood chips

The next series of experiments with EMPYRO wood pellets were conducted with the same operating conditions (i.e. T=550°C in zone 1, T=550°C in zones 2,3,4 and cooling -5°C). Only in the 14<sup>th</sup> experiment the cooling temperature was at 20°C. The maximum oil production of 63% was achieved in 12<sup>th</sup> and 13<sup>th</sup> experiment whereas in the other two experiments the production was lower.

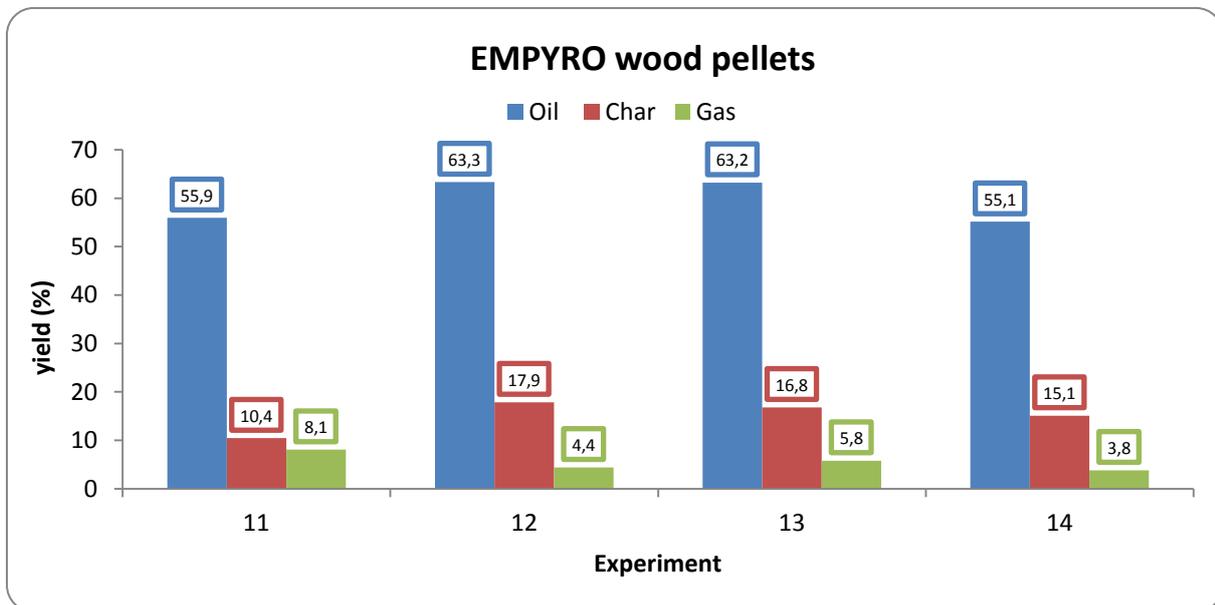


Figure 22: Oil and char yield for the EMPYRO wood pellets

Considering the operating conditions in wheat straw experiments, the pressure was close to ambient while in the last seven experiments the temperature in heating zone 1 varied between 450 to 700°C. In experiments 15<sup>th</sup> to 17<sup>th</sup> temperature in zone 1 was kept at 500°C. Furthermore, a second cooling system was added to control the temperature of the first condenser at 50°C whereas the temperature of first cooling system was kept at -5°C. The temperature effect on the product distribution of wheat straw experiments is analyzed in section 3.4.

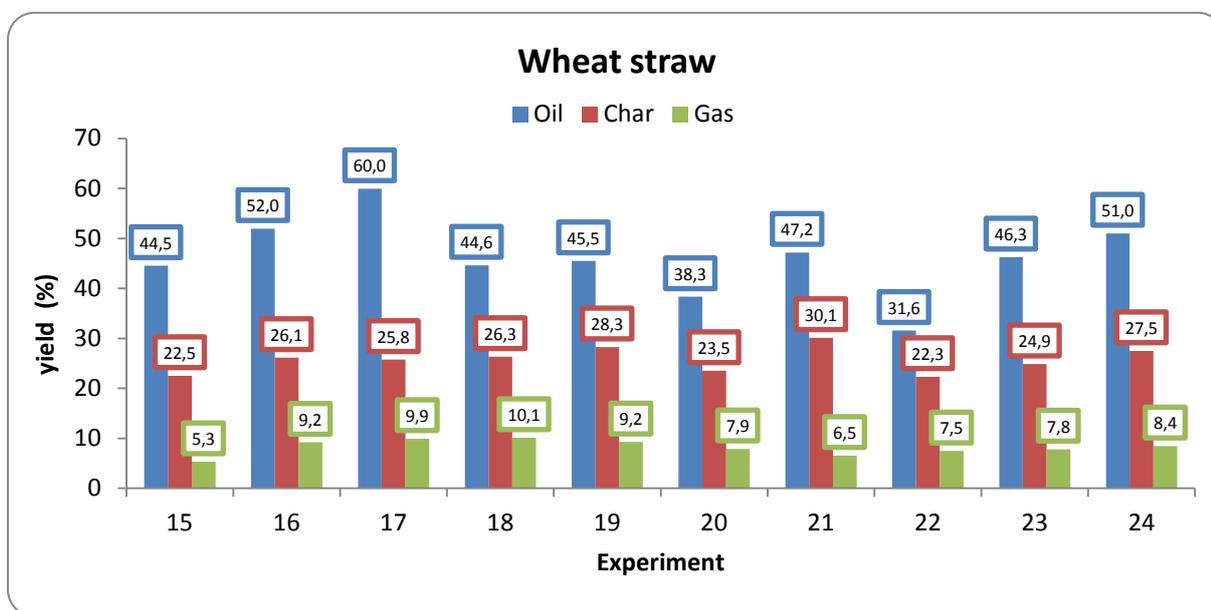


Figure 23: Oil and char yield for the Wheat Straw

The 8<sup>th</sup> and 9<sup>th</sup> DDB experiments were performed in the same temperature and pressure conditions (i.e. 550°C for zone 1 and 500°C for zones 2-4 and one cooling system at -5°C). In experiments 25<sup>th</sup> and 26<sup>th</sup>, the temperature was set to 450°C for zone 1 and to 650°C for zones 2-4. The additional cooling system (T=50°C) in the first condenser was used again. From the DDB oven tests (Figure 19) is observed a 63% of DDB to be vaporized at 450°C and 650°C while at 550°C the vaporized content drops to 52%. However, comparing the production distribution, a higher bio-oil production in experiments 8 and 9 (550°C) is noticed, while in 25<sup>th</sup>(450°C) and 26<sup>th</sup>(650°C) experiments char is the major product at the expense of bio-oil.

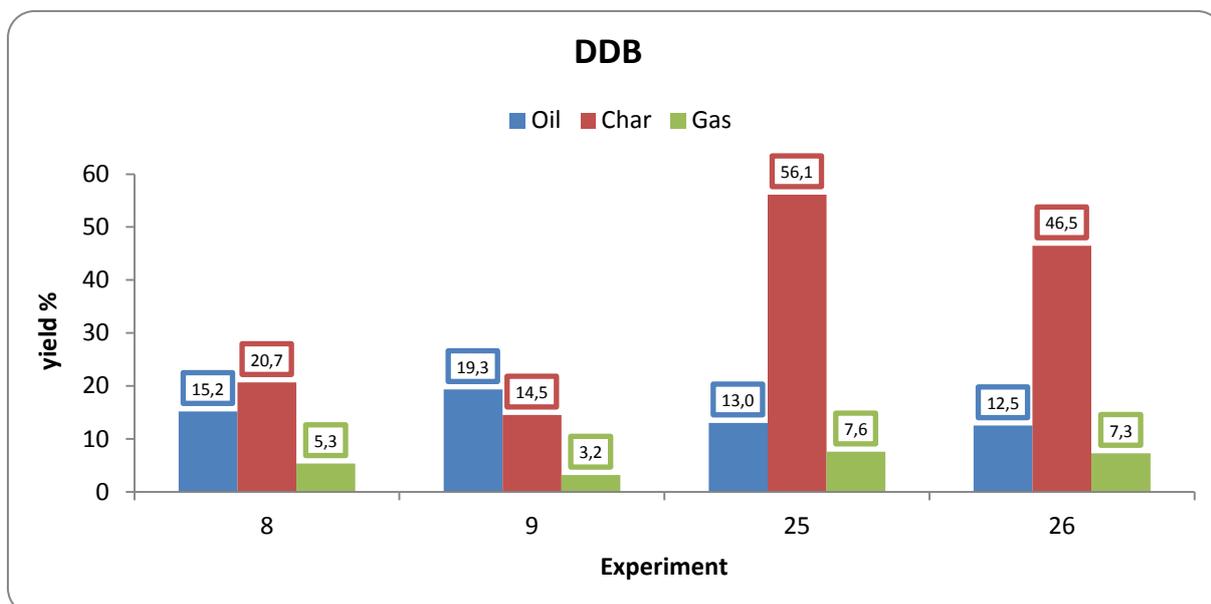


Figure 24: Oil and char yield for DDB

Figure 25 shows a comparative overview of the product yields for the experiments that have been performed in this work. Bio-oil was the main product in experiments with pine wood, wheat straw and soft wood followed by char and gas production whereas in DDB experiments char was mainly produced followed by bio-oil and gas production.

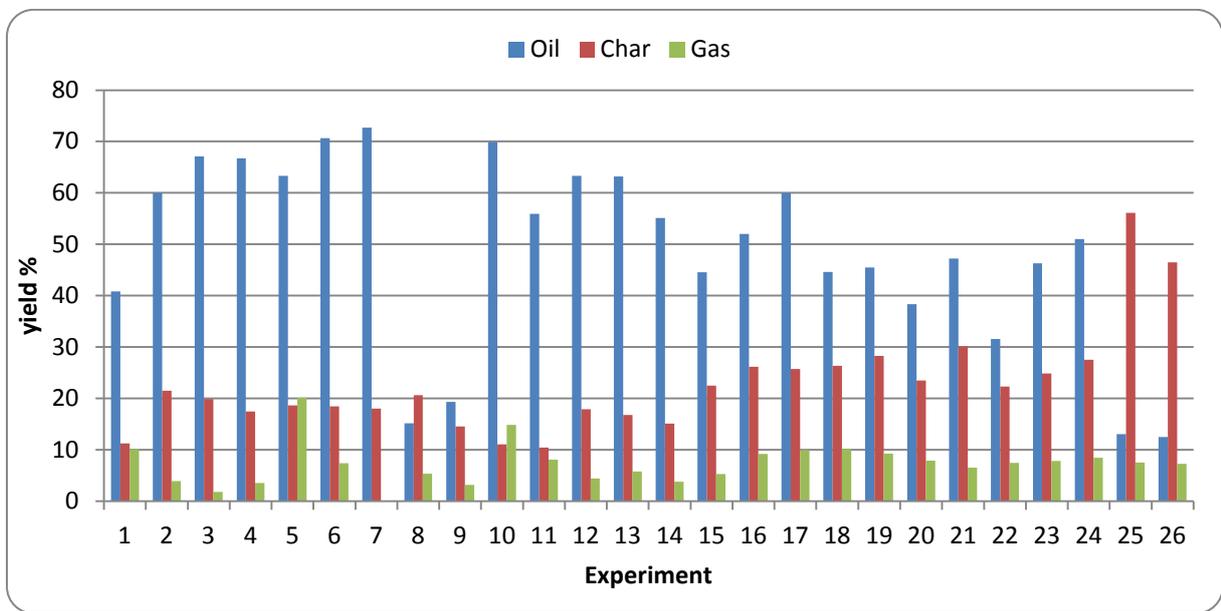


Figure 25: Product distribution for all the experiments

### 3.4 Temperature effect on wheat straw

The effect of temperature on the oil yield of wheat straw was studied in the wheat straw experiments. Figure 26 shows that the oil yield maximizes at 550°C, with a 60% to be achieved. In higher temperatures, a decrease in oil yield is observed whereas the char production remains almost stable. It is found from the literature that the optimum temperature for maximizing oil yield is 550°C. This temperature is suitable for substantial devolatilization of biomass while is not too high to promote substantial cracking of pyrolysis vapors into non-condensable gas or the polymerization of vapors into char [13].

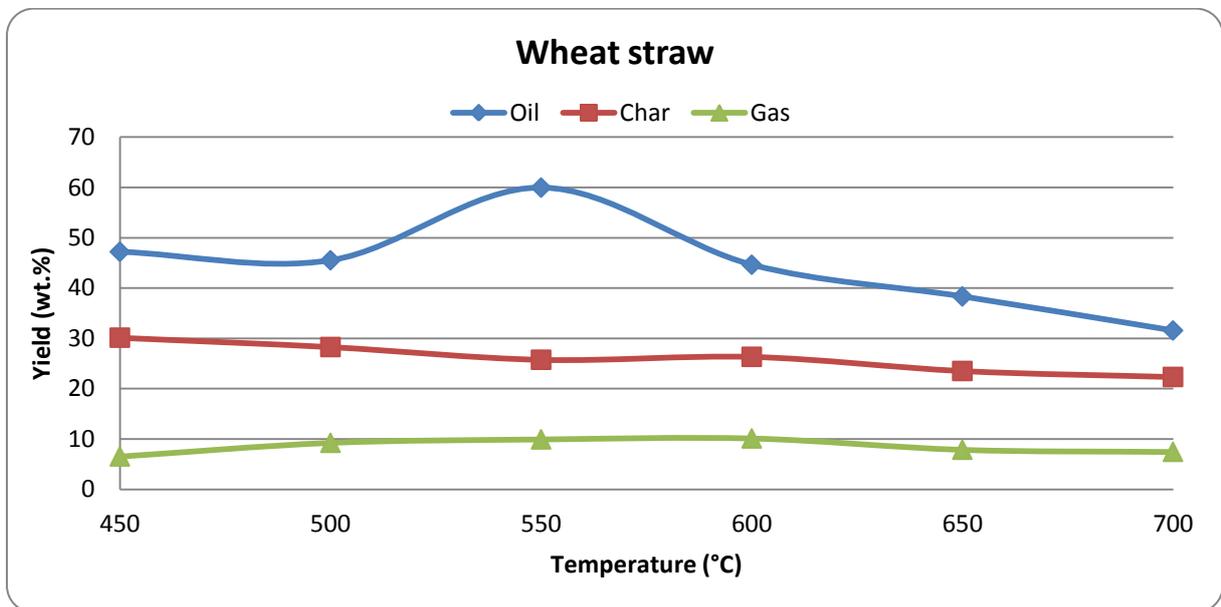


Figure 26: Effect of the temperature on the wheat straw oil yield

### 3.5 Thermogravimetric analysis (TGA)

Thermogravimetric analysis is a well established technique for measuring the change in weight of a sample as a function of temperature or time in an inert atmosphere [23, 24]. The analysis has been performed in the laboratory of the Sustainable Process Technology (SPT) group of University of Twente using a Netzsch TG 449F1 Jupiter TGA. The thermogravimetric analysis has been done to five biomass types with a heating rate of 10°C/min from room temperature until 900°C. The purge flow of nitrogen was kept at 50 ml/min along with an additional safety flow of 20 ml/min for the TG-analyzer.

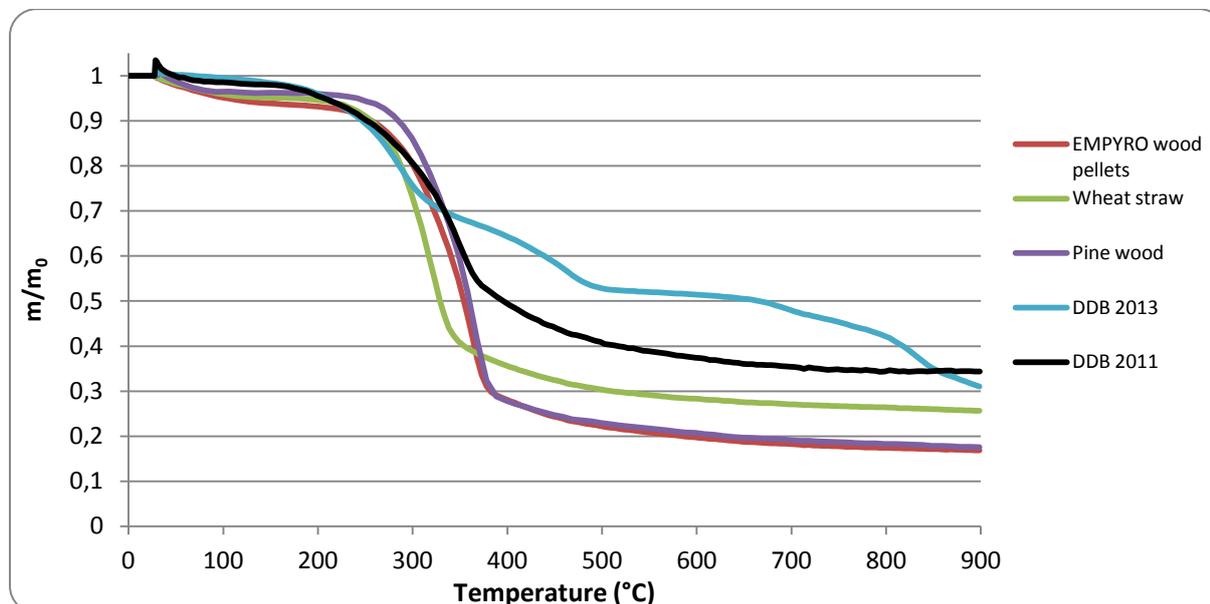


Figure 27: TGA for the biomass samples

Figure 27 plots the ratio of mass change over the initial sample mass versus the temperature. An intense mass loss occurs after 250°C in all the samples which can be ascribed to devolatilization of biomass particles. The thermal degradation of the EMPYRO wood pellets and pine wood chips follows a similar trend. In both samples we can see a sudden and intense mass loss at 250°C which lasts until 400°C. Subsequently, the mass decreases with a lower rate until 650°C where the degradation stabilizes until the end of test. The TGA test for the DDB 2013 shows a mass stability until 160°C. The degradation of the mass starts after this temperature and gradually continues until the final temperature of the test (900°C).

Figure 28 presents the differential thermogravimetry (DTG) profiles of the biomass feedstocks. As it was mentioned before, biomass is composed of three polymers that degrade in different temperature regions. The pyrolysis profiles display one characteristic weight loss peak in the region of 300°C - 380°C where the cellulose decomposition takes place. In a lower temperature, around 200 - 300°C, a shoulder peak is displayed which is attributed to the less stable hemicellulose fraction.

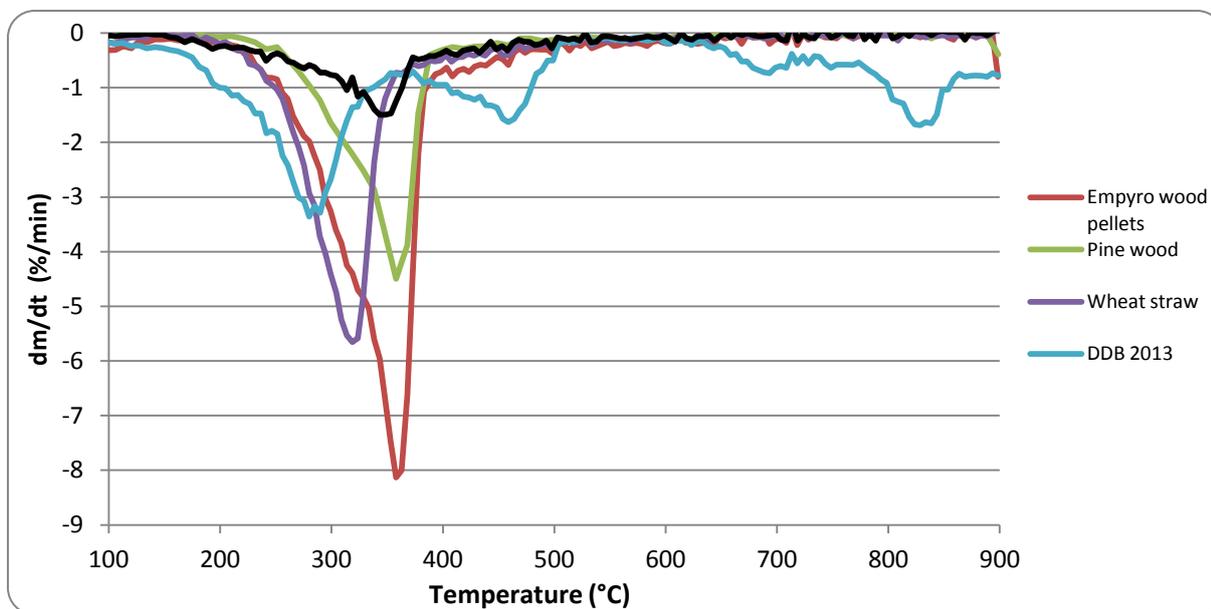


Figure 28: DTG plots for the various feedstocks

Figure 29 presents the TGA comparison between the DDB 2013, that was used in this work, and the DDB 2011. In DDB 2013 plot four distinct reversed peaks are observed which depict the decomposition of the biomass polymers. The first peak at around 250 - 300°C corresponds to the hemicellulose decomposition; the second peak at 450°C is characteristic for the degradation of cellulose. The other two peaks after 700°C might correspond to materials that were added in the biomass during bio-ethanol production. The plot of DDB 2011 displays one pronounced peak at 350°C where cellulose decomposition takes place. The degradation of hemicellulose occurs around 250°C where a small shoulder is observed.

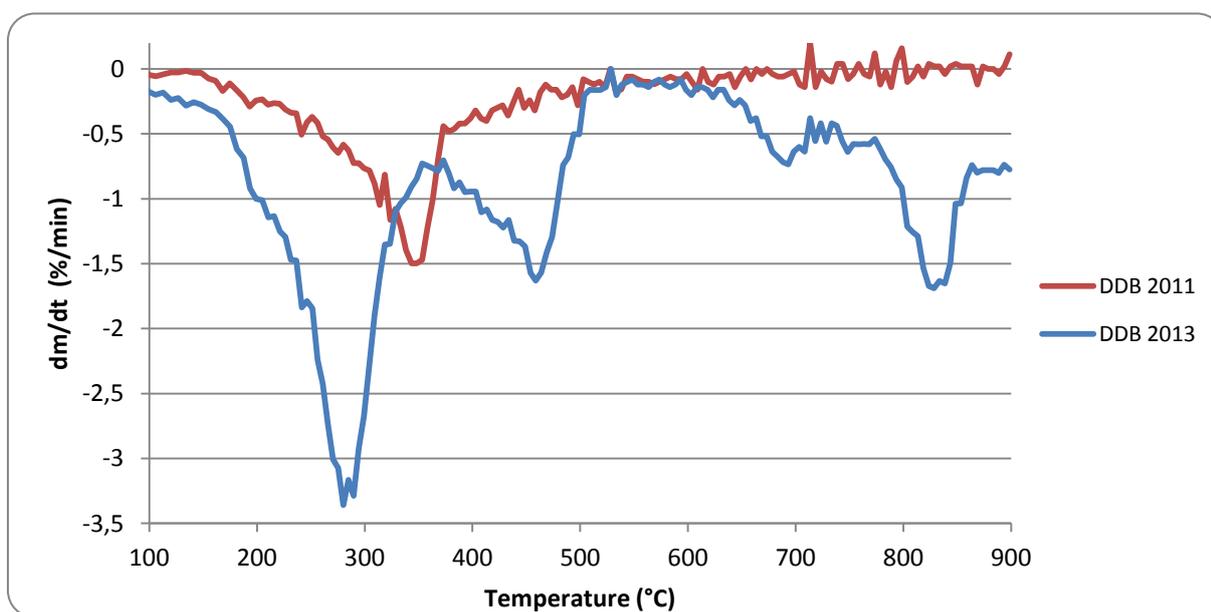


Figure 29: DTG comparison plot between DDB 2011 and 2013

### 3.6 Energetic yield

The heating values of the raw original feedstock are presented in Table 1. The calculation has been done according to section 2.4. The pine wood chips has found to be the feedstock with the higher LHV, followed by the wood pellets, DDB 2013 and the wheat straw pellets.

Feedstock	HHV <sub>Milne</sub> [MJ/kg]	LHV <sub>dry</sub> [MJ/kg]
DDB 2013	14,6	13,3
Wheat straw pellets	17,1	14,2
EMPYRO wood pellets	20,8	19,5
Pine wood	30,5	29,7

Table 2: HHV and LHV of the original feedstocks

Table 3 presents the LHV<sub>dry</sub> of the oil produced from pine wood in the first seven experiments. The average value of the LHV<sub>dry</sub> for the oil produced in the first condenser is around 12 MJ/kg whereas the LHV<sub>dry</sub> of oil produced in the second condenser for the experiments 4 and 5 is increased up to 21 and 22 MJ/kg respectively. This is a very promising result as this oil can be used as a transportation fuel after upgrading.

Pine wood	Oil 1 Exp.2	Oil 1 Exp. 3	Oil 1 Exp. 4	Oil 2 Exp. 4	Oil 1 Exp. 5	Oil 2 Exp. 5	Oil 1 Exp. 7
LHV <sub>dry</sub> [MJ/kg]	11,6	12,3	12,3	20,9	12,5	21,8	12,1

Table 3: LHV of pine wood oil

The LHV<sub>dry</sub> of wheat straw oil is shown in Table 4. This oil is the remaining concentrated organic phase, after water removal. The average calculated LHV<sub>dry</sub> value is around 20 MJ/kg which makes wheat straw oil, after upgrading process, an attractive alternative to fuels production.

Wheat Straw	Exp. 15	Exp. 16	Exp. 17	Exp. 18	Exp. 19	Exp. 20	Exp. 21	Exp. 22	Exp. 23	Exp. 24
LHV <sub>dry</sub> [MJ/kg]	19,1	19,5	19,5	19,9	19,5	21,6	19,3	23,6	21,2	19,2

Table 4: LHV of wheat straw oil (organic phase)

The calculation of LHV for the DDB shows that the concentrated organic phase has an average value of around 29 MJ/kg whereas the water phase has a lower value below 10 MJ/kg.

DDB	Extra Oil Exp. 9	Oil 1 (org) Exp. 9	Oil 1 (w.ph.) Exp. 9	Extra Oil (org) Exp. 8	Oil 1 (w.ph.) Exp. 8
LHV <sub>dry</sub> [MJ/kg]	28,7	30,6	8,1	28,1	6,9

Table 5: LHV of DDB oil for organic and water phase

The energetic yield of the oil produced has been determined, according to section 2.4, for the feedstocks under study. It was assumed that the oil produced in the first condenser corresponds to the water phase oil whereas the oil in the second condenser along with the extra oil correspond to the organic phase.

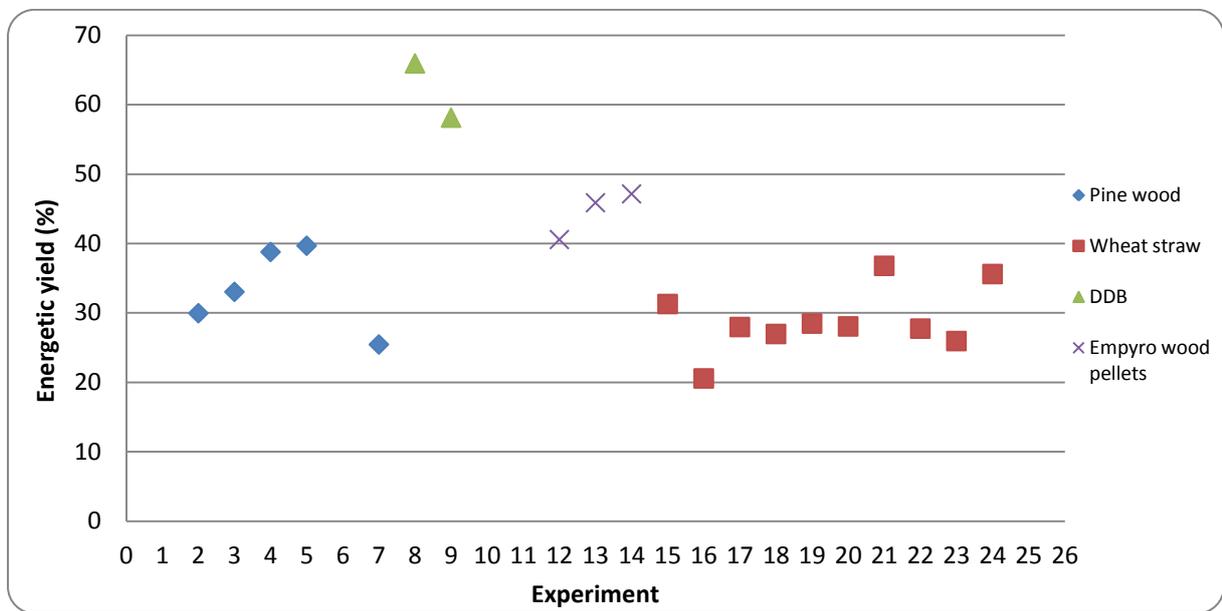


Figure 30: Energetic yields of pine wood, wheat straw and DDB oil

In Figure 30, the energetic yield for the selected feedstocks is presented. Pine wood oil ranged between 30% to 40% whereas for the wheat straw oil the energetic yield ranged between 26% and 36%. The bio-oil from the two DDB experiments has energetic yield of 58% and 65%, significantly higher compared to the energy recovered from the other three feedstocks. This result gives an extra incentive in further investigation of DDB as an alternative feedstock for fuel production.

## 4. Conclusion

The present study addressed the fast pyrolysis process in four different types of biomass in a series of experiments. The experimental setup consisted of a screw reactor that was rotating with a standard frequency facilitating the convey of biomass and adjusting the residence time of the vapors. The pine wood chips experiments produced bio-oil with an average yield of 63% and an average LHV of 12 MJ/kg, having also good mass balance closure. A novel type of biomass which holds the potential to become a promising feedstock in fuel production, the Dried Distilled Biomass (DDB), has been also investigated as it a low cost by-product. However, the bio-oil yield from these experiments were relatively low, around 15%, with the oil produced to contain a high amount of water and the balance closure to be insufficient. Considering the EMPYRO wood pellets, the oil yield was around 60% and the balance closure of these experiments was relatively good. In wheat straw experiments the temperature effect on the bio-oil and char yield was investigated. The oil production was maximized in 550°C as expected, whereas the char production was almost stable, decreasing slightly in higher temperatures.

Regarding the conduct of the experimental series, many operating problems were encountered. The major of which to be the clogging of the feeding section along with slagging in the inner part of the reactor. A possible solution in eliminating these problems could be the burn-off of the screw reactor before each experiment combined with a thorough cleaning of the whole system. Furthermore, it is considered that a higher purge flow could remove stuck biomass particles along the system. The addition of nuts in the feeding section could also facilitate sticky feedstocks as DDB to transport better through the system.

To conclude, fast pyrolysis is a promising technology in the production of storable and transportable liquid fuels. From our research, pine wood was found to be the most promising feedstock in terms of bio-oil production. However, more research needs to be done in the novel types of biomass, like DDB, in view of optimizing the process and maximizing the bio-oil yield.

## 5. References

1. BP. *BP Statistical Review of World Energy* 2013; Available from: [http://www.bp.com/content/dam/bp/pdf/statistical-review/statistical\\_review\\_of\\_world\\_energy\\_2013.pdf](http://www.bp.com/content/dam/bp/pdf/statistical-review/statistical_review_of_world_energy_2013.pdf).
2. Holechek, J.L., *Global trends in population, energy use and climate: Implications for policy development, rangeland management and rangeland users*. *Rangeland Journal*, 2013. **35**(2): p. 117-129.
3. Tilman, D., J. Hill, and C. Lehman, *Carbon-Negative Biofuels from Low-Input High-Diversity Grassland Biomass*. *Science*, 2006. **314**(5805): p. 1598-1600.
4. McKendry, P., *Energy production from biomass (part 1): overview of biomass*. *Bioresource Technology*, 2002. **83**(1): p. 37-46.
5. Bridgwater, A.V. and G.V.C. Peacocke, *Fast pyrolysis processes for biomass*. *Renewable and Sustainable Energy Reviews*, 2000. **4**(1): p. 1-73.
6. Pande, M. and A. Bhaskarwar, *Biomass Conversion to Energy*, in *Biomass Conversion*, C. Baskar, S. Baskar, and R.S. Dhillon, Editors. 2012, Springer Berlin Heidelberg. p. 1-90.
7. Naik, S.N., et al., *Production of first and second generation biofuels: A comprehensive review*. *Renewable and Sustainable Energy Reviews*, 2010. **14**(2): p. 578-597.
8. Westerhof, R.J.M., *Refining fast pyrolysis of biomass*. 2011: Enschede. p. 210.
9. Alonso, D.M., J.Q. Bond, and J.A. Dumesic, *Catalytic conversion of biomass to biofuels*. *Green Chemistry*, 2010. **12**(9): p. 1493-1513.
10. McKendry, P., *Energy production from biomass (part 2): conversion technologies*. *Bioresource Technology*, 2002. **83**(1): p. 47-54.
11. McKendry, P., *Energy production from biomass (part 3): gasification technologies*. *Bioresource Technology*, 2002. **83**(1): p. 55-63.
12. Wagenaar, B.M., W. Prins, and W.P.M. van Swaaij, *Pyrolysis of biomass in the rotating cone reactor: modelling and experimental justification*. *Chemical Engineering Science*, 1994. **49**(24): p. 5109-5126.
13. Nachenius, R.W., et al., *Chapter Two - Biomass Pyrolysis*, in *Advances in Chemical Engineering*, M. Dmitry Yu, Editor. 2013, Academic Press. p. 75-139.
14. BTG. *Fast pyrolysis process*. [cited 2013 6/12/2013]; Available from: <http://www.btgworld.com/en/rtd/technologies/fast-pyrolysis>.
15. BTG-BTL. *BTG-BTL pyrolysis process*. 11/12/2013]; Available from: <http://www.btg-btl.com/en/technology>.
16. *EMPYRO project website*. 16/12/2013]; Available from: <http://www.empyroproject.eu/index.php>.
17. Pasangulapati, V., et al., *Effects of cellulose, hemicellulose and lignin on thermochemical conversion characteristics of the selected biomass*. *Bioresource Technology*, 2012. **114**(0): p. 663-669.
18. *Ash*. 2011 20/1/2014]; Available from: <http://www.miningknowhow.info/glossary-of-terms/ash>.
19. Westerhof, R.J.M., et al., *Controlling the Water Content of Biomass Fast Pyrolysis Oil*. *Industrial & Engineering Chemistry Research*, 2007. **46**(26): p. 9238-9247.
20. ECN. *Definitions used in Phyllis*. 9/12/2013]; Available from: <https://www.ecn.nl/phyllis/defs.asp>.
21. Demirbaş, A., *Calculation of higher heating values of biomass fuels*. *Fuel*, 1997. **76**(5): p. 431-434.
22. Li, H., et al., *Application of the FactSage to Predict the Ash Melting Behavior in Reducing Conditions*. *Chinese Journal of Chemical Engineering*, 2006. **14**(6): p. 784-789.
23. Wieboldt, R., S. Lowry, and R. Rosenthal, *TGA/FT-IR: Thermogravimetric analysis with fourier transform infrared detection of evolved gases*. *Microchimica Acta*, 1988. **94**(1-6): p. 179-182.
24. Singh, S., C. Wu, and P.T. Williams, *Pyrolysis of waste materials using TGA-MS and TGA-FTIR as complementary characterisation techniques*. *Journal of Analytical and Applied Pyrolysis*, 2012. **94**(0): p. 99-107.