

Fast Pyrolysis of Woody Biomass in a Pyroprobe Reactor:

Effect of Torrefaction on the Pyrolysis Products

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Fast Pyrolysis of Woody Biomass in a Pyroprobe Reactor: Effect of Torrefaction on the Pyrolysis Products

By

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Abstract

The future depletion of conventional fossil fuel reserves, the ever increasing need for energy self – reliance and the global concern around environmental change caused by their use, have made heat and power generation from alternative and sustainable sources a primary research focus worldwide. Biomass is such a source, constituting a clean and renewable fuel, while being the third fuel resource in the world after coal and oil in terms of abundance. Through thermochemical processes biomass can be employed for energy, chemicals and transport fuel production. Pyrolysis is the thermochemical process of biomass decomposition into various useful products in the absence of an oxidation medium. Torrefaction is a mild pyrolysis process, typically carried out in a temperature range between 230°C and 300°C. This pretreatment process offers benefits with respect to biomasses energy density, while reducing the oxygen and hydrogen to carbon ratios and its hygroscopic nature.

In this work untreated and torrefied biomass species were pyrolysed under different final temperatures in a Pyroprobe 5200 reactor. In particular, raw and torrefied (at 250°C and 265°C) wood ash (*Fraxinus excelsior*) and raw and torrefied (at 300°C) Torrcoal, which consists of mixed wood residues, were investigated. The feed was reduced to a particle size less than 75 µm and the experiments were performed with a sample size of 30 mg in the temperature range of 600°C to 1000°C at a heating rate of 600°C/s, in order to achieve fast pyrolysis conditions. The main purpose of these experiments was to determine the effect of final pyrolysis temperature and torrefaction to the yield and nature of pyrolysis final products. In terms of individual gases, CO, CO₂, CH₄ and H₂ were identified using a micro GC. Tar compounds (phenol and PAHs) were identified and quantified using a HPLC system.

The aforementioned experiments produced mass closure values between 65% and 84%, which can be considered as satisfactory due to the difficulties in measuring gravimetrically pyrolytic water, higher hydrocarbon gases and light tar compounds. Increasing pyrolysis temperatures had a negative effect on char yield, however above 800°C it appeared to stabilize. Maximum values of the liquid yield were obtained at 600°C and 700°C before attaining a decreasing trend for the ash materials and stabilizing for Torrcoal materials at 900°C. Gas yields increased until 900°C for Torrcoal species and ash torrefied at 265, but for the rest species the increase continued until 1000°C. CO was the major gas produced above 800°C overtaking CO₂ at that temperature, while CH₄ and H₂ yields became significant above 700°C and 800°C respectively.

Torrefaction and increased torrefaction severity led to an increase of the char yield of the pyrolysis process. Their effect on the liquid yield was the opposite. In terms of total gases production the differences were minimal and only noticeable above 800°C. However, the quality of the pyrolysis gas was higher for the torrefied species.

Regarding the tar compounds analysis, phenol yield decreased until 800°C before reaching a plateau thereafter. PAH species yield increased steeply between 800°C and 900°C. Their production still increased above that temperature but at a slower rate. Naphthalene was the major PAH produced. Torrefaction seemed to favour phenol production while its effect on PAHs was not significant. Between the two biomass species studied, the higher phenol yield of Torrcoal pyrolysis along with its higher char and lower liquid yield are indicative of higher lignin content for this biomass.

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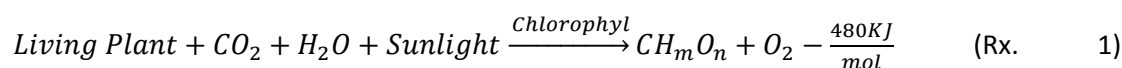
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1. Introduction

1.1 Biomass formation and composites

The reactions that lead to botanical biomass formation and growth are photochemical and biochemical and they take place when CO₂ and water are taken up by the plant and solar energy is absorbed. During these processes water is oxidized in order for electrons and protons to be obtained and carbon dioxide is reduced. The overall process is called photosynthesis and its global reaction scheme is depicted in Reaction 1. As it can be seen, the initial organic products of photosynthesis are carbohydrates. Generally, it can be said that during this process solar energy is converted to chemical energy contained in the biomass components [1, 2].



According to the reaction above the inorganic materials, CO₂ and water are converted to organic chemicals with the simultaneous release of oxygen. The photosynthetic assimilation of CO₂ from the environment involves a large number of biochemical reactions and produces sugars as initial product. Secondary products that are derived from key intermediates are polysaccharides, lipids, proteins and some other complex organic compounds, like lignin. These organic compounds are not produced in all kinds of biomass and they include simple low molecular weight organic chemicals such as acids, alcohols, aldehydes, ethers and esters. Furthermore, complex alkaloids, nucleic acids, pyrroles, steroids, terpenes, waxes and high molecular weight polymers like the polyisoprenes can be produced [1].

According to Basu [2], biomass is a complex mixture of organic materials (carbohydrates, lignin, fats and proteins) with small amounts of minerals (sodium, phosphorus, calcium and iron). Generally, it can be said that biomass is constituted by extractives, fibre or cell wall components and mineral matter. The extractives are substances present in vegetable or animal tissue that are released by dissolution in a solvent and recovery through evaporation of the solution. Proteins, oils, starch and sugars belong to this category. The fibres or cell walls provide structural strength to the plant and they are made out of lignin and carbohydrates. These carbohydrates are hemicellulose and cellulose which impart strength to the plant's structure, while lignin holds the fibres together. The cell wall components vary among plants, e.g. soybeans and potatoes also store starch and fats in their seeds and roots. Finally, ash is the inorganic component of biomass. In the following paragraphs the three main biomass components are going to be presented.

Hemicellulose (C₅H₈O₄)_n, is a heterogeneous polymer of pentoses (xylose, arabinose), hexoses (mannose, glucose and galactose), acetyl side groups and sugar acids. In contrast with cellulose, hemicellulose is not chemically homogeneous. Differences exist in hemicellulose compositions between softwood and hardwood for example. In the case of softwood hemicellulose consists mainly of glucomannans, whereas in hardwood, xylans are the main component [3]. Generally, hemicellulose is composed of all the non – cellulosic polysaccharides and related substances. Their structure resembles the one of celluloses but it contains 50 to 200 monomer units

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and it is branched in contrast to celluloses linear structure. Furthermore, they are more soluble and susceptible to chemical degradation than cellulose [4]. This is mainly due to their random, amorphous structure which has little strength. Figure 1 presents the molecular arrangement of a hemicellulose molecule (xylan). Additionally, it should be mentioned, that hemicellulose takes up 20 to 30% of the dry wood's weight, while it yields more gases and less tars than cellulose [2].

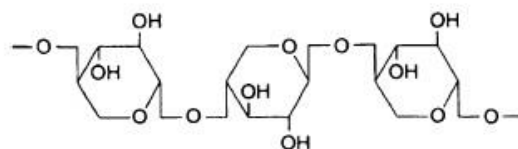


Figure 1: Molecular structure of xylan, [2]

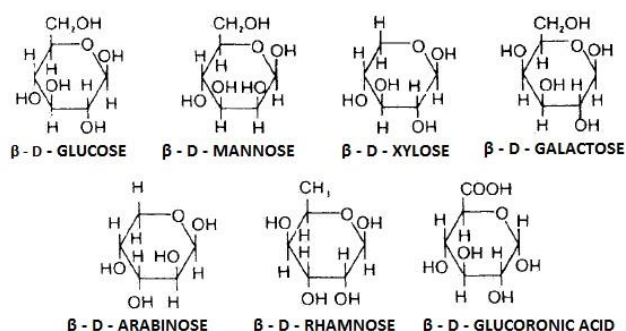


Figure 2: Hemicellulose monomers, [2]

Cellulose, with the elementary formula $(C_6H_{10}O_5)_n$, is mainly found in the protective cell walls of plants, more particularly in the stalks, stems, trunks and generally in all the woody portions of plant tissues. It is classified as an unbranched homopolysaccharide and it is composed of β - D - glucopyranose units linked by (1 $\rightarrow$ 4) glycosidic bonds. The cellulose chains in nature have a degree of polymerization of approximately 10000 glucopyranose units in wood and 15000 in native cotton [5]. The molecules that comprise cellulose are completely linear and tend to form intra- and intermolecular hydrogen bonds. Its structure is highly crystalline, because of the aggregation of those linear molecular chains within microfibriles. Consequently, cellulose's fibrous structure and strong hydrogen bonding, makes it insoluble in most solvents and gives it a high tensile strength [4]. Generally, cellulose is the most abundant organic compound on earth, its amount varying from 90% by weight in cotton to 33% in most plants. In the case of wood, cellulose amounts to roughly 40% of its dry weight [2].

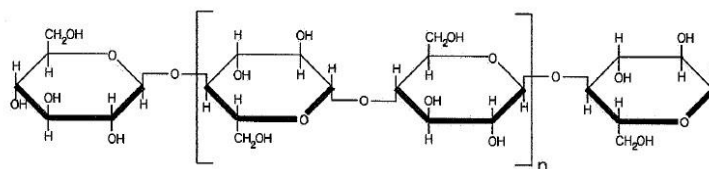


Figure 3: Cellulose structure, taken from [4]

According to [6], lignin can be defined as an amorphous, polyphenolic material arising from an enzyme - mediated dehydrogenative polymerization of three phenylpropanoid monomers, namely coniferyl, sinapyl and p - coumaryl alcohols. The biosynthesis process of lignin consists of radical coupling reactions, often followed by water addition or of primary, secondary and phenolic

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hydroxyl groups to quinonmethide intermediates. This process leads to the formation of a three dimensional polymer, which does not present the regular and repeating units that other natural polymers, such as cellulose, present. Therefore, lignin is considered a composite of physically and chemically heterogeneous materials. In the case of softwood lignin (guaiacyl lignin), its structural elements originate mainly from coniferyl alcohol and in lesser degree from p – coumaryl alcohol type units and trace amounts of sinapyl alcohol – derived units. On the other hand, hardwood lignins are comprised of discrete guaiacyl and syringyl lignins which are made up by coniferyl alcohol and sinapyl alcohol – derived units, while the methoxyl content per phenylpropanoid ranges from 1.2 to 1.5. In any case, the structural elements comprising lignin are linked by carbon – carbon and ether bonds. Nevertheless, according to the same authors mentioned above, evidence exists that lignin occasionally forms extremely stable links with polysaccharides, mainly through arabinose, xylose and galactose units in the hemicellulose components. Generally, lignin is the most abundant organic polymer on Earth after cellulose and acts as the glue for cellulose fibres holding adjacent cells together. It is highly insoluble, even in strong acids. Finally, its concentration in hardwood ranges from 18 to 25% while in softwood from 25 to 35% by dry weight [2].

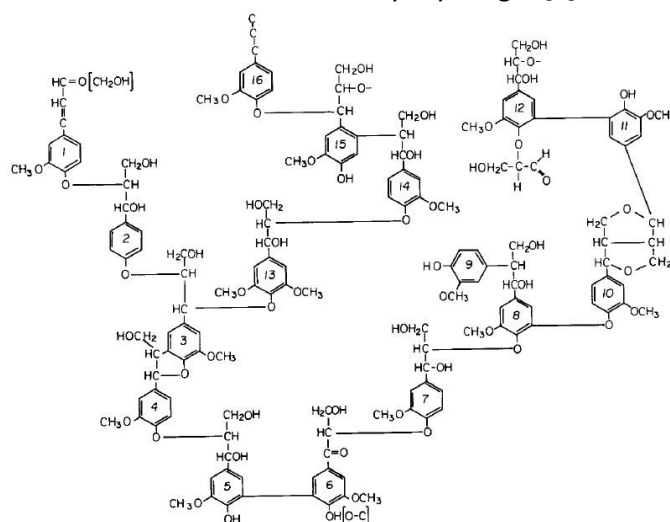


Figure 4: Structural model of spruce lignin, taken from [6].

1.2 Biomass pyrolysis

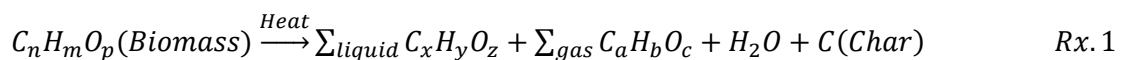
Pyrolysis is the thermochemical process of biomass decomposition into various useful products, either in the absence of an oxidation medium, or with a small presence which does not enable gasification to an appreciable extent. Pyrolysis is first chemical conversion step of gasification and it involves the devolatilization of biomass. This step occurs fast, especially in reactors with rapid mixing. During, pyrolysis large and complex biomass hydrocarbon molecules break down to relatively smaller and simpler gas, liquid and solid molecules. Additionally, biomass pyrolysis is most often performed in a lower temperature range (300°C to 650°C) compared to gasification (800°C – 1000°C) [2].

The pyrolysis process involves the heating of biomass or any other fuel with a certain heating rate, in the total absence of air or oxygen, to a maximum final temperature (pyrolysis temperature) and its stabilization there for a certain time interval. The nature of pyrolysis products depends on various factors, which include the biomass type, the pyrolysis temperature, the heating rate and the residence time. The main phenomena occurring during pyrolysis are [7]:

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- Heat transfer from a source to the fuel, in order to increase its temperature and to remove any moisture present.
- Initiation of the main pyrolysis reactions at the final temperature, which leads to volatiles release and the production of char.
- The flow of hot volatiles towards the less hot solids, leads to heat transfer between those volatiles and the part of the fuel which has not been pyrolysed yet.
- Condensation of some volatiles in cold fuel pieces, followed by secondary reaction can lead to tar formation.
- Autocatalytic secondary pyrolysis reactions take place while primary pyrolysis reactions occur at the same time in competition.
- Further thermal decomposition can also occur, as well as reforming, water gas shift reaction, radicals recombination and dehydrations. These are influenced mainly by the processes' residence time, temperature and pressure profile.

Initial pyrolysis products comprise of condensable gases and char. Condensable gases can break down further into non – condensable gases (CO, CO₂, H₂ and CH₄), liquids and more char. This decay occurs mainly through homogeneous gas – phase reactions and partly through heterogeneous thermal gas – solid phase reactions. In gas – phase reactions, condensable vapour breaks down to smaller non – condensable permanent gases molecules (CO, CO₂, etc.). Generally, the pyrolysis process can be described by the following reaction [2]:



In Figure 5, a simplified pyrolysis reactor unit is presented. Biomass is fed into the pyrolysis chamber which includes hot solids (fluidized bed) where degradation is initiated. Condensable and non – condensable gas released leave the chamber, while the char produced partly remains in the chamber and partly in the gas as aerosols. Gas is separated from the char and is cooled downstream of the reactor. Condensable gas is liquefied into bio – oil or pyrolysis oil, whereas non – condensable gas exits the condenser as product gas. This gas can be fired in a burner in order to produce heat for the pyrolysis, or to be used in other applications. Likewise, the char can be exploited commercially or fired in a different chamber for heat production. Since the gas does not contain oxygen it can be re – circulated in the pyrolysis chamber as a heat carrier or as a fluidization medium [2].

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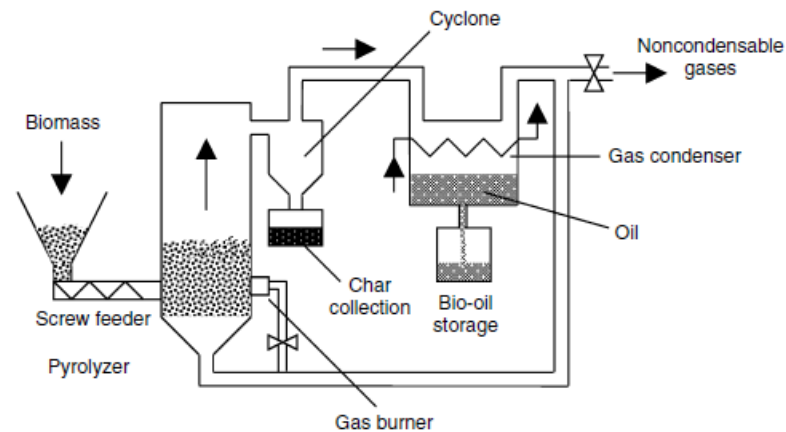


Figure 5: Simplified layout of a pyrolysis unit [2].

1.2.1 Pyrolysis products

As it was mentioned before, pyrolysis leads to the degradation of big molecule complexes into much smaller molecules. The products of this process can be divided into three categories which are presented below.

1.2.1.1 Solid Product

The solid product yield of pyrolysis is char and it constitutes mainly of carbon which can reach a mass based content of up to 85% and it contains lesser amounts of oxygen and hydrogen. Depending on the pyrolysis (final) temperature, the char fraction contains inorganic material and in some cases unconverted organic solids and carbonaceous residues derived from the thermal degradation of organic components. In comparison with fossil fuels, biomass derived fuels usually contain much less inorganic matter (ash), a fact that, along with other reasons to be mentioned later on, leads to lower solid pyrolysis yield in comparison. It should also be mentioned that the lower heating value of biomass char (32 MJ/kg) is significantly higher than that of the parent biomass or its liquid product [2]. Generally, the heating value of pyrolysis char is comparable to the ones of lignite and coke. Furthermore, it can be used in the preparation process of activated carbon, due to its porous structure and its appropriate surface area [8].

The amount and type of inorganic compounds in the final product are very important aspects in biomass applications. The main constituents of ash in biomass feedstocks are potassium, calcium, sodium, silicon, phosphorus and chlorine. The ash content –both in terms of amount and elemental composition- of biomass depends highly on the kind that is investigated. Normally, in softwoods it is less than 1% while in herbaceous biomass and agricultural residues ash can be found in percentages as high as 15%. During pyrolysis, those constituents and especially potassium and calcium can catalyse biomass degradation and promote char – reforming reactions. The char formed through these reactions can end up in the liquid product and make it problematic for installations like steam boilers, diesel engines or turbines, as the release of ash and alkali metals can hinder their operation [9].

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1.3.1.2 Liquid Product

The liquid product of pyrolysis, or bio – oil is a dark brown, free flowing organic liquid that is comprised of highly oxygenated compounds. Other terms used to describe bio – oil are the following ones: pyrolysis oil, pyrolysis liquid, pyroligneous acid, liquid wood, etc. Pyrolysis liquids are formed through the rapid and simultaneous depolymerisation and fragmentation of cellulose, hemicellulose and lignin caused by a rapid temperature increase. The subsequent quenching freezes in the intermediate products of this fast degradation and traps the products that could react further if the residence time in high temperatures was sufficient. Bio – oil is a mixture of water, guaiacols, catecols, syringols, vanillins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid and other carboxylic acids. Additionally, hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics are also contained in its composition [7]. The properties of bio – oils are significantly different than the ones of petroleum – derived oils, since their chemical composition also differ. Generally, bio – oils are multicomponent mixtures comprised of molecules with different sizes, which originate from depolymerisation and fragmentation reactions of cellulose, hemicellulose and lignin. Consequently, the elemental composition of bio – oils is similar to the parent biomass [10]. According to Mohan, et al. [7], oligomeric species in bio – oil, that are formed as part of the aerosols originate mainly from lignin and partially from cellulose. To conclude the description of bio – oil composition, it can be stated that it is a microemulsion where the continuous phase is an aqueous solution of holocellulose decomposition products and small molecules derived from the decomposition of lignin. The continuous liquid phase stabilizes a discontinuous phase mainly constituted out of pyrolytic lignin macromolecules.

The lower heating value (LHV) of bio – oil ranges from 13 to 18 MJ/kg (wet basis), while the parent biomass's values are lower and specifically in the region of 19.5 to 21 MJ/kg (dry basis) [2]. The biomass derived oils can be used as fuel oil substitutes, as it is indicated from tests that show that their combustion in standard or slightly modified boilers and engines is effective even in rates close to those of commercial fuels. Nevertheless, problems arise due to their high water content which hinders ignition and the presence of organic acids that are corrosive for most of the materials currently used in such installations. Furthermore, char that is still contained in the liquid yield can lead to blockage of injectors and erosion of turbine blades. Additionally, it should be noted, that bio – oil aging leads to the formation of larger molecules. This increases the viscosity of the liquid and therefore lowers the rate of combustion. Finally, the high oxygen content of bio – oil makes it acidic, unstable, immiscible with oil and also reduces its lower heating value [11]. Consequently, upgrading of bio – oil is necessary in order to successfully employ them in such processes. Oxygen containing functional groups are removed through processes like HDO and zeolite cracking [11]. In general techniques like hydrodeoxygenation, catalytic cracking of pyrolysis vapours, emulsification and steam reforming are used for the stabilization and upgrading of bio – oil [12]. Except from their use as fuels, bio – oils can be used for chemicals synthesis, glues, fertilizers, etc. [8]. Regarding the last, proposals exist that bio – oils can be converted to nitrogen slow – release fertilisers by reaction with nitrogen sources like ammonia, urea and proteinaceous materials like manure. In this modified form bio – oil is not hazardous for soil micro – organisms [13]. In particular, this method has been already patented [14] and it involves the chemical combination (through mixing and heating between 60°C and 150°C) of biomass pyrolysis liquid products and nitrogen compounds containing a –NH₂ group for the formation of an organic nitrogen compound. These compounds polymerize and solidify upon heating to produce stable, nitrogen releasing products.

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1.3.1.3 Gaseous Product

As it was mentioned previously, the primary decomposition of biomass leads to the formation of condensable (vapour) and non – condensable gases (primary gas). The vapours, constituted out of heavier molecules, can be condensed by cooling and included in the liquid pyrolysis yield. The same does not apply for the non – condensable (permanent) gases, which include low molecular weight gases (CO_2 , CO , CH_4 , C_2H_6 , C_2H_4 , etc.) [2]. Additional amounts of non – condensable gases can be formed through secondary reactions which take place in the vapour phase, or between vapour and solid phase. As it can be easily understood, this leads to a reduction of the liquid yield of the process. The secondary reactions that are important in pyrolysis are cracking, reforming and the water – gas shift reaction ($\text{H}_2\text{O} + \text{CO} \leftrightarrow \text{H}_2 + \text{CO}_2$) which take place at temperatures higher than 973K and lower than 1083K respectively. The main limitations for the occurrence of those reactions are low temperatures (below 923K), small residence times of gases and vapours (roughly below 2s) and the quick separation of char. In commercial pyrolysis process conditions, reactions like reforming, carbon – steam and carbon – carbon dioxide conversions are negligible [15]. According to Basu [2], the lower heating value of primary gases is around $11\text{MJ}/\text{Nm}^3$ and the one of secondary gases is much higher ($20\text{MJ}/\text{Nm}^3$). It should be mentioned, that primary reactions include the depolymerisation of the basic biomass constituents (hemicellulose, cellulose, lignin). The volatile species formed (vapors and aerosols) can undergo secondary reactions with the nascent char along their diffusion path out of the particle (intraparticle), with other particles (interparticle) or in the vapour phase (homogeneous vapour – phase reactions) [16]. Generally, the heating value of pyrolysis gases is comparable to those of producer gas or coal gas, but it is much lower than that of natural gas [8].

1.2.2 Types of pyrolysis

1.2.2.1 Flash pyrolysis

In flash pyrolysis, biomass is heated rapidly ($>1000^\circ\text{C}/\text{s}$ [17]) in the absence of oxygen to a relatively medium temperature range between 450°C and 600°C . The product which contains condensable and non – condensable gases is removed after a short residence time (30 to 1500ms). After the cooling, the vapour is condensed to bio – oil. The difference between this process and fast pyrolysis lies in the shorter residence time of the gases in the present case and less in the heating rate. Usually, the amount of bio – oil produced by flash pyrolysis processes can reach to 70 – 75% of the total pyrolysis yield [2]. Nevertheless, this process has certain technical limitations, some of them being the bad thermal stability and corrosiveness of the oil, the increase of viscosity through time due to char catalytic action, the dissolution of alkali concentrated in the char in the oil and finally the production of pyrolytic water [17].

Ultra – Rapid pyrolysis can be viewed as a kind of flash pyrolysis. This process involves the rapid mixing of biomass with a heated solid, which leads to very high heat transfer rates and consequently to a very high heating rate. Subsequently, the main product of the pyrolysis is rapidly cooled down within the reactor. Afterwards, the hot solids are separated from the main product which is constituted from non – condensable gases and vapours. The hot solids are then returned to the mixer by a non – oxidizing gas (mainly nitrogen), while the gases and the vapours are heated to a separate reactor. In order to achieve a high efficiency process the short – uniform residence time need to be precisely controlled. It should also be noted, that for maximum gaseous yield a pyrolysis

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temperature of 1000°C is required, while for liquids the corresponding temperature is roughly 650°C [2].

1.2.2.2 Fast pyrolysis

Fast pyrolysis takes place in a time interval of a few seconds, or even less. Therefore, apart from the chemical reaction kinetics, also heat and mass transfer phenomena heavily influence the process. The most critical issue is to achieve optimal process temperature and minimization of the exposure of biomass particles to intermediate – lower temperatures that lead to charcoal formation. A possible route to achieve this goal is the use of small particles. Other methods are focused on the fast transfer of heat only to the particle surface that comes to contact with the heat source (ablative processes) [18].

During fast pyrolysis biomass decomposes and produces mainly vapours, aerosols and partially charcoal. After the subsequent cooling and condensation, bio – oil is formed with a heating value almost half of that of conventional fuel oil. Despite the fact that this process is similar to traditional pyrolysis processes for charcoal production, fast pyrolysis controlled parameters are chosen carefully in order to maximize liquid yield. In the following lines the typical process of fast pyrolysis is described [18].

- Very high heating (1000 to 10000°C/s [2]) and heat transfer rates at the reaction interface. In order to achieve this, finely ground biomass feed is required.
- The pyrolysis temperature needs to be approximately 500°C, while the vapour phase temperature should be in the area of 400 to 450°C.
- The residence time of vapour should be short, typically less than 2 seconds.
- In order to achieve maximum bio – oil product the pyrolysis vapours need to be cooled down rapidly.

A typical bio – oil yield is in the region of 75% wt. on dry feed basis. In this, also the by – product char and gas are included, since they are used within the process. The only waste streams of the process are the flue gases and ash. Furthermore, it should be noted that in fast pyrolysis the feed needs to be dried to less than 10% water [18]. The reason for that is that the amount of water in the bio – oil should be low, although a percentage up to 15% can be acceptable. Additionally, as it was mentioned before, the feed should be grinded to ensure sufficiently small particle size (roughly 2mm for fluid bed reactors). Finally, separation of solids (char) from the liquid product is also necessary [18].

1.2.2.3 Slow pyrolysis

Carbonization is a slow pyrolysis process, that has as a goal the production of charcoal or char and it is the oldest pyrolysis method since it has been employed for thousands of years. Biomass is heated slowly (heating rates below 100°C/min [19, 20]), in the absence of oxygen, at relatively low temperatures (roughly 400°C) for a significant time period. This extended time period allows the condensable vapour to be converted into char and non – condensable gases [2].

On the other hand, conventional (slow) pyrolysis includes all three types of pyrolysis products (gas, liquid and solid). In this process, the biomass is heated at a slow rate up to a final temperature of roughly 600°C. The vapours' residence time is long (5 to 30 minutes). This way the

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components that are in the vapour phase continue to react with each other, which lead to the formation of solid residues and liquids [10]. Nevertheless, slow pyrolysis has certain technical limitations that render its employment for fine quality bio – oil production difficult. The cracking of the main product due to the long residence time can reduce the quantity and the quality of the produced bio – oil. Furthermore, the long residence time and the low heat transfer rate increase the energy demanded for the process [21, 22].

1.2.2.4 Pyrolysis in the presence of a medium

In this category we find two pyrolysis methods, namely hydropyrolysis and hydrous pyrolysis, which are presented in the following paragraphs.

In hydropyrolysis, the thermal decomposition of biomass takes place in an environment containing hydrogen under high pressure. This process can increase the amount of volatiles produced as well as the percentage of low molecular weight hydrocarbons [23]. Hydropyrolysis is different from hydrogasification of char and the greater amount of volatiles produced can be attributed to the hydrogenation of free radical fragments. Those fragments can repolymerize and form char, but before that they are stabilized through this process [2].

Hydrous pyrolysis (hydrothermal treatment) is the thermal cracking of biomass in the presence of high temperature water. The first stage of this process takes place in pressurized water at a temperature range between 200 and 300°C. In the second stage, the produced hydrocarbons break down to lighter ones at 500°C. a significant drawback of this process is that in contrast with hydropyrolysis, a high amount of oxygen is included in the final product [2].

1.2.3 Pyrolysis end product

Pyrolysis end product is highly dependent of the following factors [2]:

- Biomass composition
- Presence of mineral catalysts
- The pyrolysis unit and in particular the following factors
 - o Heating rate
 - o Pyrolysis (final) temperature
 - o Residence time in the reaction zone
 - o Pressure
 - o Ambient gas composition

Some of those factors and their effect on the pyrolysis yield are examined in this chapter.

1.2.3.1 Effect of biomass composition – particle size

According to Di Blasi [24], for low heating rates at moderate temperatures the following temperature ranges for the decomposition of each components are given. Furthermore, in Figure 6 an example of the decomposition behaviour of each compound is given by means of a multi – component devolatilization mechanism modelling attempt based on TGA findings.

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- Hemicellulose: 225 – 325°C
- Cellulose: 325 – 375°C
- Lignin: 250 – 500°C

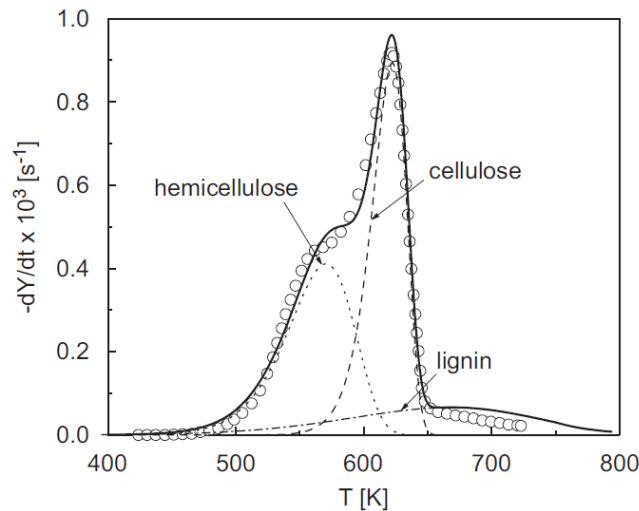


Figure 6: Observed (symbols) and simulated (solid line) differential curves for beech wood heated at 5 K/min. The various style lines show the predicted volatile evolution from the three components [24].

The same author claims that as the heating rate is increased, due to the narrow range corresponding to each component's degradation the different peaks tend to merge. The differences in the thermal behaviours of the biomass components are attributed to the differences in their chemical structure. Hemicellulose is the least thermally stable component due to its amorphous nature, while cellulose has this thermal behaviour due to its strong intra – molecular bonds. Lignin is a complex, highly branched and heavily cross – linked polymer and therefore is more thermally stable compared to the other two components [25, 26]. Generally, bio – oil is mainly derived from cellulose, while the char and aromatics mainly come from lignin. This is also proved by its composition which is really similar to the one of lignin [17]. Nevertheless, according to Mohan et al. [7], the pyrolysis of lignin yields phenols via the cleavage of ether and carbon – carbon linkages. Cellulose pyrolyzes mainly to levoglucosan, which above 500°C vaporizes contributing almost exclusively to the gas and liquid yields [27]. Hemicellulose contributes mainly to volatile production, especially non – condensable gases, while it yields less tars and char than cellulose [7]. Additionally, most of the acetic acid produced during pyrolysis can be attributed to the decomposition of hemicellulose [7].

Apart from the composition of biomass, its size, shape and structure influence the pyrolysis process as well, mainly due to their effect on the heating rate. The thermal conductivity of biomass is particularly low, namely 0.1W/mK along the grain and circa 0.05W/mK cross grain. Therefore, mainly gas – solid heat transfer takes place, something that means that the biomass particles need to be really small in order to ensure rapid heating and consequently high liquid yields. Temperature increases in the area of 10000°C/s are possible within the thin reaction layer but such temperature gradients are unlikely throughout the whole particle. Generally, when particle size increases, secondary reactions within the particle become more significant, as the escape of primary pyrolysis products becomes more difficult [13]. Consequently, smaller biomass particles favour liquid production whereas the opposite applies for char production [28].

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1.2.3.2 Effect of pyrolysis temperature

As it was already mentioned before, during pyrolysis the biomass particles are heated under a predetermined heating rate, from ambient temperature to a final temperature (pyrolysis temperature). As it can be easily understood, the pyrolysis temperature influences heavily the nature, the composition and the quantity of the pyrolysis final product.

The only way to determine the influence of the pyrolysis temperature on the final product is by examining it under constant heating rate, as it influences the procedure significantly. Generally, by increasing the pyrolysis temperature the amount of produced char is decreased and the amount of the produced gas and liquid is increased (Figure 7) [28, 29]. However, when exceeding a certain temperature the liquid yield starts decreasing again. Furthermore, as it will be presented later in the results section of this thesis the effect of pyrolysis temperature is also very significant for the composition of the gas products and the amount and nature of the tar products.

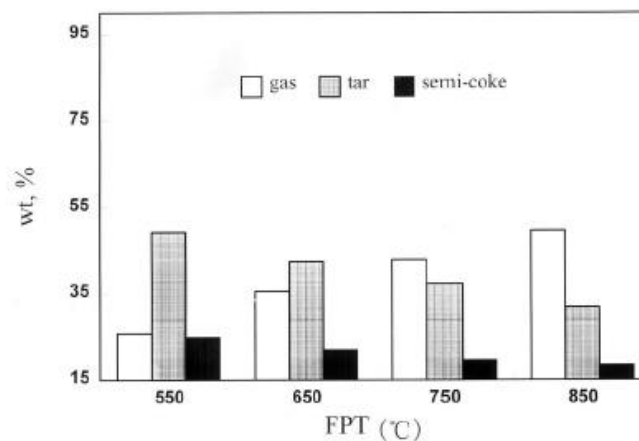


Figure 7: Influence of final pyrolysis temperature (FPT) on pyrolysis product yields of wood chips in a rotary kiln. The char yield is mentioned as semi – coke in this figure [29].

1.2.3.3 Effect of heating rate

The heating rate of biomass particles influences strongly the amount and the composition of the final product. Pyrolysis reactions take place over a broad temperature range and therefore the early products of this process go through further decomposition and transformation through a series of consecutive reactions. The rapid heating of biomass tends to limit those secondary reactions, leading to the increase of the volatiles yield and therefore to the increase of the liquid and gaseous product. The opposite occurs for the char in this case. Nevertheless, the heating rate cannot determine the final product irrespectively of the rest of the experimental conditions. Through the combined effect of those factors (pyrolysis temperature, residence time and heating rate) the following conclusions can be derived [2]:

- Liquid product is favoured by small particles pyrolysis, under a fast heating rate to moderate pyrolysis temperatures (450 – 600°C) and short gas residence time.

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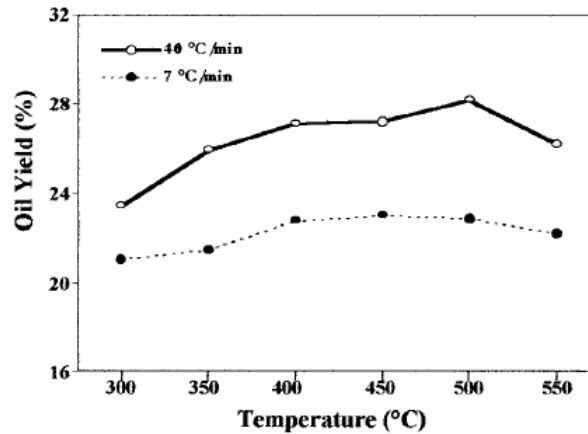


Figure 8: Effect of heating rate on the liquid (oil) yield of pine chips pyrolysis at various final temperatures [30].

- Char production is favoured by the pyrolysis of larger particles, under slow heating rates to low final temperatures and long gas residence time.

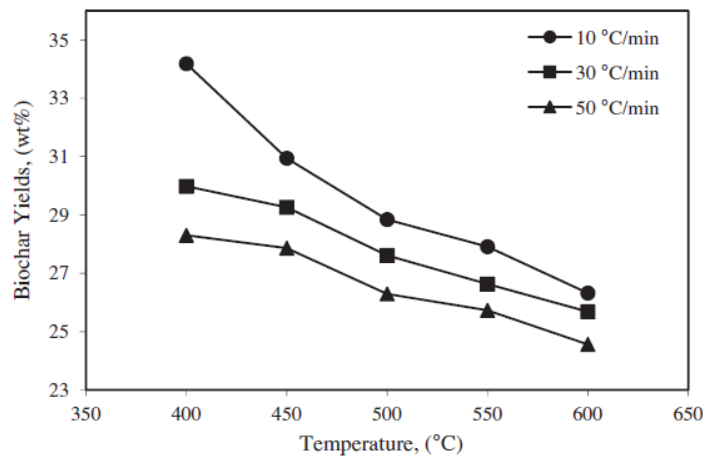


Figure 9: Effect of pyrolysis final temperature and its heating rate on the char yield of safflower seed cake pyrolysis in a fixed bed reactor [31].

- In order to maximize gas production, slow heating rates are needed to a high final temperature (700 – 900°C) and a long gas residence time.

1.3 Fundamentals of torrefaction

Torrefaction is a mild pyrolysis process carried out typically in a temperature range of 230°C to 300°C in the absence of an oxidizing agent. It is a method of thermal pretreatment of biomass which can improve the material's energy density while reducing its oxygen to carbon (O/C) and H/C ratios and its hygroscopic nature. During torrefaction, the biomass material dries and devolatilizes partially, which leads to a mass reduction while the energy content is largely preserved. Mainly water (H₂O) and CO₂ are removed from the material. This leads to two very significant results regarding the properties of the new material. Firstly, thermodynamic losses are reduced due to the lower oxygen content and secondly the relative carbon content of the biomass is increased [32]. As it was reported by [33], usually 70% of the initial biomass mass is retained after torrefaction, while up to 90% of the initial energy content can be retained, depending on the feedstock. This means that

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the torrefaction process offers a high transition of the chemical energy of the feedstock and in the same time the fuels properties are improved.

The components of biomass that are more easily combustible, mainly hemicelluloses, are the ones that decompose first, through carbonization and devolatilization. Consequently, the weight loss during torrefaction is because of the reaction of hemicellulose mainly and extractives (e.g. resins, fats and fatty acids) at a lesser extent. On the other hand lignin and cellulose decomposition is very limited compared to hemicelluloses but their overall chemical structure is altered by this thermal treatment [16, 34]. This particular behaviour can be also observed in Figure 10 which presents the evolution of the mass loss rate during the combustion of raw and torrefied wood biomass (Eucalyptus) through thermogravimetric (TGA) analysis at different temperatures. This curve presents a shoulder and two peaks in the case of raw biomass (RE). This shoulder can be attributed to the decomposition of hemicellulose components. The fact that this shoulder is not evident in the case of the torrefied biomass samples (TRE-1 at 240, 260 and 280°C) further supports the conclusions derived above [35].

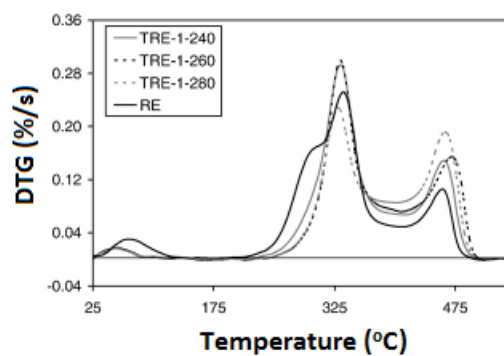


Figure 10: Mass loss rate for raw (RE) and torrefied (TRE-1) eucalyptus combustion from TGA in a thermobalance under a constant heating rate of 15°C/min [35].

Generally, hemicellulose decomposes between 225°C and 325°C, which corresponds well to the temperatures realized during torrefaction. The largest part of the hemicellulose content of biomass is devolatilized in this temperature range (Figure 11). Lignin, which as it was mentioned earlier is the binder component of biomass, starts to decompose above its glass – softening temperature which is around 130°C. This behaviour enhances the densification of torrefied biomass. On the other hand the decomposition of cellulose starts at temperatures higher than 250°C [32]. Furthermore, at temperatures below 160°C moisture (H₂O) and CO₂ are released [36, 37]. These two products do not add to the total energy of the product gas, but they constitute a considerable portion of it in terms of mass. At temperatures above 180°C, the reaction becomes exothermic and gases with small heating values are released. Until 250°C hemicellulose is depolymerized and carbonized, a process which causes the polysugar structures to alter and to be rearranged. Lignin and cellulose are also partially decomposed, but at a much lower extent, with simultaneous chemical changes in their structures which however do not lead to significant mass loss. At temperatures between 250 and 300°C the main part of carbonization takes place. In this temperature regime hemicellulose decomposes into volatiles and a char – like solid product. Lignin and cellulose also devolatilize and carbonize within this regime, but to a much lower extent [38].

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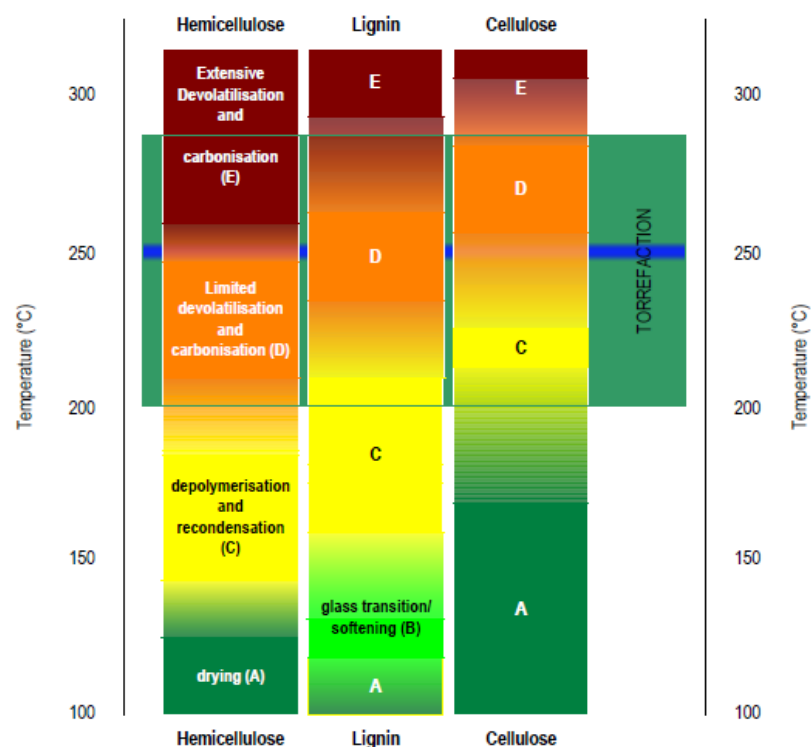


Figure 11: Stages of torrefaction of lignocellulosic biomass materials [38]

Park, et al [39] investigated the transformation of loblolly pine, which can be categorized as a softwood, during torrefaction. They concluded that the volatile matter release can be attributed mostly to the release of hydrocarbons and especially hemicellulose. Furthermore, in agreement with other authors too [35, 40], they reported an increase in fixed carbon content with the increase in torrefaction degree, which was naturally accompanied by a decrease in oxygen content. Those changes in the elemental analysis showed that torrefied biomass can be compared to lignite in the Van Krevelen diagram and in terms of heating value [39]. Generally, during torrefaction more oxygen and hydrogen are lost than carbon, which leads to the decrease of the H/C and O/C ratios. At this point it should be mentioned that torrefaction should not be considered the same process as carbonisation. Carbonisation takes place at much higher temperatures and yields charcoal with considerably lower H/C and O/C ratios [32].

Another interesting derivation from [39] was that the amount of solid residues after acid hydrolysis treatment of the biomass, showed an increased amount of lignin, which might indicate the formation of condensed structures into thermally modified products. More specifically, it was argued that the cleavage of ether bonds in lignin and the condensation of lignin by linking carbons directly are favoured by thermal treatment. Additionally, the modification of lignin was associated with the extent of demethoxylation, as it was claimed to be able to generate additional reactive sites and lead to higher amounts of condensed lignin during thermal modification. Such a claim was also made earlier by [41]. Nevertheless, the increased amount of acid – insoluble residues can be also attributed to carbohydrate fractions in lignocellulosic biomass. Finally, it was found that those condensed solid products generated during the early stages of torrefaction were mainly of aromatic structure at least until some point during the process. This attribute of the torrefied biomass can be linked to its increased hydrophobicity.

The choice of the torrefaction conditions (i.e. temperature and residence time) depend on the kind of biomass input and on the desired application for the end product. The torrefied biomass

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attributes are influenced in a different way by variations of those operating parameters. Regarding the proximate analysis, as it was investigated by [42], the moisture and volatile matter decrease for an increase in the torrefaction temperature and residence time respectively. On the other hand, the ash and fixed carbon content increase with increasing temperature but they decrease for increasing residence time. Furthermore, the mass and energy yields decrease when the torrefaction temperature and residence time increase, with the effect of temperature being more evident than that of residence time. This can be attributed to the decrease of the moisture and volatile content of the biomass. Concerning the energy density of the torrefied biomass, it is generally higher compared to untreated biomass. This is due to the loss during this process of water vapour and carbon dioxide, which have a lower heating value of zero. Therefore more mass is lost than energy. The energy density increases with temperature as it was reported by [42, 43], while both these teams of authors reported that while it was expected that energy density would also increase for higher residence times, the effect of these parameter was negligible in the final product. Finally, according to [38] the H/C and O/C ratios of torrefied biomass become lower with increasing reaction temperature and residence time.

A mean to evaluate the torrefaction process is the degree of torrefaction, which can be calculated by dividing the released volatiles by the initial volatile content of the raw material on dry-ash free basis [40]. In this study, the pyrolysis of torrefied palm kernel shell was studied. This group of authors claim that the release rate of oxygen is faster compared to carbons as the torrefaction degree increases. Experimental work showed that the amount of released volatiles drops linearly to the degree of torrefaction, under a constant residence time, which means that the reactivity of biomass is reduced by torrefaction. Regarding gas species production, it was found that CO and H₂ were the main components of the released volatile matter, followed by CH₄ and CO₂ during high temperature devolatilization. For pyrolysis at a temperature below 550°C CO₂ and CO were dominating followed by a small quantity of CH₄. Of course, the amount of volatiles produced still depends on various other factors, such as the pyrolysis heating rate.

Generally, the effect of varying operational conditions of torrefaction (e.g. particle size, residence time, process temperature, heating rate) is rather inconclusive, as many trade – offs exist between them. For example, for lower residence times, a higher biomass throughput can be achieved, something that leads to lower operational costs. Nevertheless, such a process requires smaller particle sizes in order to achieve sufficient heat transfer. Furthermore, severe torrefaction can produce a torrefied product with very high energy density, though at the same time the efficiency of the system and the transportation chains becomes lower. Another example of such trade – offs, is the fact that for severely torrefied biomass, additional binding materials may be required [34]. In the same study, Table 1 is included, according to which mild torrefaction presents the best option regarding the degree of torrefaction. Severe torrefaction yields an end material with high heating value but is not cost effective. On the other hand, light torrefaction does not lead to adequate improvement of the biomass characteristics.

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Table 1: Effect of torrefaction severity on biomass properties [34]. This table is adapted from [44] and is derived from the investigation of bamboo wood torrefied at 245°C (light), 255°C (mild) and 265°C (severe) in regards to the mentioned properties.

Attribute	Degree of torrefaction		
	Light	Mild	Severe
Densification effort	++	-	-
Grindability of biomass	-	++	+++
Self-heating	+++	+	-
Heating value	-	++	+++
Reactivity	+++	+	-
Cost of production	+++	++	-

1.3.1 Advantages of torrefaction

One of the most significant advantages of torrefaction is that it improves the lower heating value of the biomass fuel. As it was mentioned above, biomass loses relatively more oxygen and hydrogen than carbon. This leads to an increase of its calorific value. According to [38], depending on the torrefaction conditions the LHV can be between 18 and 23 MJ/kg and the HHV (dry basis) between 20 and 24 MJ/kg. It should be mentioned that LHV_{dry} of coal is 25 – 30 MJ/kg, for charcoal around 30 MJ/kg and for untreated wood 17 – 19 MJ/kg.

One of the most important characteristics of torrefied biomass is its higher grindability compared to untreated biomass. Through torrefaction the physical characteristics of biomass are improved as it loses its tenacious nature and partly its fibrous structure. Grinding energy requirements are reduced, the co-gasification process is improved as well as the biomass energy supply chains [33, 34]. More specifically, raw biomass is composed out of large particles and fibres that give it a highly fibrous nature. The fact that the fibres form links between the particles, understandingly makes the handling of raw biomass difficult. Through torrefaction though, the particle size decreases and the fibres mostly disappear. This decrease in particle size corresponds to the rise in temperature and the increase of residence time, of the torrefaction process. This transformation that biomass undergoes through this process, actually leads to more spherical particles. Consequently, through torrefaction the grindability of biomass can be improved along with its handling characteristics and its ability to flow through tubes [35]. Those improvements facilitate the co – firing of biomass in pulverized coal fired boilers or its gasification in entrained flow reactors [32].

Another advantage of torrefied biomass is its increased hydrophobicity and decreased biological activity. Hemicellulose, which is considered as the most hydrophilic compound in the biomass structure decomposes during the torrefaction process [16]. After being torrefied biomass is almost completely dried (1 – 6% moisture), but also the uptake of moisture is very limited. The hygroscopic property of biomass is lost to a great extent during torrefaction because of the destruction of OH groups during dehydration. This largely prevents the formation of hydrogen bonds [32, 38]. Additionally, unsaturated – non – polar structures are formed, causing the material to become hydrophobic. This leads to a reduction of its biological activity, which means that it can be preserved for longer times compared to untreated biomass [38]. Generally, due to the sustained high temperature torrefied biomass is sterilized. This, along with the increased hydrophobicity and the removal of monosaccharides and hemicelluloses prevent the appearance of fungi when the feedstock is in storage. Furthermore, the loss of solid matter limits biochemically induced self –

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heating of stored feedstock. Consequently, torrefied biomass presents improved storage properties which can lead to significant cost reductions compared to untreated biomass [16].

Regarding fast pyrolysis bio-oil production, biomass feedstocks with lower oxygen content, result in oil containing a lower oxygen content that is more stable than the oil derived from conventional pyrolysis feedstocks. Such a property leads to easier storage, transportation and upgrading to commercial vehicle fuel [45]. Moreover, the produced pyrolysis oils were claimed to be less acidic and of higher energy content than those that were produced through one stage fast pyrolysis. On the other hand, it was observed that an increased degree of torrefaction leads to a decrease of the pyrolysis oils yield and energy recovery from them. The same authors claim that sugar content is lost in the torrefaction process, something that renders it as a poor pretreatment method for biofuel production through biochemical methods. More information regarding this subject will be presented along with the experimental results of this work.

1.4 Tars

1.4.1 Basics and classification

Tar is a mostly unavoidable by – product of thermal conversion processes. Tar is a thick, black, highly viscous liquid that condenses in the low – temperature zones of a gasifier, creating obstacles in the smooth operation of the system. Among the problems that arise by the appearance of tars are the plugging of downstream equipment caused by their condensation, formation of aerosols and their polymerization into more complex structures. Tar is a complex mixture of condensable hydrocarbons, including oxygen – containing 1 to 5 – ring aromatic and complex polyaromatic hydrocarbons. Generally, the components of products derived by thermal conversion with a molecular weight higher than benzene are identified as tars [32]. Among the numerous definitions available in the literature, in this study the one of [46] will be used together with the one mentioned before: ‘The organics produced under thermal or partial – oxidation regimes of any organic materials are called tars and are generally assumed to be largely aromatic. Finally, it should be mentioned that according to the European tar measurement standard definition [47], tar is “*a generic (unspecific) term for entity of all organic compounds present in the gasification product gas excluding gaseous hydrocarbons (C1 through C6)*”.

The presence of tars is considered as a major obstacle in gasification processes operation mainly because their condensation in exit pipes and on particulate filters can lead to blockages and clogged filters [48]. Their condensation on gas – cleaning equipment fouls it and the liquid tar droplets entering prime movers have a very negative impact on the operation of these end – use applications of syngas. Furthermore, the effect of tars in wastewater management is also negative. When a water based method is used for gas cleaning, the mixing of water and tars, leads to a significant water treatment problem. The main reason for that is the poisoning behaviour of some tar components (e.g. phenol) in biological wastewater treatment systems [49]. Additionally, the quality and usability of the product gas derived from biomass gasification is greatly influenced by tars. In direct – combustion systems, since the gas is fired while it is still hot, the tar related problems appear in the pipeline between the gasifier exit and the burner inlet. Tar depositions can block the pipes, leading to hazardous conditions and the flue gas produced after combustion can contain pollutants. In internal – combustion engines, where the gas is cooled before usage, condensation of the tars can occur in the engine or in the fuel injection systems. Moreover,

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problems can arise with the piston – cylinder system which is not designed for solid handling. Regarding gas turbines, the limits of allowed tar concentration are even lower, as their blades are very sensitive to deposits from the gas. Moving over to syngas applications, tar is also unwanted as it poisons the catalyst [32].

Generally, tar leads to fouling when the product gas becomes over – saturated with it, leading to aerosol formation and depositions in various places in the installation. At this point it should be noted that fouling phenomena do not appear when the tar is in the gas phase but when it condenses. It is widely perceived, that tar related problems are not connected that much with tar quantity, but with its properties and composition. The condensation of tar is affected by each and every one of its components, as the all contribute to the total vapour pressure of it. When the saturation pressure is exceeded the tar becomes over – saturated according to Raoult's law. Thus, the saturated vapour is condensed. Consequently, the tar dew point (the temperature at which the total partial pressure of tar is equal to its saturation pressure) is of major importance regarding tar handling [50].

Tar is produced primarily through depolymerisation during the pyrolysis stage of gasification [32]. Their formation is highly dependent on reaction conditions. At high temperature regimes, secondary reactions take place in the gas phase converting oxygenated tar compounds to light hydrocarbons, aromatics, oxygenates and olefins before forming higher hydrocarbons and larger PAH [50]. Elliot, after reviewing the composition of biomass pyrolysis and gasification tars from experiments performed at various temperatures, proposed the scheme presented in Figure 12 as the transition path from primary products to finally aromatic hydrocarbons [51].

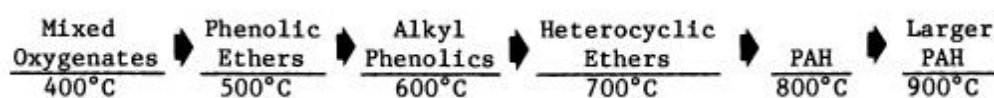


Figure 12: Tar maturation scheme as proposed by Elliot [51]

According to [46], a systematic approach to classify tars can be used to compare products from various pyrolysis or gasification reactors. The four major classes were identified as a result of gas – phase thermal cracking reactions:

- 1) Primary tars. In this class cellulose – derived products such as levoglucosan, hydroxyacetaldehyde and furfurals are included, along with analogous hemicellulose derived products and lignin derived methoxyphenols. Primary tars are produced during primary pyrolysis (200° – 500°C).
- 2) Secondary tars. This class is characterized by phenolics and olefins. According to [32] at temperatures higher than 500°C, primary tars start to rearrange, producing more non – condensable gases and heavier molecules which consist the secondary tars.
- 3) Alkyl tertiary tars. This class includes methyl derivatives of aromatics, such as methyl acenaphthylene, methylnaphthalene, toluene and indene.
- 4) Condensed tertiary tars. Here polycyclic aromatic hydrocarbons are included without substituents: benzene, naphthalene, acenaphthylene, anthracene/phenanthrene and pyrene.

It should be noted, that according to the authors [46], the primary and tertiary products are mutually exclusive, as the primary products are destroyed before the tertiary ones are formed. The

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latter can be derived from cellulose and lignin. Nevertheless, higher molecular weight aromatics can be formed faster from lignin – derived products. In Figure 13, the distribution of the four tar classes according to temperature is presented. From there it can be derived that at that high temperatures affect negatively primary tars but not the tertiary ones.

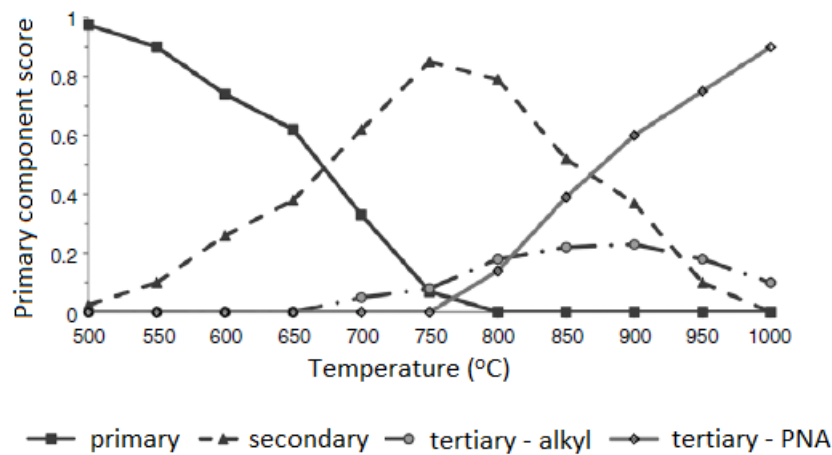


Figure 13: Effect of temperature on tar distribution produced from wood pyrolysis with a 300 ms residence time. Adapted from [46].

In [52] a different classification system is encountered, proposed by the authors in cooperation with the Energy research Centre of The Netherlands (ECN), Toegepast Natuurwetenschappelijk Onderzoek (TNO) and University of Twente (UT) within the framework of the project 'Primary measures for the inhibition /reduction of tars in biomass fuelled fluidised-bed gasifiers', funded by the Dutch Agency for Research in Sustainable Energy (SDE). This approach is based on the solubility and condensability of the tar compounds instead of their reactivity. According to this study, the following five tar classes can be identified:

- 1) GC – undetectable. This class includes very heavy tars that cannot be detected by GC.
- 2) Heterocyclic. Here, tars that contain hetero atoms are included along with highly water soluble compounds. Representative compounds are pyridine, phenol, cresols, quinoline, isoquinoline and dibenzophenol.
- 3) Light aromatic. This class is comprised usually by light hydrocarbons with a single ring. These compounds do not pose problems regarding condensability and solubility. Representative compounds are toluene, ethylbenzene, xylenes and styrene.
- 4) Light polyaromatic. This class includes two and three ring compounds. They condense at low temperatures and even at a very low concentration. Representative compounds are Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene and anthracene.
- 5) Heavy polyaromatic. This class includes larger than three ring compounds that condense at high temperatures at low concentrations. Representative compounds are fluoranthene, pyrene, chrysene, perylene and coronene.

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1.4.2 Phenol

In this chapter, some general information is given regarding the phenol tar specie. This specie is treated separately since only this was identified and quantified from the heterocyclic tar class.

Phenol is the parent substance of a homologous series of compounds containing a hydroxyl group which is bound directly to a carbon atom in a benzene ring. Since a hydroxyl group is included in its structure it belongs to the family of alcohols, constituting its simplest aromatic member. The OH group determines its acidity, while the benzene ring determines its basicity. A similar definition is also given by Milne, et al. in [46], where phenols are defined as aromatic hydrocarbons with at least one OH group (e.g., phenol, cresols). Generally, phenol has a low melting point, it can crystallize in colourless prisms and its odour is slightly pungent. When molten, it is a clear, colourless and mobile liquid. Phenol can be easily dissolved in most organic solvents (aromatic hydrocarbons, alcohols, etc.) and less easily in aliphatic hydrocarbons [53].

Lignin is a major source of phenolic compounds since it is composed of phenylpropane units which upon thermal degradation yield those compounds. The production of phenolic compounds from thermochemical conversion of biomass is favoured by small biomass particle size, low reactor residence time, low pressure and moderate pyrolysis temperature. The mainly occurring chemical reaction in the transformation of biomass to phenols is initiated by the dehydration of OH – groups in the alkyl chain of the lignin phenylpropane basic unit and is followed by the cleavage of interaromatic bonds, with the β -O-4 aryl ether bond being the most frequent linkage. Additional elimination of carbonyl entities in the alkyl side chain in the form of low molecular weight compounds (HCHO and CO) can also take place during this stage of thermal degradation [54].

1.4.3 PAH formation

According to Frenklach and Wang [55], aromatic rings grow by a sequential two – stage process. The first one is H – abstraction which leads to the activation of the aromatic molecules and the subsequent one is acetylene addition which propagates molecular growth and PAH cyclization (HACA sequence). More specifically, the abstraction of the hydrogen atom activates a singlet hydrocarbon molecule which produces a radical intermediate able to grow further through a reaction with acetylene. Higher PAH containing an extra aromatic ring can be derived from a ring closure reaction. Regarding the pyrolysis of hydrocarbon fuels, the authors claim that initially reactions of aromatic rings with species other than acetylene take place, but as the process progresses the HACA sequence becomes dominant. When stable molecules like pyrene or coronene are formed, the change in Gibb's free energy is so large that the reactions are practically irreversible. Consequently, the reaction sequence moves forward towards the formation of larger PAH molecules. Other acetylene addition steps are highly reversible though, like the reaction from phenanthrene to benzo[ghi]perylene and thus create a thermodynamic barrier to PAH growth.

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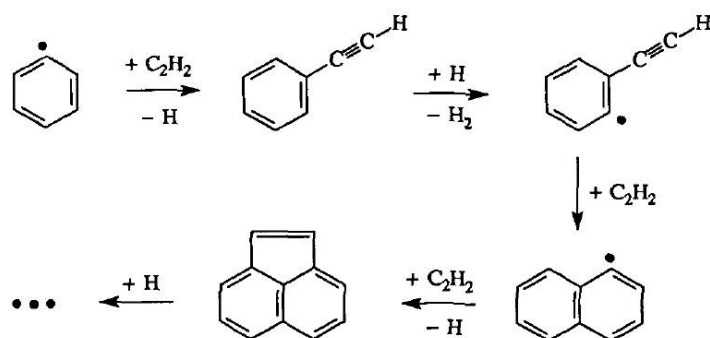


Figure 14: H – abstraction and C₂H₂ – addition reaction pathway of PAH growth according to the HACA sequence (Taken from [56])

At this point it should be mentioned that two alternative pathways of the HACA sequence regarding the sequential addition of two acetylene molecules exist. The first was presented by Frenklach, et al. [57, 58]. According to the authors, the distinctive feature of the probable reaction pathways is the transfer of the hydrogen atom between carbon atoms of the aromatic rings and those of the side chains. This migration plays a crucial role, because the reactant and the products can constitute intermediates of aromatic growth for hydrocarbons. As we see in Figure 15, in the forward direction, the hydrogen in ring position 2 is transferred to the radical site in the side chain, thus moving the radical vacancy to the ring. Consequently, the addition of acetylene to the radical site of the product can lead to the formation of another aromatic ring. Therefore, the second acetylene molecule adds to the activated aromatic ring. On the other hand a model proposed by Bittner and Howard in [59], proposes a different route, where the second acetylene molecule adds to the first one.

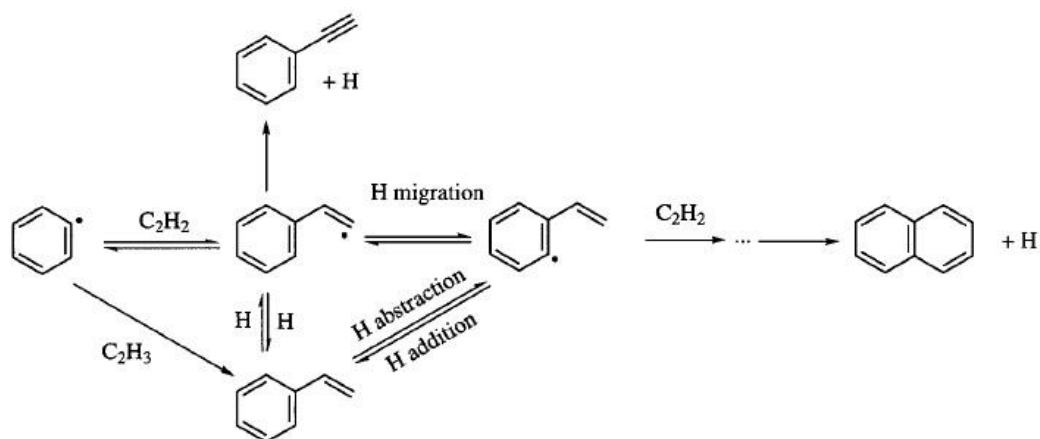


Figure 15: Reaction path diagram showing the role of H migration in the overall reaction path from phenyl to naphthalene, as proposed by Moriarty, et al. in [58].

An alternative scheme developed by Miller and Melius and described in [60] does not involve acetylene molecules at all. The researchers, through a series of flame experiments and kinetic modelling efforts, proposed several paths that lead to the formation of benzene and subsequently naphthalene formation. According to their findings, the first pathway that leads to benzene production is the self – reaction of propargyl radicals and the second the reaction of

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propargyl radicals with allyl radicals. Regarding naphthalene production, the two main paths involve resonantly stabilized radicals. These are the reaction of benzyl and propargyl radicals and the self – reaction of cyclopentadienyl radicals.

The third mechanism of PAH synthesis was proposed by Siegmann and Sattler and is described in [61]. This scheme does not include radical species in the description of the PAH growth process and the authors claim it to be the dominant route for PAH growth in methane combustion. According to their findings the acetylene molecule acts as a dienophil and effectively closes bay regions in such PAHs as biphenyl, phenanthrene, etc. This process takes place in two stages, the first being the cycloaddition of C_2H_2 to produce a Diels – Alder adduct. Subsequently, H_2 abstraction from the adduct takes place leading to a higher PAH. The authors claim that this process can explain the successive formation of more compact and pericondensed PAHs in methane combustion.

Finally, the work of Yu, et al. [62] links the process of PAH formation to the major biomass components (i.e., cellulose, hemicellulose and lignin). Through experimental work, they suggest that phenols and their derivatives are major lignin components. On the other hand BTEX and various other hydrocarbons along with PAHs are the major components for cellulose and hemicellulose. Furthermore, they observed that by increasing the temperature from 800 to 1000°C the amount of produced PAH increases for each of the three components. Nevertheless, in the case of lignin this due to the conversion of phenolic substances, while for cellulose and hemicellulose the further reaction of miscellaneous hydrocarbons and BTEX lead to the increase in PAH production. According to the authors two mechanisms for PAH generation exist, one with benzene as a precursor and another with phenol as the precursor. To begin with, for the first one, benzene is formed through a diene synthesis reaction taking place between the decomposition products of cellulose and hemicellulose, propylene and butadiene. Then, benzene generates bicyclic or polycyclic PAHs through the desorption of hydrogen atoms, the addition reaction of ethylene molecules or by the benzene ring condensation reaction of PAHs. When phenol is the precursor, the following process takes place. The ether bond in lignin breaks and phenol is formed under acidic conditions. Subsequently, a CO radical leaves the phenolic compounds, which results to the formation of cyclopentadiene. Almost simultaneously, through H abstraction of cyclopentadiene, a cyclopentadiene radical is formed which further combines to naphthyl. The latter gives an H atom and a relative radical is formed, which when combined with a cyclopentadiene radical forms higher than two rings aromatic compounds.

1.4.4 Tar removal and conversion

Tar derived by the thermal conversion of coal includes products like benzene, toluene, xylene and coal tar that have a high commercial value. On the other hand, the same does not apply for biomass derived tar which is highly oxygenated and of little commercial value. Consequently, a major focus of the researchers delving in the fields of biomass thermochemical conversion is on the development of efficient methods for tar removal in an economically feasible and efficient way. Moreover, it is very important that the method of tar removal employed, does not significantly affect the formation of useful products. The methods that are currently in use by researchers all over the world can be divided into two main categories: (1) in – situ or primary tar reduction which takes place inside the gasifier and prevents tar formation and (2) post – gasification or secondary reduction that takes place outside the gasifier [32, 63, 64].

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1.4.4.1 Primary methods for tar reduction

In – situ or primary methods are the measures taken in the gasification process to prevent the formation of tar in the gasifier, or to convert it. Ideally, the concept of in – situ methods completely eliminates the need for post – gasification treatments. Consequently, in order to obtain high quality exit gas, the gasifier's performance needs to be optimized. The most decisive factors in this direction are the proper selection of operating conditions, the use of suitable bed material or catalyst and the gasifiers design [63].

The amount of tar included in the syngas produced by gasification, is influenced by many of the gasifiers operating parameters and mainly the following: gasification temperature profile, equivalence ratio (ER – the ratio of the actual air - fuel ratio to the stoichiometric air - fuel ratio), steam to biomass ratio (S/B), gasifying agent, gasifying ratio (GR – the ratio of steam – oxygen to biomass). Regarding the effect of those parameters on tar removal, higher temperature, GR, ER and S/B lead to lower tar yields [63-67]. Additionally, regarding the effect of temperature on tar formation, it was found that despite the fact that the increase of temperature leads to a total reduction of tars formed during gasification, it actually leads to a rapid formation of 3- and 4- ring aromatics and a simultaneous decrease of 1- and 2- ring aromatics. The same observation has been made for ER, as its increase stimulates the formation of polyaromatic compounds. [63, 65]. Additionally, Kinoshita et al. [65], reported also an increase in toluene and indene until an ER of 0.27 but a decrease for higher values. Furthermore, as it was investigated in the previously mentioned study, the effect of residence time is negligible regarding tar yield, but it is more important for tar composition. In particular, it was found that 1- and 2- ring compounds (excluding benzene and naphthalene) yield decreases, while the 3- and 4- ring compounds yield increases for an increase in residence time. Finally, regarding the gasification agent, according to [63] the use of CO₂ seems promising, as tar reduction is enhanced by dry reforming reactions of CO₂ which is also a gasification product. Gil et al [68], compared the tar yield of biomass gasification for three gasifying media (steam, steam – O₂ and air). The lower tar yield was obtained for air gasification followed by steam – O₂ and pure steam gasification.

Another primary method for tar reduction that has been extensively studied by researchers is the use of bed additives that can be employed for catalytic tar reduction. Catalysts accelerate the steam reforming reaction and the dry reforming reaction that lead to tar reduction [32]. Some of these catalysts are Ni-based, calcined dolomites and magnesites, zeolites, olivine, limestone, char and iron. According to [69], the criteria for the catalysts used can be summarized as follows:

- The catalysts must effectively decrease tar yield.
- When syngas is produced, the catalyst has to be able to reform methane.
- The syngas ratio for the intended process should be suitable.
- The catalyst should be resistant to deactivation as a result of carbon fouling and sintering.
- The regeneration of the catalyst should be easy.
- The catalyst needs to be strong.
- The catalyst should be inexpensive.

Generally, the catalysts used in biomass conversion applications can be categorized in to two groups according to the position of the catalytic reactor relative to the gasifier's. Primary catalysts are added directly to the biomass before the gasification. This is done either by wet impregnation of

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biomass material (on small – scale) or by dry mixing of the catalyst with it. The main focus of this process is tar reduction, while the conversion of CH_4 and C_{2-3} hydrocarbons in the product gas are minimally effected. Their operating conditions are the same as the gasifiers and usually they are made out of cheap, disposable material, as they cannot be regenerated. On the other hand the second category catalysts are placed in a secondary reactor downstream from the gasifier and therefore they can operate under different conditions. Those catalysts can reform hydrocarbons and methane [69]. In a review performed by Devi et al [63], it is mentioned that seven critical observations can be made regarding the performance of active bed additives during gasification:

- 1) The distribution of the product gas is altered.
- 2) The amount of tar decreases.
- 3) Catalytic tar reduction is highly influenced by gasification conditions.
- 4) Hydrogen production increases.
- 5) The amount of CO decreases in contrast with the amount of CO_2 .
- 6) The production of CH_4 is not affected.
- 7) Severe problems of catalyst deactivation and carryover of fine particles were reported.

The influence of the gasifier design on the gasification tar yield is particularly high, as it determines the place where pyrolysis happens, the way that tar reacts with oxidants and the temperatures under which those reactions take place. The four main types of gasifiers are the following: updraft, downdraft, fluidized bed and entrained bed. As it was reported by Basu [32], the tar concentration in the product gas is negligible for entrained flow gasifiers and below 1 g/Nm^3 for downdraft gasifiers. For fluidized beds and updraft gasifiers the corresponding values are 10 g/Nm^3 and 50 g/Nm^3 respectively. Apart from these general design aspects there are also modification that can be applied to gasifiers in order to reduce their tar yield. To begin with, secondary air injection can lead to significant tar reduction as higher temperature can be achieved this way. Another design that can be employed is the two – stage gasifier. Its operation principal is that the pyrolysis zone is separated from the reduction zone. Consequently, tars are formed during pyrolysis in the first stage and are decomposed in the reduction zone. These two designs can also be combined and with the addition of char can lead to effective tar decomposition. By using a moving bed, two – stage gasifier were in the first stage pyrolysis is performed and in the second the char is gasified in a bed of char, the tar yield can be reduced dramatically. This reduction can be even higher with the injection of air in the second stage, as it can increase the temperature of the bed [32, 63].

1.4.4.2 Secondary methods for tar reduction

Post – gasification or secondary methods, treat the hot product gas of the gasifier and they are chemical or physical in their nature. The chemical methods include thermal or catalytic tar cracking downstream of the gasifier. On the other hand physical methods include the use of cyclones, baffle, ceramic, electrostatic and fabric filters, rotating particle separators and scrubbers [63].

Secondary methods can be further divided into dry and wet gas cleaning. Dry gas cleaning is employed before the cool - down of the gas where the temperature is higher than 500°C and partly below 200°C after the gas has been cooled. On the other hand, wet gas cleaning is used after the gas has been cooled at temperatures around $20 - 60^\circ\text{C}$. For example, the use of cyclones, rotating and

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electrostatic precipitators and filters are equipment of dry gas cleaning applications, while spray and wash towers, scrubbers, etc. are used in wet gas cleaning [70].

Regarding the chemical methods, cracking is the breaking of large molecules into smaller ones. By this process, tar is converted into permanent gases like H_2 or CO and so its energy content is recovered through these smaller molecules. This procedure does not require condensation of the tar and it involves its heating to high temperatures or its exposition to catalysts at lower temperatures ($\sim 800^\circ\text{C}$). In thermal cracking, the temperature depends on tar composition, as for example, oxygenated tars can crack around 900°C . Nevertheless, usually, higher temperatures ($\sim 1200^\circ\text{C}$) are required. Additionally, during this process, oxygen or air can be added and partial combustion can take place, as a measure to increase the temperature. Another thermal cracking technique involves the use of electric arc plasma, but the product gas has a lower energy content compared to the other methods. For thermal cracking, the main reactions that take place in such a reactor are steam reforming and dry reforming. Those reactions are endothermic and consequently combustion can be performed inside the reactor in order to produce the required heat. In those reactors, the dirty gas passes over catalysts that can be metallic or non – metallic. Non – metallic catalysts like dolomite, zeolite and calcite are less expensive and the problems associated with their use are attrition and deactivation. Metallic catalysts include Ni, Ni/Mo, Ni/Co/Mo, NiO, Pt, and Ru on supports like silica-alumina and zeolite. Most of them are used in the petrochemical industry and consequently can be obtained easily and the most important issue with their use is that they also need reactivation. For both metallic and non – metallic catalysts, tar – laden gas is used in the reactors, which operate in temperature between 750°C and 900°C [32].

Generally, secondary methods are very effective in tar reduction, since they are being widely studied and are rather well understood processes. Despite that fact, the production of gas with very low tar content often requires a complex and economically unviable process [63].

1.5 Research questions and methodology

The aim of this study was to answer the following main research question:

“What is the effect of torrefaction of woody biomass types on their thermochemical conversion under fast pyrolysis conditions?”

In order to address this main subject the following research sub - questions were formulated:

- How do different final temperatures influence the product yields of pyrolysis?
- What is the effect of torrefaction and its severity on the solid, liquid and gaseous yield of pyrolysis?
- How do torrefaction and its severity (in terms of final temperature) affect the formation of tar compounds?
- How do the results obtained compare to those of relevant other experimental studies?

For this purpose, fast pyrolysis experiments of woody biomass materials were performed in a Pyroprobe 5200 reactor under various final temperatures. The woody biomass materials studied were torrefied materials and their untreated parent species. In particular the species studied were

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Ash (hardwood) and a commercial torrefied wood product from the company Torrc coal, which consists of a mixture of wood species. The pyrolysis products of those experiments were quantified gravimetrically (solid residue and liquid product) and with the use of a micro – GC (gases). Furthermore, tar compounds that were formed were identified and quantified by a HPLC analyser. The results were compared with relevant studies that were obtained during the literature study performed.

2. Materials and methods

2.1 Biomass feedstocks

Wood ash (*Fraxinus excelsior*) and a commercial product, Torrc coal, which consists of mixed wood residues, were the two biomass species studied within this thesis. Wood ash was provided by ECN (the Netherlands), while Torrc coal was provided by the Torrc coal company. The torrefied and the untreated version of these materials were studied in this work. Wood ash (ECN Ash) was torrefied at 250°C (ECN 250) and 265°C (ECN 265) for 30 minutes. Torrc coal (white Torrc coal) was torrefied at approximately 300°C for two minutes according to the information given by the company. Torrefied Torrc coal (black Torrc coal) is a biofuel already available on the Dutch market. All the biomasses were received in pelletized form and were subsequently ground and sieved to a size less than 75µm.

2.2 Pyroprobe

The CDS Analytical Pyroprobe 5000 is a pyrolysis instrument which can perform multistep – platinum filament heated pyrolysis, in order to provide gas samples for gas chromatography, mass spectrometry or FTIR. The principle behind its operation is that by calculating the resistance of the filament at set - point temperature, the very temperature of the filament can be controlled by varying the voltage. There are three basic operational modes, with the main one being single step or sequential pyrolysis, with which the pyrolysis experiments are performed. The other two methods are the 'dry method' for removing solvent from a sample deposited in a solution and 'clean' for removing residual material from the filament between runs. The temperatures for the pyrolysis filament can reach up to 1400°C and the heating rates range from 0.01°C/min to 20000°C/sec, while the interface temperatures can be set to 350°C [71]. In the following lines the experimental procedure followed for the experiments performed within this thesis is going to be presented.

A 2.1mm quartz tube was used as a sample holder. In order to keep the 30mg of sample into the holder, quartz wool was placed on each side of it, caging the sample in between (Figure 16). The sample holder and the quartz wool were carefully cleaned with pressurized air and seared, to avoid the presence of any contaminants during pyrolysis. The holder including the biomass sample is then inserted in the probe rod. After the apparatus for tar and gas collection has been prepared and the nitrogen flow has been regulated the experiment can be started. The filament temperature was set in the temperature range between 600 and 1000°C with a heating rate of 600°C/s. It should be mentioned at this point, that the set filament temperature differs from the actual temperature. As it is indicated by the manufacturer, the temperature inside the quartz tube is approximately 100°C

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lower than the filament temperature. Furthermore, according to the manufacturer's instructions the oven temperature was set at 325°C in order to prolong the life of the rotor used in the valved interface which lies on the back part of the reactor. The initial temperature of the interface was 50°C and the corresponding heating rate 100°C/min. Consequently, the interface is heated at 300°C in roughly 2.5 min. This part of the process is necessary in order to remove the moisture that the sample contains. Then pyrolysis takes place as the probe filament is heated up to the set pyrolysis temperature. Finally, with the interface temperature still at 300°C the experiment continues for 5 more minutes in order to ensure complete collection of the gaseous and tar product. The pyrolysis time for the experimental series in this work was set at 10s. The time at final temperature as it is set in the Pyroprobe software also includes the time required for the filament to reach this particular temperature. As a result, in order to achieve 10s of pyrolysis for any given pyrolysis temperature this time interval (holding time) should be set accordingly. In Table 3, the holding time for different pyrolysis temperatures is presented as it was measured through blank Pyroprobe runs.

Table 2: Pyroprobe holding time for each pyrolysis temperature

Actual Temperature (°C)	Holding Time (s)
600	11
700	11.4
800	11.8
900	12.1
1000	12.4

For the tar collection a trap and an impinger bottle were used. A syringe was inserted after the impinger tube to collect the gases for the gas analysis, which was performed using a micro - GC. The volatile flow from the pyrolysed sample was carried by a 15 – 20ml/min nitrogen flow initially through the trap. The syringe for gas collection was inserted at the end part of the trap – impinger assembly just before the initiation of pyrolysis after the interface temperature had reached 300°C and it was taken off after the completion of the experiment. Regarding tar collection, part of the tar content was condensed in the trap due to the lower temperature (50°C) and the filter of the trap was used to block char particles from reaching the impinger tube. The tube contained 2ml of isopropanol which was the solvent used in the tar analysis. After the completion of each experiment, the trap was weighted in order to determine the gravimetric tar content. Subsequently, the trap was inserted in a testing tube which contained the 2 ml of isopropanol from the impinger and an additional 3ml of isopropanol. The trap was left in the tube for 30 to 40 min, in order for the tars to dissolve in the isopropanol. Afterwards, the solvent was passed through a filter for particle separation and collected in a vial. This vial was refrigerated, before the tar analysis in the HPLC.

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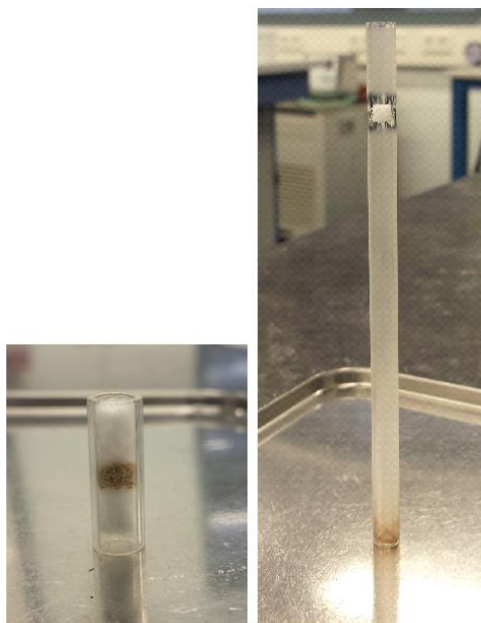


Figure 16: Sample holder containing the biomass sample and the quartz wool (left) and trap (right)

For every experiment, several gravimetric measurements were performed. Initially, the weight of the holder with one piece of quartz wool on one end was measured. Afterwards, the weight including the biomass sample first and subsequently also the other piece of quartz wool was measured. It should be noted that the weight measured during this procedure also includes the moisture of the sample. Furthermore, before the initiation of the experiment the weight of the empty trap is also noted. After the completion of the experiment both the weight of the holder and the trap are measured again. This way, the amount of volatiles released and the gravimetric tar content of the biomass are measured. Additionally, the total amount of gas that is collected in the syringe is measured as it is used in the gas yield determination.

At this point it should be mentioned that the Pyroprobe reactor setup was modified in the course of the experiments. In Figure 17, the original setup and the pathways of the carrier gas and the product gas stream are presented. Of course, as it was mentioned earlier, for the experiments conducted within this thesis, an impinger bottle was connected right after the trap for the collection of tars. Therefore, the subsequent pathway is irrelevant for the present study. The first three experimental series (white and black Torricol and ECN 250) were performed with this setup. However, many problems would arise frequently. In particular, the escape of char particles which could not be fully prevented by the use of the quartz wool would cause blockages in the tube that connected the reactor chamber and the upper valve. The high amount of downtime forced by those blockages led to the decision to simplify the setup (Figure 18). Both valves were completely removed and the gas was fed directly in the reactor chamber. The gases that exited the reactor chamber were fed directly in the trap. This setup, offers the advantage of less blockages due to the absence of the valve. Additionally, in the previous setup, during idle operation, the carrier gas followed a different pathway before its venting into the atmosphere. Under these conditions, the constant flow of gas through the same pathway as for the gases during an experiment, offers constant cleaning of the remaining tubes. It should be noted that, after the aforementioned changes the setup was never again blocked. Furthermore, it was observed that the duplication of the experiments for the last two series (ECN 265 and ECN Ash) became easier since the gravimetric results became more consistent.

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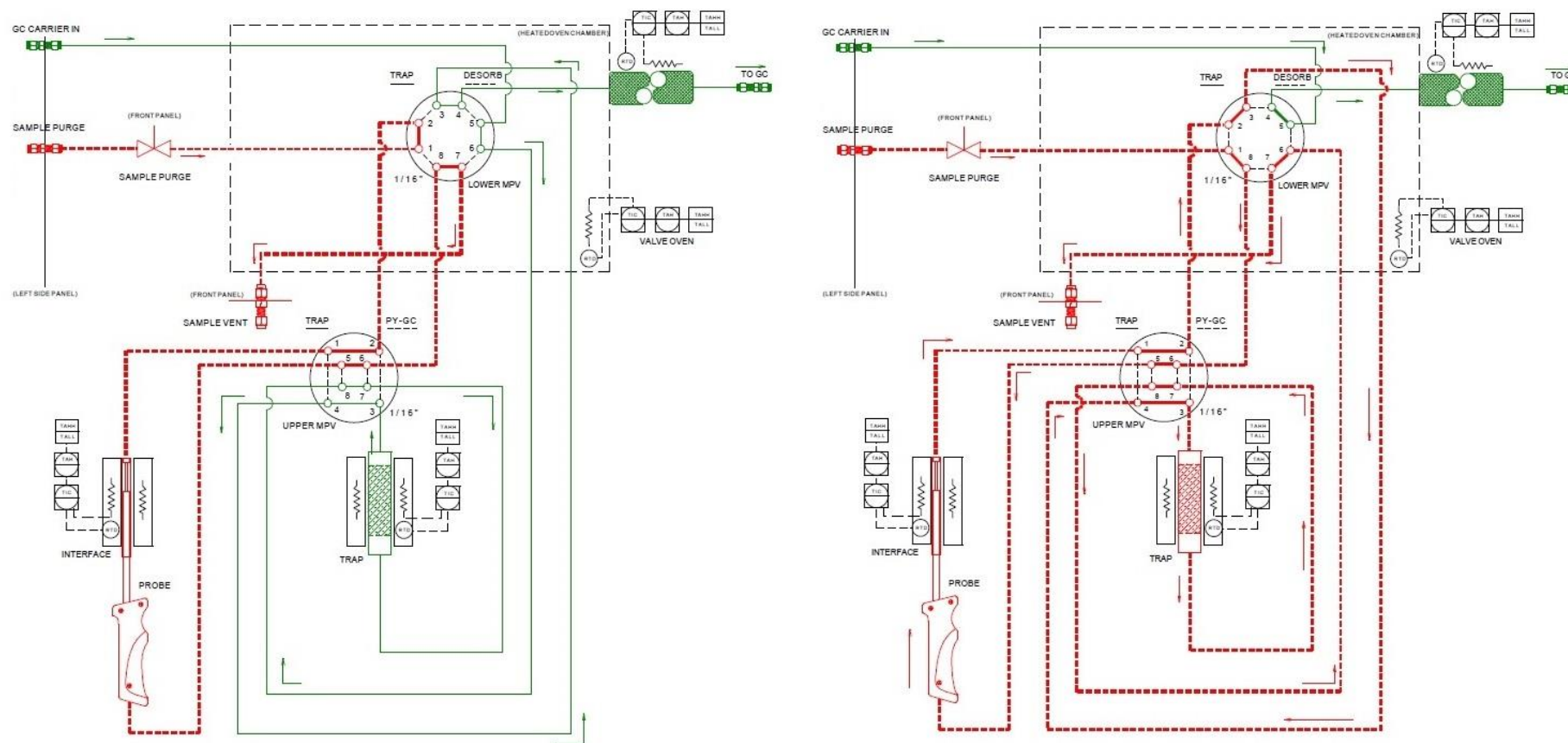


Figure 17: Pyroprobe setup. On the left are depicted the pathways during idle operation and on the right the pathways during an experiment

2. Materials and methods

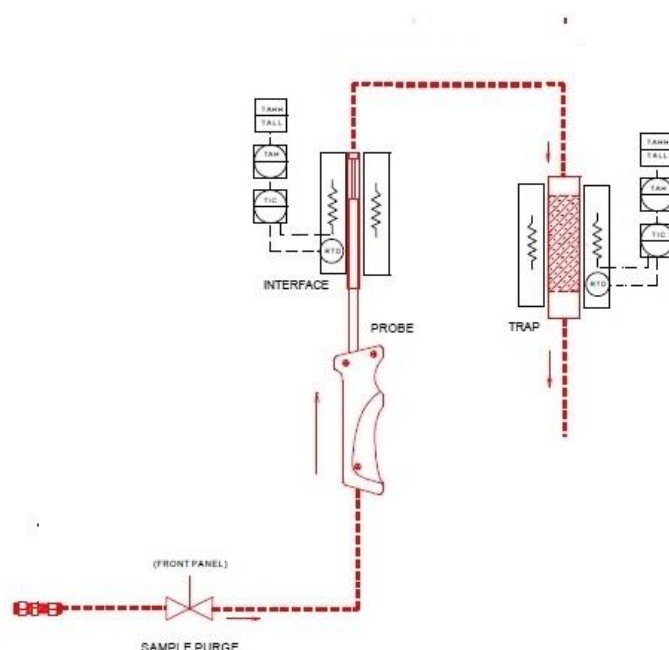


Figure 18: Simplified Pyroprobe setup

In order to obtain a complete understanding of the pyrolysis process in the Pyroprobe, the time required for the produced gases to leave the reactor and enter the trap was calculated. It appears that 51 to 68 seconds are needed for the gases to leave the reactor chamber depending on the nitrogen flow (15 – 20 ml/min). This particular area is initially at 50°C and its temperature reaches 300°C within 2.5 min, right before the filament begins to heat up which signals the initiation of the pyrolysis process. As it was mentioned before the experiments were conducted under a nitrogen purge-flow of 15 to 20 ml/min, so these calculations were performed between those bounds. Consequently, the produced gases stay in the reactor chamber for roughly 1 minute at a temperature of 300°C. Afterwards, they pass through the valve oven where the temperature is maintained during the whole experiment at 325°C. the time needed to pass through the 0.0345 inches tubes is significantly less, namely 0.75 – 1 sec. The latter values correspond to the simplified Pyroprobe setup. For the initial setup the required time was more than double (1.7 – 2.3 sec). It should be mentioned at this point, that by removing the extra tubes and the valves from the product gas pathway, the total distance for the gases was reduced from roughly 95 cm to 41.5cm.

Regarding the heat transfer phenomena taking place and leading to the realization of the pyrolysis reaction, not much emphasis was given since the modelling of this process is outside the scope of the present study. However, some general information is provided here. As it was mentioned earlier, according to the Pyroprobe manufacturers there is a difference between the set filament temperature and the actual temperature inside the quartz tube (holder). The correspondence between the two values was calculated by measurements performed with the use of thermocouples which were inserted inside the quartz tube which however was not performed by the author. The results differed from the manufacturer's estimation (100°C difference) and they are presented in Table 2.

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Table 3: Actual and set filament temperature correspondence

Actual Temperature (°C)	Set Temperature (°C)
100	120
200	248
300	375
400	503
500	630
600	758
700	885
800	1013
900	1141
1000	1268

Heat transfer in the Pyroprobe is a complex process since it involves many mechanisms. The main heat transfer medium is the filament surrounding the quartz tube, but the heat is transferred to the biomass particles through the following routes [2, 72, 73]:

- 1) Heat is transferred by conduction and radiation from the filament to the quartz tube walls. Furthermore, the nitrogen gas flowing around the quartz tube is also heated. The initial layers of the gas that come into direct contact with the filament are heated conductively and then convection takes charge of the heating of the remaining gas. Therefore, if assumed that also the nitrogen gas that comes into contact with the quartz tube walls is heated, the quartz tube walls are also heated conductively through the nitrogen – wall boundary layer.
- 2) Subsequently heat conduction perpendicular to the quartz tube wall takes place
- 3) It is fair also to assume that the nitrogen that passes through the quartz tube is also heated by the mechanism described earlier. Consequently, nitrogen can be considered as a second heating medium.
- 4) The biomass particles that are in contact with the quartz tube walls are heated by solid – solid conduction. Furthermore, heat is transported to the particles outer surface by radiation and convection.
- 5) Thereafter, it is transferred inside the particle by conduction and pore convection.

The discussion above is far from a complete presentation of the heat transfer phenomena taking place and it is meant to be indicative for the reader since a modelling attempt is lacking at the moment for this type of reactor. It should not be omitted that after the biomass particle is heated, first moisture is removed and afterwards pre – pyrolysis and main pyrolysis reactions take place. Due to the reaction heat changes from the chemical reactions and phase changes a non – linear and time dependent temperature gradient is formed within the bed. This gradient is also caused by heat transfer limitations for the mechanisms described earlier. The volatiles produced by the pyrolysis, which are removed by the nitrogen gas, also participate in heat transfer process as they flow through the particles pores and the biomass bed [72]. The rate of the pyrolysis reactions depends on the local temperatures. In order to minimize the temperature gradients, a relatively small sample size (30mg) and small biomass particles (<75µm) were used in the experiments within this thesis project. However, the short pyrolysis regime employed (roughly 10s) has the reverse effect. The time provided may not be sufficient to create a uniform temperature within the biomass bed.

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Another important consideration for the pyrolysis process taking place is the endothermicity or exothermicity of the pyrolysis reactions. Dehydration, depolymerisation and secondary cracking reactions are endothermic. Nevertheless, reactions between intermediate pyrolysis products can be both exothermic and endothermic. As a general indicator, the pyrolysis of hemicellulose and lignin is exothermic. For cellulose, its pyrolysis becomes exothermic at higher temperatures [2]. Consequently, in order to build a model regarding heat transfer for a pyrolyzer this factor also needs to be considered. However, such an investigation is outside the scope of this thesis.

2.3 Thermogravimetric analysis (TGA)

The TGA experiments were performed in a SDT Q600 V20.9 thermobalance, with an alumina cup and a 100 ml/min nitrogen purge flow. The method employed for each experiment followed the sequence described below.

- Equilibration of temperature at 30°C (initial temperature).
- Increase of temperature until 110°C under a 30°C/min heating rate.
- Isothermal operation for 15 min in order to remove the sample's moisture.
- Increase of temperature until 900°C under a 10°C/min heating rate.
- Isothermal operation for 10 minutes to ensure the sample has fully devolatilized
- Isothermal operation for 15 min in order to combust the remaining char. For this interval the nitrogen flow rate is replaced by air with the same flow rate (100 ml/min).
- Cooling of the machine.

2.4 Gas and tar analysis

The gas analysis was performed in a Varian μ -GC CP4900 equipped with a column module which measured continuously the volumetric fraction of N₂, H₂, CO, CO₂ and CH₄ (1 m CP-COX column). The sampling procedure was described in the previous chapter. More on the gas sampling process can be also found in Appendix IV which includes the experimental protocol.

The analysis of the condensed tar species was performed using a high performance liquid chromatography (HPLC) on a KNAUER System. PAH separation was achieved on a UltraSep ES PAH QC, 60×2.0mm column with a mobile phase of water/acetonitrile at a flow rate of 0.5 ml/min. The analysis temperature and time were 25°C and 17 min, respectively. Determination of tars composition was accomplished through a combination of ultraviolet-visible (UV) and fluorescence detectors. Due to the limited amount of strongly fluorescent compounds, the fluorescence detection is highly selective for PAHs. The HPLC chromatogram of each sample was analysed by both detectors (UV and fluorescence). Phenol separation was carried out with a Kromasil Eternity XT 5-C18 4.6×150 mm column, at 25°C with a mobile phase of methanol/water and analysis time of 5 min. Phenol detection was accomplished by a UV detector (λ =254nm).

3. Experimental results

3.1 Fuels analysis

3.1.1 TGA results

TGA experiments were performed for torrefied and untreated (black and white, respectively) Torrrcoal. The analysis was performed using two different sample sizes, namely roughly 15 and 20 mg of sample in order to investigate possible effect of the initial sample size in the process. The results of the proximate analysis which are also presented in Table 4 showed that the effect of this parameter is negligible at least for such small differences. Furthermore, in this chapter the mass loss (%) and devolatilization rate curves versus temperature are also presented, for the 20mg samples. TGA tests were also performed for ECN ash, untreated and torrefied at 250°C and 265°C but this time only for one sample size. The results for ECN ash are presented in Table 5.

Table 4: Proximate analysis for black and white Torrrcoal based on TGA tests with two sample sizes

Biomass	White Torrrcoal		Black Torrrcoal	
Sample size (mg)	15.9	21.5	15.3	20.6
Moisture (%)	7.3	7.5	4.7	4.9
Volatiles (% d.b.)	76.7	76.8	66.2	66.3
Fixed carbon (% d.b.)	21.4	22.2	31.8	32.5
Ash (% d.b.)	1.9	0.9	1.9	1.2

Table 5: Proximate analysis for ECN ash (torrefied and untreated) based on TGA tests

Biomass	Moisture (%)	Volatiles (% d.b.)	Fixed carbon (% d.b.)	Ash (% d.b.)
ECN ash	4.7	79.3	19.9	0.7
ECN 250	5.7	72.4	27	0.5
ECN 265	5.8	68.6	30	1.4

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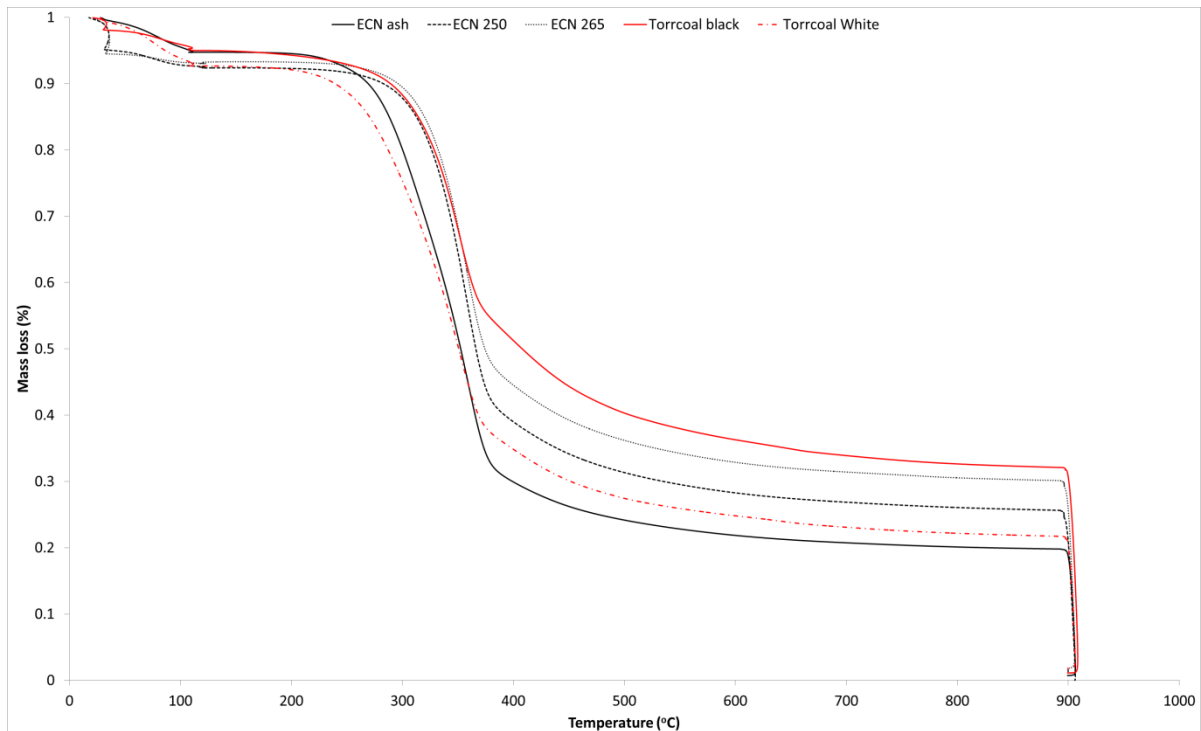


Figure 19: Mass loss versus temperature curves for Torrocoal and ECN ash (untreated and torrefied) under a 10 °C/min heating rate and a 100 ml/min nitrogen flow

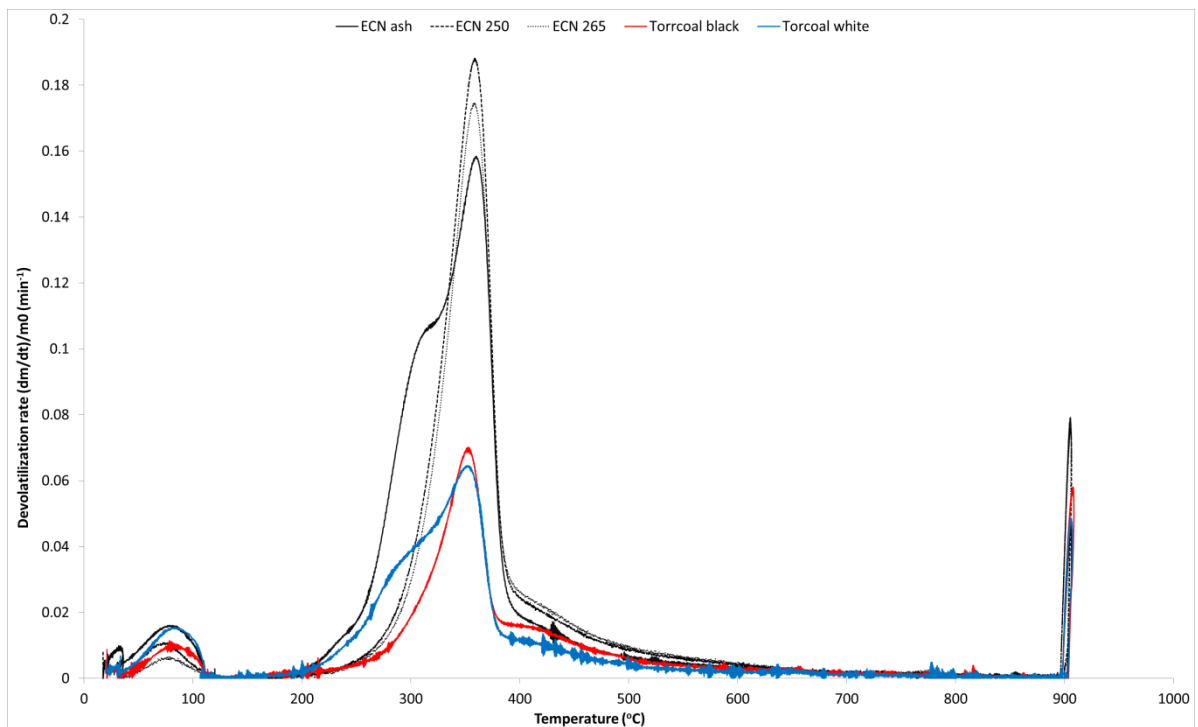


Figure 20: Devolatilization rate versus temperature curves for Torrocoal and ECN ash (untreated and torrefied) under a 10 °C/min heating rate and a 100 ml/min nitrogen flow

It can be concluded from the proximate analysis, that the amount of moisture was higher for the untreated Torrocoal (white). This result was expected since a portion of the treated biomass moisture was removed during the torrefaction process. On the contrary, in the case of ECN ash, the moisture content of the biomass material was increased after torrefaction. Probably this has to do with the pelletization process or the storage of the torrefied biomass. Additionally, it can also be

3. Experimental results

observed that the amount of volatiles decreased in contrast with the amount of fixed carbon for both woody biomasses studied. This behaviour can be explained by the loss of volatiles due to the torrefaction process which renders the torrefied wood more concentrated in the thermally non – reactive carbon [38, 42, 45, 74]. The amount of ash was not particularly influenced by the process as it is shown by the results. This contradicts the findings of the aforementioned studies which report an increase in the ash content when torrefaction was performed. Nevertheless, as it is also indicated in [35] due to the low ash content of woody biomass the effect of torrefaction can be considered as negligible. Additionally, Bridgeman et al. [75] reported only a small increase in the ash content of willow between the untreated and treated samples (from 1.7 to 2.3 % d.b.).

By studying the mass loss curve, it can be observed that the main mass portion is devolatilized between 200°C and 500°C for the white Torrrcoal and between 250°C and 500°C for the black Torrrcoal. For ECN ash the highest percentage of mass change again occurred between 200°C and 500°C while for Ash 250°C and Ash 265°C the main part of the devolatilization occurred between 250°C and 500°C. This increase in the initial decomposition temperature is indicative of the increased thermal stability of the torrefied biomass compared to the untreated one [76, 77]. The initial drop in both curves is attributed to the loss of moisture while the sudden drop in the end is attributed to the pyrolysis of the char. The total mass loss was lower in the case of black Torrrcoal due to the reduction of volatile content through the torrefaction process. This observation can also be made for ECN ash, since the total mass loss was reduced with the increase of the torrefaction severity. When comparing the two biomasses, the mass loss was higher for ECN biomass, despite the fact that the volatile content was higher for Torrrcoal and torrefied Torrrcoal.

Moving over to the devolatilization curve, it can be noted immediately that the ‘shoulder’ corresponding to hemicellulose decomposition disappears after torrefaction for both biomasses studied. This behaviour was expected as it was mentioned in Chapter 1.3, since hemicellulose is the main component that devolatilizes during torrefaction. Furthermore, it was observed that white Torrrcoal decomposition was faster until 330°C and slower for higher temperatures when compared to black Torrrcoal. The exact same behaviour and at the same temperature point can be observed for treated and untreated ECN ash. Nevertheless, with the increase of the torrefaction severity the devolatilization rate decreased until 380°C, remaining however significantly higher than the raw biomasses. After this temperature the rate of ECN ash torrefied at 265°C exceeded slightly the corresponding rate for ash torrefied at 250°C. The disappearance of the ‘shoulder’ corresponds to the lack of hemicellulose in the torrefied sample, while the increased devolatilization rate shows an increase in the reactivity of the wood sample after the torrefaction. At this point it should be mentioned that the reactivity of a biomass feedstock is proportional to the maximum devolatilization rate and inversely proportional to the temperature that corresponds to this rate [78, 79]. In both the cases of Torrrcoal and ECN ash, the maximum devolatilization rate value increased with torrefaction, while the corresponding temperature remained unaffected. Finally, by observing the 400°C – 500°C temperature range it can be seen that torrefaction resulted in a rise in the devolatilization rate for both feedstocks. Additionally, this effect was also apparent with the increase of the torrefaction severity. As it was mentioned earlier this particular range corresponds to the decomposition of lignin, but in the case of torrefaction the total lignin content of the biomass is not increased. Therefore, this rise can be attributed to secondary reactions of carbon – containing residues [36, 37], since the fixed carbon content of the biomass is increased through torrefaction. Finally, between the two biomass species it was observed that the devolatilization rate was higher for the case of treated and untreated ECN ash.

3. Experimental results

3.1.2 Ultimate analysis

In this chapter the table containing the ultimate analysis for the biomass fuels studied is presented. The data it contains will be used for the analysis following in the coming chapters.

Table 6: Ultimate analysis of wood and wood torrefied at various temperatures

Biomass	C ^a	H ^a	N ^a	S ^a	O ^{a,c}	LHV (MJ/kg) ^{b,c}
ECN ash white	46.6	5.9	0.1	0.8	41.5	17.6
ECN ash 250	50.6	5.5	0.1	0.8	36.7	19.1
ECN ash 265	51.8	5.3	0.1	0.7	35.3	19.5
Torrcoal white	46.6	5.8	0.2	0.8	39.7	17.3
Torrcoal black	53.5	5.2	0.5	0.7	34	19

^a on a.r. basis, ^b O₂ content is calculated via difference, ^c calculated based on [80]

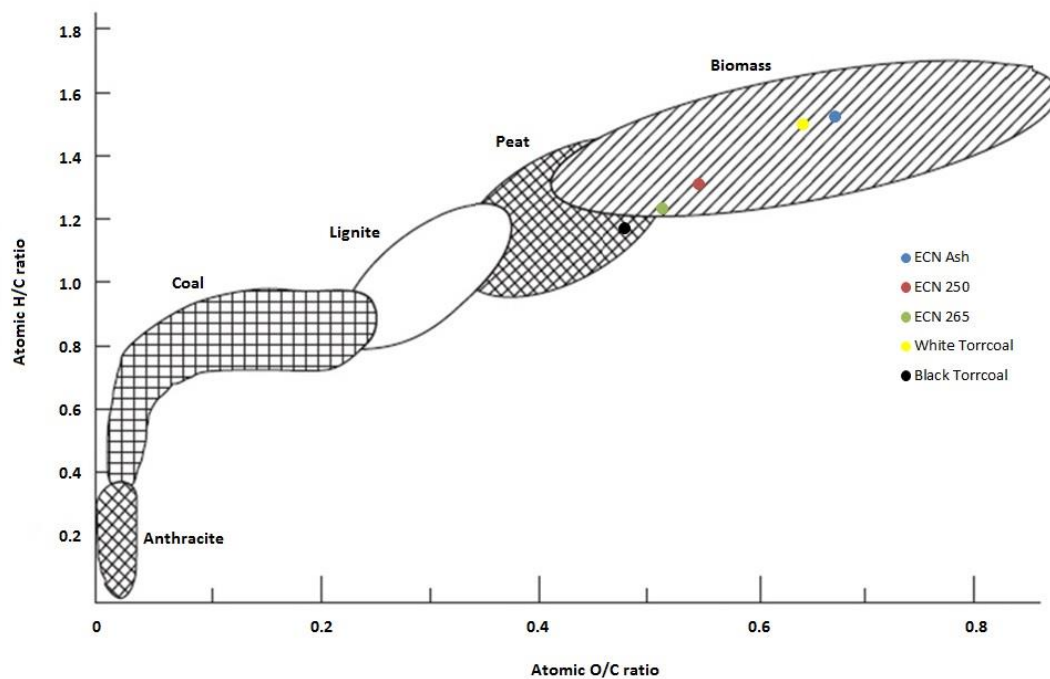


Figure 21: Van Krevelen diagram of the biomass species studied (adapted from [16]).

In the above figure the Van Krevelen diagram of the biomass species studied within this thesis is presented. In general, the lower the atomic O/C and H/C ratios are the higher the energy content of the material described in [81]. As it was expected, the torrefied biomass species appear to have higher energy content than the parent biomass. This is also apparent from their higher heating values (Table 6). Furthermore, it can be seen that as torrefaction severity increases (black Torrc coal was torrefied at 300°C), the materials tend to resemble the behaviour of fossil fuels like peat and lignite as their relative carbon content is increased.

3. Experimental results

3.2 Pyroprobe results

3.2.1 Mass balances

In this section the experimental results of the Torrcoal (untreated and torrefied) and Ash samples fast devolatilization in the Pyroprobe reactor are going to be discussed. More specifically, the liquid (tars), solid (residue) and gaseous products of the experiments were collected and measured gravimetrically. In the following paragraphs the results derived from these measurements are presented. It should also be mentioned that these experiments were performed at least twice. Therefore, the presented values are the mean values of two experiments performed under the same conditions. The Tables containing the arithmetic values are included in Appendix II.

In Figure 22 and 23, the mass balances derived from the fast devolatilization of white Torrcoal and ECN Ash are presented. The corresponding figures for the torrefied species are included in Appendix II. In order to perform these calculations it was assumed that the dry mass of the sample was converted in its entirety to the gaseous, liquid (tars) and solid products.

The average value of the mass balance closure was 75.5 wt% (d.a.f. basis) and no significant effect of temperature was noticed in that respect in the case of white Torrcoal. The mass closure values ranged from 73 to 78.6 wt% (d.a.f. basis). For black Torrcoal the corresponding value was 76.6 wt% (d.a.f. basis), but this time the percentages appeared to drop slightly with temperature ranging from 72.8 to 83.9 wt% (d.a.f. basis). From comparing the two experimental series, it can be concluded that the torrefaction process did not influence the experimental results in terms of mass balance closure.

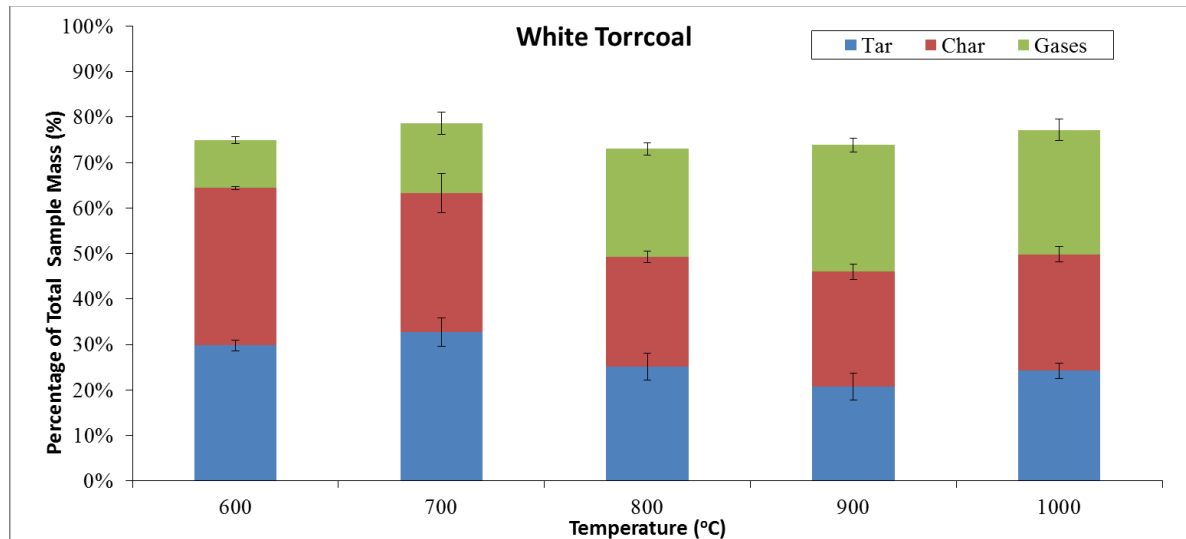


Figure 22: Mass balance of untreated (white) Torrcoal pyrolysis (d.a.f. basis)

For ECN ash the average value of mass closure for all five experiments was 73.9% with the values ranging from 80.6% (600°C) to 66.1% (1000°C). In this case a drop can be noticed as the pyrolysis temperature was increased. This behaviour can be attributed to the reduction of the liquid and char yields which is not matched by the increase in the gaseous yield. It should be noticed that the micro – GC employed in the experimental series performed is not able to detect higher hydrocarbons like ethylene, which yields are increased along temperature. Furthermore, it is possible that also tar compounds evolved at higher temperatures, failed to condense in the trap and

3. Experimental results

subsequently were also not detected by the micro – GC. In the case of ECN ash torrefied at 250°C the mass balance closure ranged from 76.5% at 700°C to 66.7% at 1000°C, with an average value of 71%. Also in this case the same behaviour along temperature rise was noticed as in the case of untreated ash. On the other hand for ECN ash torrefied at 265°C the mass balance closure values decreased from 74% in 600°C to 64.9% in 800°C before starting to rise again by 1000°C. The average value for this experimental series was 68.6%. Generally, by looking at the average values of the mass closure for each species it can be noted that the mass balance closure values experienced a slight but noticeable decrease along the increase of torrefaction degree and through the torrefaction process initially. These differences in the mass closure values between treated and untreated species are mostly attributed to the decrease of liquid yield from torrefaction, which is mostly observable at lower temperatures especially for ECN 265. However, at 1000°C the results were similar for all three species, since also the difference in the liquid yields becomes smaller.

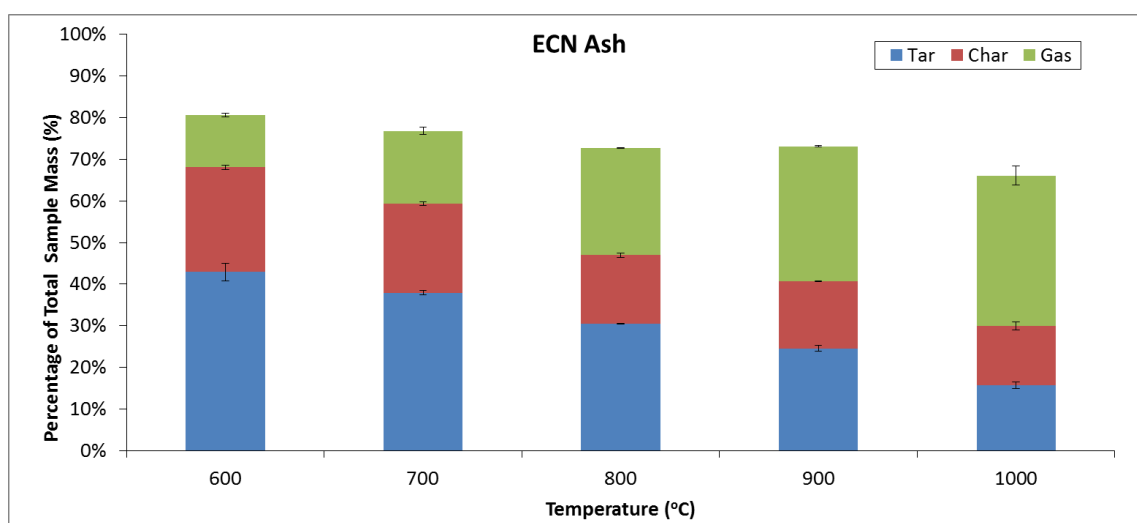


Figure 23: Mass balance of untreated ECN ash pyrolysis (d.a.f. basis)

For all the experiments conducted within this thesis, there are a number of reasons why the mass balance closure does not reach 100%. First of all, as it was observed during the cleaning of the Pyroprobe reactor, some tars can condense before the trap where the temperature is 325°C. This could be avoided by increasing the temperature in this particular area, but unfortunately this is not possible for this apparatus since the local temperature (oven) cannot be increased above 325°C. Furthermore, some losses may occur from the evaporation of very volatile compounds which manage to escape in the time interval between the trap removal from the reactor and the insertion in the isopropanol filled testing tube. Another reason that leads to an unclosed mass balance originates from the inability of the micro – GC to measure gas species constituted by higher hydrocarbons, mainly C_2H_4 , C_2H_6 , C_3H_6 and C_3H_8 . As it was proposed by Hajaligol et al. [82], these gaseous products are derived from secondary decomposition of tar and therefore their yield is increased with temperature. From the literature [83-86] it is indicated that the total yield of these products can sum up to a 2 – 5 wt% dry depending on the experimental conditions and the biomass feedstock used. Furthermore, the water produced during the pyrolysis process which is included both in the liquid and gaseous product was also not measured by either the micro – GC or the HPLC. As it was found in the literature [7, 13, 87], pyrolytic water can account for 10 – 12 wt% of the dry feed. The pyrolytic water can be quantified through a Karl – Fischer apparatus, which unfortunately was not available for this study. Another source of losses in the mass balance is introduced by the

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inability to measure gravimetrically the light tars that escape the trap and condense in the isopropanol filled impinger bottle. Finally, there is always the possibility of error during the gravimetric measurements of the liquid and solid product as well as in the determination of the gaseous products through the micro – GC and the ideal gas law implementation.

3.2.2 Solid product

The solid residue (char), produced from the pyrolysis experiments was measured gravimetrically after the completion of each experiment. Starting with the case of Torrrcoal and specifically white Torrrcoal, it was observed that the char percentage dropped from 600°C until 800°C before attaining a steady value at 900°C and 1000°C. On the other hand, the values for black Torrrcoal kept dropping until 1000°C. Nevertheless, the char values dropped by roughly 11% from 600°C to 700°C and by 10% from 700°C to 1000°C an observation that shows that the char production rate was reduced significantly at higher temperatures. Furthermore, as it was expected, there was a significant difference in the char yields of torrefied and untreated material. The difference was more apparent in at lower temperatures, as at the higher ones it was reduced (16.6% of initial sample weight (d.a.f. basis) at 600°C, 5.3% at 1000°C).

Regarding the ECN ash wood fast devolatilization, the char yield decreased by approximately 11% in the temperature range studied. Its behaviour was similar as in the case of white Torrrcoal, since the values were at the same levels at 800°C and above. For ECN ash torrefied at 250°C and at 265°C the same trend was experienced but to a lower extent. For both the torrefied samples, above 800°C there was a drop of roughly 1% in the char yield for each one of the last two temperatures studied. The effect of torrefaction on the pyrolysis of biomass was also apparent for ECN ash. As it can also be seen in Figure 24, the torrefied materials pyrolysis produced more char than the untreated material. With the increase of the torrefaction degree this difference increased further from an average of 12% to 16% of initial sample weight (d.a.f. basis). It is also noticeable that despite the small difference in the torrefaction temperatures there this rise in the char yields from 250°C to 265°C was observed. By comparing the results for treated and untreated ECN ash and Torrrcoal, it can easily be concluded that the amount of char produced was higher for Torrrcoal before and after the torrefaction. This difference can be attributed to the higher fixed carbon and ash content in both black and white Torrrcoal. With the increase in torrefaction temperature, the amount of fixed carbon increased for ECN ash. As it can be seen from the following figure, the difference between black Torrrcoal and ECN ash char yield is reduced for an increase in the torrefaction severity. Generally, char yield is favoured by high carbon and ash content, low oxygen content, low H/C ratio and higher content of coke forming components like lignin [88-90]. Despite, the fact that the lignocellulosic composition of the biomasses studied is not known, it can be assumed by these results that Torrrcoal white has higher lignin content than ECN ash.

3. Experimental results

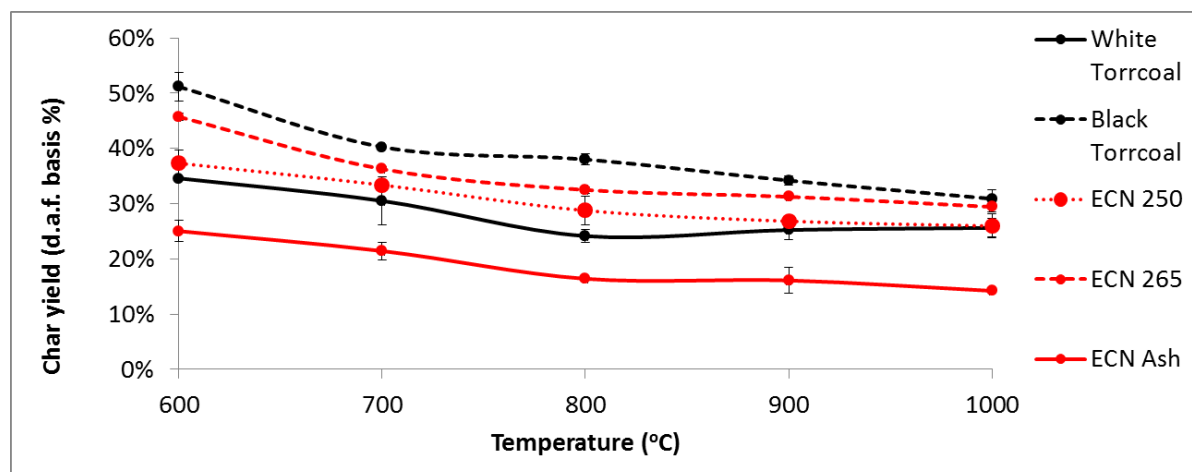


Figure 24: Char product from the pyrolysis of Torrcoal and ECN ash (torrefied and untreated) in the Pyroprobe at various pyrolysis temperatures

As it was expected, the char product yields decreased for higher temperatures, since the pyrolysis conversion is lower at low temperatures. Generally, in the case of wood materials char is also formed by recondensation of liquid intermediates like tar, generated by early bond breaking of the substrate. This is mainly due to the high aromatic content of wood which makes it have stronger coke formation tendencies [84]. This argument will be further evaluated in the chapter regarding tar analysis. The char yield is reduced with the increase of the temperature due to greater primary decomposition of the sample (hemicellulose, cellulose and lignin decomposition) or due to secondary decomposition of the char which also produces non – condensable gases [91]. At low temperatures less volatiles can be released from the solid/liquid decomposing biomass by vaporization and sublimation [92]. Products due to secondary reactions are expected to be limited in the case of the Pyroprobe reactor due to the brief pyrolysis time interval (10s). Regarding the pyrolysis behaviour of the char products, the trends extracted from the experimental series conducted are also reported in most of the studies in the literature [83, 84, 93-99]. The values obtained from the experiments are also in good agreement with several other researches focused on woody biomass in similar facilities [83, 93, 98-101].

From the above presented results it can be concluded that the structure of both Torrcoal and ECN ash was changed through torrefaction and the cross – linking that occurred during pyrolysis led to an increase of the char yield [100]. In fast pyrolysis, active cellulose with a degree of polymerization between 200 and 400 is firstly formed from cellulose. Consequently, active cellulose can decompose further towards the production of anhydrosaccharides (mostly levoglucosan) which can undergo parallel pathways to form char, liquids and non-condensable gases. Nevertheless, during torrefaction the active cellulose produced undergoes cross – linking before it is subsequently introduced in the pyrolyzer. The severe carbon – carbon crosslinking of the biomass carbohydrates prevents the production of volatiles. Thus, the subsequent crosslinking and charring of cellulose produces predominantly char leading to higher values for torrefied biomass compared to the untreated material [77, 102-104]. The above described process is presented in the following figure. Furthermore, the increase of the relative lignin content subsequent the torrefaction process attributed significantly in the observed increase of the char yield, since as it was mentioned in the previous chapters lignin is the main source of char in biomass materials [102, 105]. These results, along with the increase in carbon content, show that torrefaction predisposes the biomass to be converted to char during pyrolysis [45, 96].

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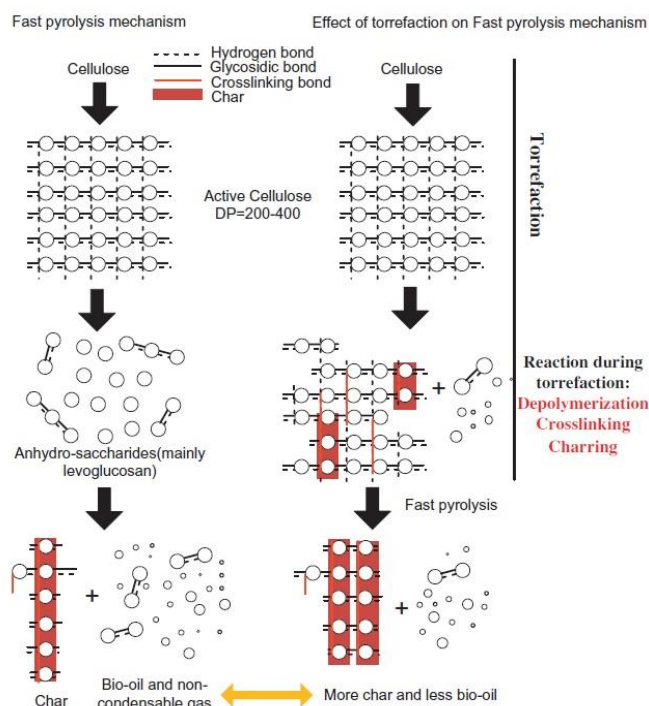


Figure 25: Effect of torrefaction on fast pyrolysis mechanism of cellulose [106]

3.2.3 Liquid product

The liquid product of the Pyroprobe experiments contains the tars, of which the definition was given in the previous chapter and the pyrolytic water. As it was mentioned earlier the exact amount of pyrolytic water produced was not measured in these experimental runs. During the gravimetric determination of the liquid yield which was performed by comparing the weight of the trap before and after the experiment, droplets that could be condensed vapour were observed on the trap walls. This is mainly due to the fact that the outer part of the trap is at room temperature while the part that is inserted inside the Pyroprobe at a 50°C region of the apparatus, causing the water vapours to condense in it. Therefore, it is safely assumed that part of the pyrolytic water produced is accounted for in the liquid product. Nevertheless, the part of the water vapour that failed to condense and was condensed in the isopropanol or collected in the syringe could not be measured due to the limitations of the micro – GC employed. Furthermore, part of the tars produced during pyrolysis possibly failed to condense in the trap walls at the certain temperature and they were also not measured by the micro – GC or the HPLC. In a similar study performed earlier using the same Pyroprobe reactor [107], it was found that volatile compounds like benzene and toluene fail to condense in the trap and do so in the impinger. The same occurred also for a fraction of the PAHs that were produced. As it is mentioned by Mohan et. al in [7] the complete detection of all the species contained in the bio – oil is impossible. Higher – molecular weight species, mainly the degradation products of lignin, pentoses and hexoses cannot be detected by the HPLC or micro – GC employed in this study and the can constitute up to a 25% fraction of the total bio – oil produced. Thus, keeping in mind that the real tar yield could be higher than the one presented here, we proceed with the presentation of the results.

Starting with the case of Torrocoal biomass, for white Torrocoal the peak in liquid production was observed at 700°C (32.8% d.a.f. of initial sample weight). At higher temperatures the liquid

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content decreased until 900°C before increasing slightly for 1000°C. This is probably due to measurement errors, as it can be concluded from the standard deviation values which are higher (3%, 2.97% and 1.69% of initial sample weight for 800°C, 900°C and 1000°C) compared to the other experiments. Empirically, it can be mentioned that in order to increase the repeatability of the experiments in the Pyroprobe reactor, the trap should be weighed immediately after the completion of the experiment in order to avoid vaporization of the liquid products condensed on its walls. Since this was the first experimental series to be conducted, it will become apparent from the following experiments that even this small -in terms of time- variation improved significantly the quality of the results.

Moving over to black Torricol, the observed trend was a steady decrease of the tar content until 900°C, since the last two values were at the same levels. By comparison with the white Torricol, it can be easily concluded that the torrefaction process leads to a reduction of the liquid yield with the difference ranging from 5.3% of initial sample weight (d.a.f. basis) at 600°C to 11% at 700°C. Furthermore, there was a shift in the liquid production maximum temperature from 700°C to 600°C. It is also noteworthy that the shape of the two curves in Figure 26 is quite similar which shows that the torrefaction process despite altering the pyrolysis process in terms of yields it does not affect the trends in the liquid products formation. Finally, by studying Figure 26, the reader can see that the standard deviation values decreased significantly with the improvements employed in the liquid collection method.

For ECN ash the maximum liquid production value was observed at 600°C. The values kept on decreasing for higher temperatures, resulting to a final value of 15.7% of initial sample weight which is roughly 2.7 times less the initial one. The torrefaction process led to a significant reduction in terms of the liquid product which increased along the torrefaction degree. The values for ECN 250 were in average 11% lower and for ECN 265 19% lower in comparison with the untreated material. Generally, the impact of torrefaction appears to be decreasing for higher temperatures, and the trends observed for all three versions of the material are also quite similar. The only difference among them in those terms is that in the case of ECN 250 the maximum values of the liquid product yield was obtained at 700°C in contrast with the other two experimental series where it was obtained at 600°C.

By comparing the results of the two woody biomasses studied, it can be readily concluded that the untreated ECN ash pyrolysis led to the production of a higher liquid yield compared to the untreated Torricol. The difference is at its highest point at 600°C (13% of initial sample weight (d.a.f. basis)), before being reduced to roughly 5% for the following three temperature points. At 1000°C, the liquid yield of white Torricol exceeds the one of ECN ash. As it was also mentioned earlier, this behaviour of the white Torricol was also observed for black Torricol, indicating a consistency regarding this trend for this biomass. This particular behaviour can be explained in two different ways. The first is that at 1000°C secondary reactions of condensable gases take place that lead to the formation of liquid product. The extra amount of liquid product can also originate from char reactions. On the other hand, the differences between the liquid yield values are small especially in the case of black Torricol. Therefore, it could also be that the liquid yield levels are not particularly influenced by temperature above 800°C in the case of Torricol and perhaps it can be argued that the liquid yield remains more or less stable above this temperature. Regarding the torrefied samples, black Torricol and ECN ash torrefied at 250°C produced approximately the same amount of liquids at almost every temperature. With the increase of the torrefaction severity for ECN ash, the liquid yield of ECN ash 265°C became lower than black Torricol. This result contradicts the proximate

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analysis conducted that indicates a higher volatile content for torrefied ECN ash. Nevertheless, as it is going to be presented in the next section, more gases were produced in the case of torrefied ECN ash. This, along with the previously described uncertainty on the liquid product estimation, can explain these results. Generally, as it was also derived from the solid product gravimetric analysis, it appears that Torrcoal has higher lignin content and a relatively lower cellulose and hemicellulose content when compared to ECN ash. This argument is further supported by this part of the experimental results. However, it should be mentioned that the effect of the parameters of the torrefaction and pelletization processes should not be neglected (additives for pelletization, storage of the materials, etc.). For example, alterations in the structure of biomass caused by the pelletization process and the torrefaction (embrittlement) can lead to a different thermal behaviour of the material. The samples introduced in the Pyroprobe included only particles smaller than 75 μm , but it was not possible to ensure uniform size. Therefore, despite the lower volatile content of black Torrcoal, it is possible that smaller particle size or an increased porosity of the particles led to more efficient heat transfer and therefore to higher biomass to liquid conversion. Nevertheless, these comments are more or less hypothetical due to the complete lack of information regarding the torrefaction and the pelletization process and the relatively small particle size which could render any differences in heat transfer phenomena negligible. More information on this subject can be derived through the subsequent tar analysis.

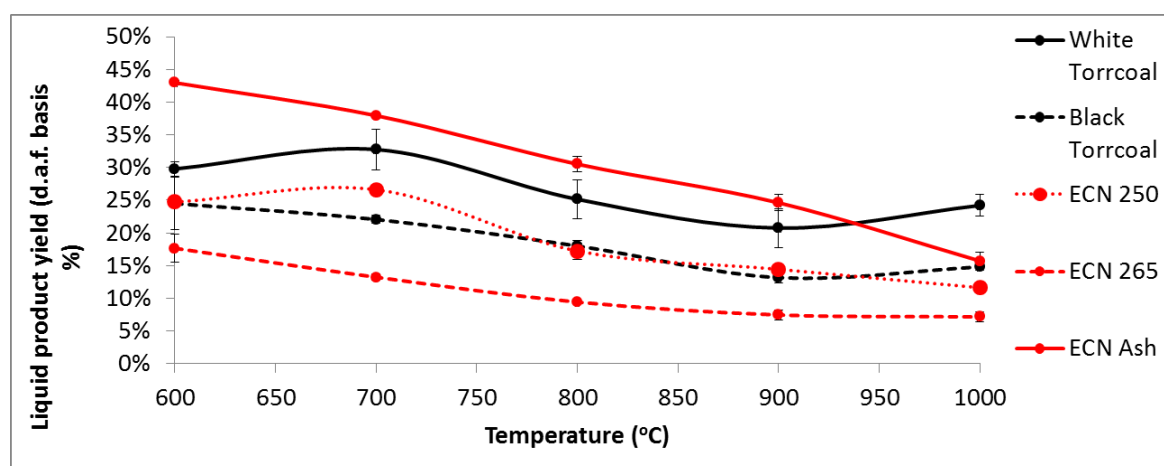


Figure 26: Liquid product from the pyrolysis of Torrcoal and ECN ash (torrefied and untreated) in the Pyroprobe at various pyrolysis temperatures

As it was observed from all the experimental series performed the liquid yield decreased with temperature producing its maximum value mostly at 600°C and at two cases at 700°C. The decrease in the yield above 700°C can originate from secondary cracking of tar products to lighter volatiles (H_2 , CO , CH_4 , C_2H_4 , etc.) despite the short residence time in the apparatus employed in this study [82, 84] or from rigorous scission reactions in the decomposing biomass [92]. It is interesting to note that Nunn et al [84] suggested the evolution of primary pyrolysis products can produce two broad classes of tars, the one being thermally labile and other essentially unreactive. With the increase of temperature the first decomposes either to lighter volatiles or produces more unreactive tar. According to the author, this explains the decrease in tar content and the fact that this decrease becomes less significant in higher temperatures. It can also explain, in our case, the smaller differences between the liquid yields of treated and untreated biomass at higher temperatures. The general trends regarding liquid production from pyrolysis and the temperatures of maximum yields

3. Experimental results

are agreed upon by many researchers [82, 83, 94, 96, 97, 99, 108, 109]. The values of the liquid yield obtained through the present experimental series are comparable with similar studies found in the literature [93, 96, 97, 99, 106, 108-111].

Generally, as it was mentioned in the previous chapter the severe carbon – carbon crosslinking of the biomass carbohydrates prevents the production of both liquid and gaseous products and favours char production. This explains the differences between the torrefied and untreated biomass which also increases along the torrefaction degree. Additionally, the amount of volatiles released during torrefaction, include mainly hemicellulose and to a lesser content cellulose which are the main sources of liquid products [102, 104]. Therefore, the decrease in the liquid yield can be attributed to the crosslinking, the carbonization and the devolatilization of biomass during torrefaction. Furthermore, it should be noticed that torrefied biomass contains less water (moisture) than the untreated one, a factor also contributing in the amount of liquid produced [74]. Similar observations regarding torrefied biomass pyrolysis were made also by other researchers [40, 45, 77, 102, 112]. Generally, the low carbon conversion to bio – oil suggests a reduction in the reactivity of biomass with torrefaction [40, 74], which contradicts our previous TGA findings. Nevertheless, this contradiction arises mainly from the debate in the scientific community on the definition of the term reactivity.

3.2.4 Gaseous Product

In this chapter the behaviour of the gaseous products of pyrolysis are studied for both woody biomasses investigated in the present work. Starting with Torrcoal, it was apparent in both the treated and untreated cases that the amount of gases produced increased for an increase in temperature. White Torrcoal pyrolysis produced 10.5% of initial sample weight (d.a.f. basis) gases at 600°C and 27.4% at 1000°C. The values rose until 800°C, as in the two final temperatures the gas yield was almost the same. The same behaviour was observed for black Torrcoal although the yield values were slightly lower (0.3 – 4%). Nevertheless, the observed difference was very small when compared to the corresponding ones from the liquid and char yield and it becomes apparent only at 800°C due to higher CO₂ production by white Torrcoal.

Regarding the pyrolysis of ECN ash the gas yield increased along with temperature, from an initial 12.5% of initial sample weight (d.a.f. basis) to 36% at 1000°C. The same trend was observed for torrefied ECN ash, both at 250°C and 265°C, for which the reported values were almost identical having a less than 1.5% difference. The only exception was noted at 1000°C where the gas yield for ECN 265 was roughly 4% higher (29% of initial sample weight (d.a.f. basis) opposed to 33%). However, the standard deviation for this experimental point of ECN 265 was much greater than for the rest (2.24% compared to less than 1%), so it is possible that the real difference between the two values is lower than the one presented in Figure 27. Torrefied biomasses gaseous yield was lower than for the untreated material for every temperature, but the difference becomes significant only above 800°C.

3. Experimental results

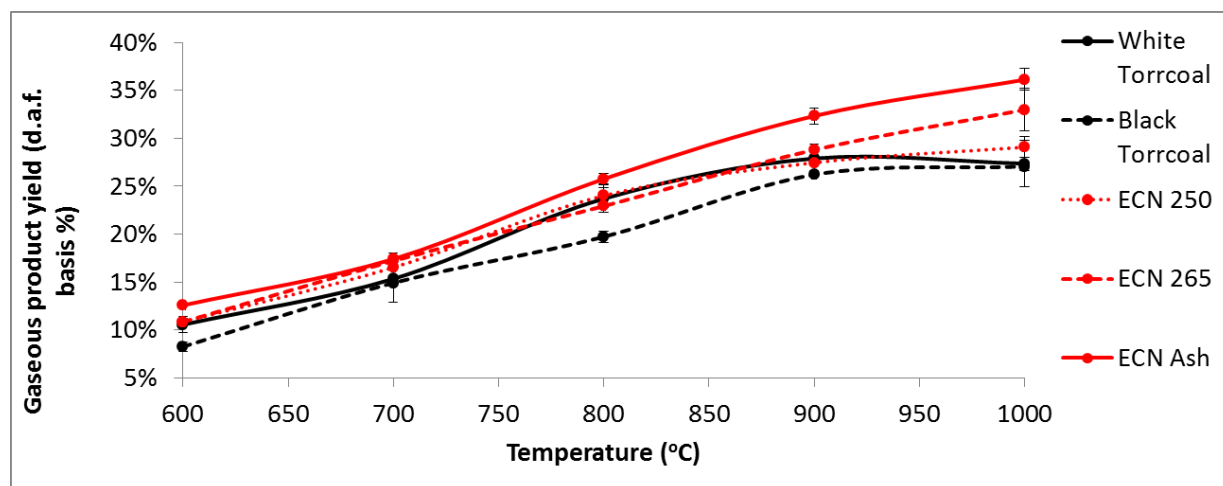


Figure 27: Gaseous product from the pyrolysis of Torrcoal and ECN ash (torrefied and untreated) in the Pyroprobe at various pyrolysis temperatures

When comparing the derived experimental results for the different kind of biomasses studied within this thesis, it becomes apparent that the gaseous yield of ECN ash is higher than for white Torrcoal. Until 800°C the gas product of ECN ash is only roughly 2% (abs.) higher, but for 900°C and 1000°C the difference rises to approximately 4.5% and 7% (abs.), respectively. In the cases of the torrefied materials the differences between the two biomasses remain, but they appear to become steadier over the temperature range studied. These conclusions are supported by the proximate analysis performed that indicates a higher volatile content for ECN ash both treated and untreated. As it was mentioned in the previous section, the amount of liquid product from the pyrolysis of black Torrcoal was almost equal to the yield from the pyrolysis of ECN 250 and significantly higher than the one of ECN 265. In order to investigate this observation, it is useful to look to the amount of volatiles released from the pyrolysis of the torrefied materials in terms of the sum of the liquid and gas product. These data are presented in Figure 28.

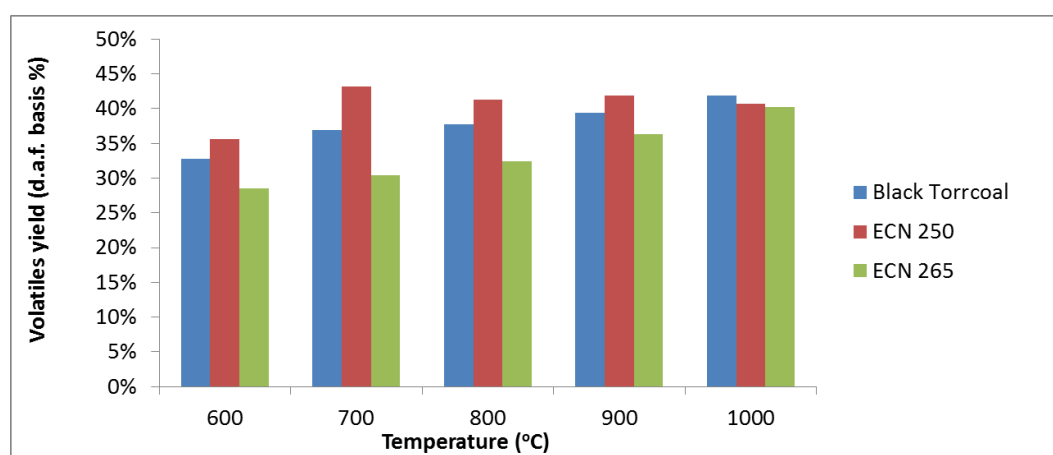


Figure 28: Volatiles yield from pyrolysis of torrefied Torrcoal and ECN ash

By studying the figure it can be immediately concluded that ECN ash torrefied at 250°C produces the higher amount of volatiles. Its production peaks at 700°C (43% of initial sample weight (d.a.f. basis)) and afterwards remains steady around 41% of initial sample weight (d.a.f. basis). This peak corresponds to a higher liquid production as it was also reported before. The other two biomasses experience a more gradual increase in terms of volatiles production, with ECN 265 rising

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from an initial 28.5% of initial sample weight (d.a.f. basis) at 600°C to a final 40% at 1000°C and Black Torricol ranging from roughly 33% of initial sample weight (d.a.f. basis) at 600°C to 42.5 at 1000°C. It is also interesting to note at this point that for all three torrefied species, the volatiles production maxes out at approximately similar percentages. Regarding the comparison of the different species, it can be observed that a higher amount of volatiles was produced by black Torricol pyrolysis compared to ECN 265. This contradicts the proximate analysis that indicated a 66% d.b. volatile content for black Torricol and roughly 69% d.b. for ECN 265. However, the reported difference that averages at 4.2% is not so significant if the uncertainty introduced by the incomplete capturing of the pyrolytic water and higher hydrocarbon species is considered. Furthermore, there are also differences in the torrefaction and pelletization procedures which, as was mentioned in Section 3.2.3, can result to differences in the structure of the samples. Finally, Torricol is constituted from various wood residues. Therefore, the probable non – uniformity of the material, even after the torrefaction, introduces some uncertainty especially regarding the TGA process. Specifically, the reported difference between the volatile contents of ECN 265 and black Torricol (approximately 3%) is not significant enough to lead us to the conclusion that indeed the volatile content of black Torricol, which was torrefied at 300°C, is lower. On the contrary, the experimental results robustly indicate that in fact the opposite is true.

For both biomass species included in this study, the pyrolysis experiments performed showed that there, despite the fact that after torrefaction the gas yield decreases, the effect of this process is not so significant in this regard. Similar conclusions are also presented by other researchers [74, 102]. Additionally, other researchers [45, 112, 113] also reported a slight increase in the syngas yield of torrefied biomass pyrolysis for an increase in the torrefaction temperature. In particular Zheng et. al [104], reported an increase in the non-condensable gas yield with an increase of the torrefaction degree from 240°C to 260°C and a subsequent decrease for a further increase in the torrefaction temperature to 320°C. The authors claim that as the carbonization of biomass increases along with the torrefaction severity leading to a reduction of the gaseous product.

In the following paragraphs, the yields of each gas species are presented and analysed. Starting with CO₂, in the case of ECN ash its production ranged from approximately 8% of initial sample weight (d.a.f. basis) to 11% increasing temperature from 600°C to 1000°C. For ECN ash torrefied at 250°C the corresponding values ranged from 6% of initial sample weight (d.a.f. basis) to 8.5%, while for ECN 265 from 6% to 11%. For the white Torricol pyrolysis 7% of initial sample weight (d.a.f. basis) was the production of CO₂ at 600°C and roughly 11% at 1000°C. For black Torricol, the CO₂ values were slightly lower (5% - 9.5% of initial sample weight (d.a.f. basis)). It is obvious that CO₂ production was only slightly affected by the torrefaction process. In the case of Torricol the average reduction of the CO₂ yield was 1.6%. The average difference between untreated ECN ash and ECN ash torrefied at 250°C was 1.7% and it was reduced by the increase of torrefaction temperature to 1.15%. Generally, as it can also be derived from the Figure 29, the CO₂ yield appears to be more or less stable above 800°C for all the biomasses studied. However, as it can be seen in Figure 29, the value of CO₂ experiences a steep increase at 1000°C for ECN 265. This phenomenon is discussed in Chapter 3.3.4 after the presentation of more relevant data.

Moving over to the presentation of CO production behaviour, firstly it should be mentioned that above 800°C it was the major gas product of the pyrolysis process for all the experiments conducted. Its production at low temperatures was below 5% of initial sample weight (d.a.f. basis), but as the pyrolysis temperature rose, its yield increased significantly compared to CO₂ which is the next majorly produced gas. Between the two biomasses studied ECN ash pyrolysis yielded more CO

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by an average value of 3.5% for all the temperatures studied. At 600°C roughly 4% on a d.a.f. basis of the initial weight were produced, while at 1000°C the percentage rose up to 22% at 4.3% average rate per 100°C. The corresponding values for white Torricol were between 3% and 14%. In contrast with ECN ash, in this case the average increase in the yield was significantly lower (2.6% of initial sample weight (d.a.f. basis)). Also, CO production appears to be stable above 900°C, behaviour also noted for black Torricol. As it can be concluded by Figure 29 not much is different for treated and untreated Torricol in terms of CO production. Only at 800°C a roughly 2% difference was noted in favour of white Torricol, while at the rest temperature points it can be considered as negligible (approximately 0.3% of initial sample weight (d.a.f. basis) on average). For ECN ash, the difference between treated and untreated material CO yield increased in favour of the untreated material as the pyrolysis temperature increased. The average variation between torrefied and non torrefied ash is around 1.5% of initial sample weight (d.a.f. basis) for both cases and is mainly due to the difference noted at high temperatures. The impact of torrefaction severity on CO production can be described as non – existent, according to the present findings as the average difference between the yields of ECN 250 and 265 approached zero. Nevertheless, it should be mentioned that in order to fully assess the effect of torrefaction severity on the CO yield higher torrefaction temperatures should be studied. As it is indicated by some researchers presented in the previous paragraphs of this chapter, the amount of produced gases can be reduced for an increase on the torrefaction severity. Finally, when comparing the torrefied samples, it can be readily concluded also by the previous findings that torrefied ECN ash produces more CO at all temperatures studied.

Regarding the production of CH₄, as for the rest of the pyrolysis gaseous products, its values increased with the increase of the pyrolysis temperature. In all the cases studied its production was insignificant at and below 700°C (1.5% of initial sample weight (d.a.f. basis) or less). Due to the low production values, the differences between the various biomass species are very small. On average CH₄ yield increased after the torrefaction for both cases studied and after the increase on the torrefaction severity for ECN ash. Between the two parent biomass species ECN ash pyrolysis CH₄ yield was higher, starting from an initial 0.2% of initial sample weight (d.a.f. basis) at 600°C and rising up to roughly 4% at 1000°C. The corresponding values for Torricol were 0.2% of initial sample weight (d.a.f. basis) and 3%, respectively. The same trends were also noted for the torrefied species with ECN 265 producing the highest CH₄ yield over the whole temperature range (0.4% - 4% of initial sample weight (d.a.f. basis) between 600°C and 1000°), followed by ECN 250 (0.4% - 3.5%) and black Torricol (0.2% - 3%).

Finally, the H₂ produced from the pyrolysis experiments was also detected. Its production was very limited not exceeding 1% of initial sample weight (d.a.f. basis), but still in significant amounts. However, some trends that can be excluded will be presented for the sake of completeness. In both cases studied torrefaction did not influence the hydrogen yield (0% for Torricol and 0.03% of initial sample weight (d.a.f. basis) for ECN ash on average). Generally, the increase of the temperature led to an increase of the H₂ yield, however only above 800°C it is produced at considerable amounts. Finally, for both treated and untreated materials ECN ash pyrolysis produced more H₂ than Torricol.

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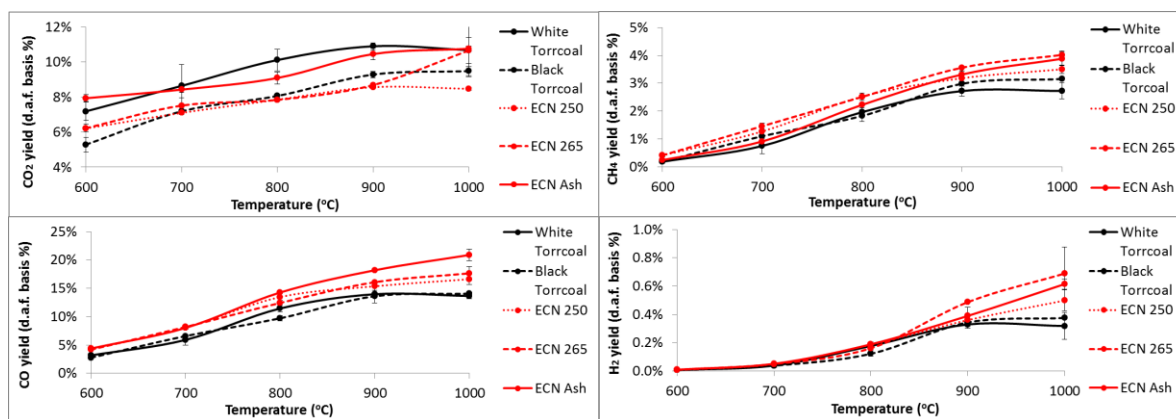


Figure 29: Yields of gas species from the pyrolysis of Torrrcoal and ECN ash (torrefied and untreated) at various pyrolysis temperatures applied in the Pyroprobe

Generally, the total gaseous yield increased along the pyrolysis temperature, a result also confirmed by many other researchers [29, 93, 96-98, 110]. However, regarding the values themselves it is difficult to find much agreement between researchers mainly because of differences in terms of different experimental conditions, biomass feeds and differently expressed yields. In any case there is a study from Kitsiou [93] that confirmed the experimental results of this work. In [93] 10 mg of wood residues were pyrolysed between 600°C and 1000°C in a heated foil reactor. Therefore, the similar experimental conditions in terms of feedstock and reactor type explain the similarities observed. The reader should also keep in mind that there is not much literature available regarding pyrolysis over this temperature range, rendering the collection of relevant data particularly difficult. In terms of the individual gases formed, both the trends and the values obtained are comparable to those of other researchers [83, 91, 93, 94, 98, 108].

Generally CO₂ and CO production levels are indicative of the oxygen content of the parent biomass, since they originate from the cracking of partially oxygenated organic compounds, while light hydrocarbons such as CH₄ are formed by the reforming and cracking of heavier hydrocarbon and tar in the vapour phase [17]. As it was also concluded by the experiments conducted within this thesis, the increase of the gaseous yield was accompanied by a decrease in the liquid yield which mainly contains various tar species. Furthermore, in the same work it is reported that the increase of the pyrolysis temperature leads to a sharp increase of the H₂ yield and a slower increase of the CO yield. The same result came up during the present analysis. Despite the fact that the yield of H₂ was very low, its production rate increase along temperature was significantly higher than the corresponding values for CO. Additionally, it was noted that above 800°C the yields of CO, CH₄ and H₂ presented a small increase for treated and untreated ECN Ash, while their values were stable for both black and white Torrrcoal. The important secondary reactions for a pyrolysis process are cracking, above 700°C, and the water – gas shift reaction ($H_2O + CO \leftrightarrow H_2 + CO_2$), below 810°C [15]. At this temperature range, an increase in the yields of those gaseous species can be attributed to secondary decomposition of tar compounds (cracking) [82, 84], since primary decomposition has ceased. This is also apparent by the relatively stable char and CO₂ yield in all cases studied at this temperature range since they are considered as products of primary devolatilization. First of all, this explains the fact that CO becomes the predominant gas species above 800°C in every case. However, it is obvious that less secondary reactions are occurring for both Torrrcoal species in comparison to treated and untreated ECN Ash. Despite the fact that secondary reactions are supposed to be limited in the present setup their occurrence at high temperatures cannot be totally prevented

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apparently. These findings will be further evaluated in the chapter regarding tar compounds analysis. Furthermore, it was apparent that the CO₂ yield was only slightly reduced through the torrefaction process. This was not so expected, since hemicellulose which decomposes at a great extent through torrefaction is mainly responsible for the release of CO₂. This is mainly due to its higher carboxyl content in comparison to cellulose and lignin which are mainly responsible for CO and H₂ – CH₄ production respectively [114]. On the other hand, the almost negligible differences observed between the three torrefied species are explained from this fact. Therefore, regarding the parent species (white Torricol and ECN Ash) it can be argued that they have similar and perhaps low hemicellulose content. CO₂ is also produced from lignin and cellulose pyrolysis and probably this was the case in this experimental investigation. However, the determination of the structural biomass components quantities in the samples is necessary in order to verify the conclusion above.

In order to determine the quality of the pyrolysis gas produced from the pyrolysis of the biomasses studied, its lower heating value was calculated at every temperature point. The results are presented in Figure 30. The values were calculated using the LHV of gases as they were reported in [115]. As it was expected, the increase of the pyrolysis temperature and the subsequent increase in the production of CH₄ in particular led to an increase of the LHV of the produced gas. Furthermore, at every temperature the torrefied species pyrolysis produced gas of higher heating value compared to the parent biomasses. This reflects the higher methane and at a lower extent the higher hydrogen yield derived from the pyrolysis of those species. Finally, between the two different biomass species studied, ECN ash pyrolysis (treated or untreated) produced higher quality pyrolysis gas.

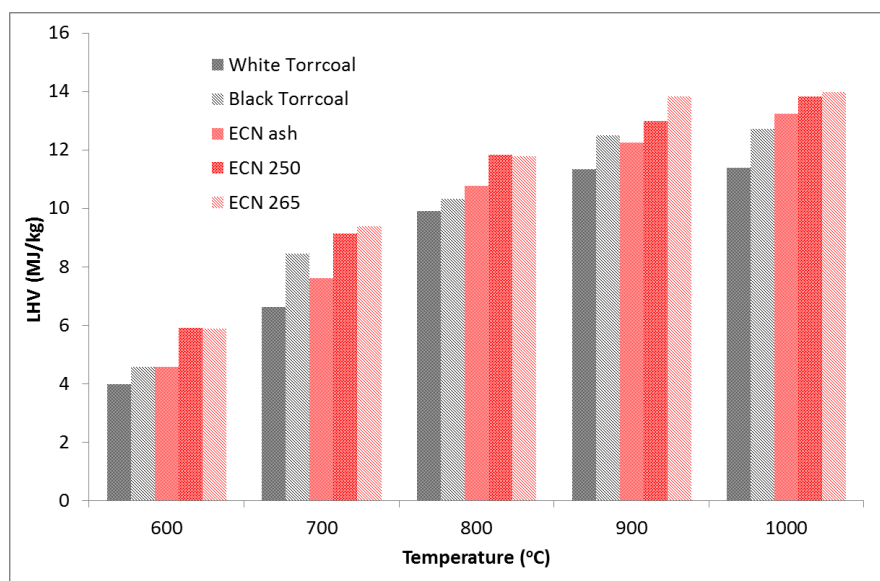


Figure 30: Lower heating value of produced pyrolysis gas in the Pyroprobe at every experimental temperature for the five biomass species studied. The results are presented at MJ per kg of produced gases.

3.3 Tar analysis

3.3.1 Amount of identified tar species

To begin with, in Figures 31 and 32 the total amount of tars identified by the HPLC analysis performed are presented for all the biomass species studied. The results are presented in milligrams per gram of biomass samples mass on a dry ash free (daf) basis. It should be mentioned that these results concern only the species for which standards were available. The ones included are for the

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heterocyclic tars class phenol, for the light polyaromatics class naphthalene, phenanthrene, anthracene and fluorene and from the heavy polyaromatics class fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(k)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, indeno (1,2,3-cd)pyrene and benzo(g,h,i)perylene. The fact that important tar compounds that mainly belong to the light aromatics class like styrene, indene, toluene and ethylbenzene and also hydrocarbons like benzene are missing from the analysis does not allow a broad and complete understanding of the process of tars evolution for the biomass species studied. Nevertheless, the data available were more than enough to indicate trends on tar compounds formation during the pyrolysis of untreated and torrefied biomass species at various temperatures.

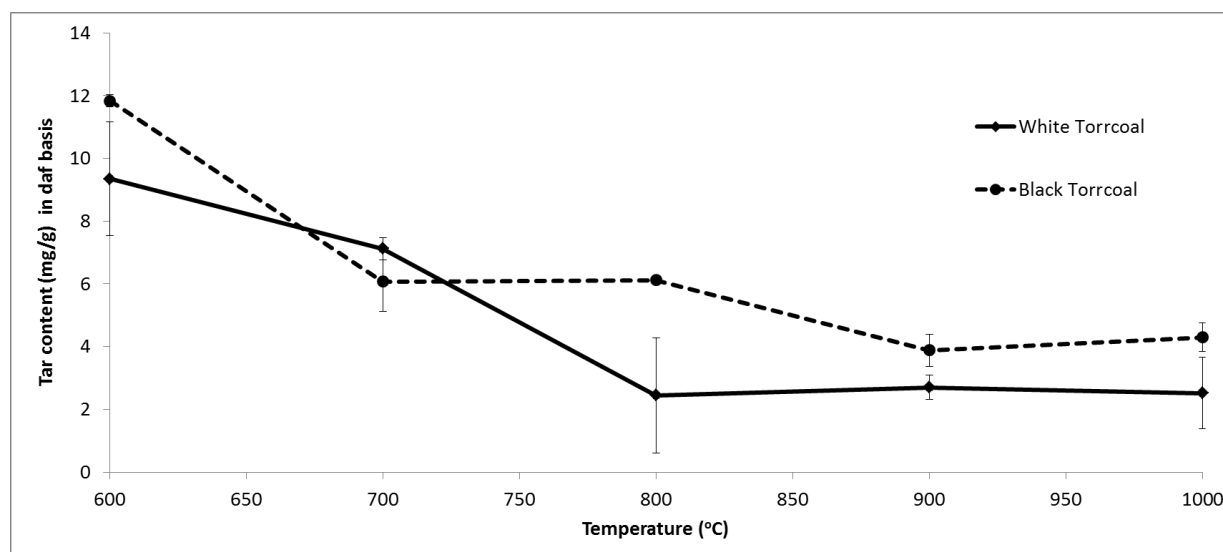


Figure 31: Total amount of identified tar compounds for the pyrolysis of untreated and torrefied Torrrcoal

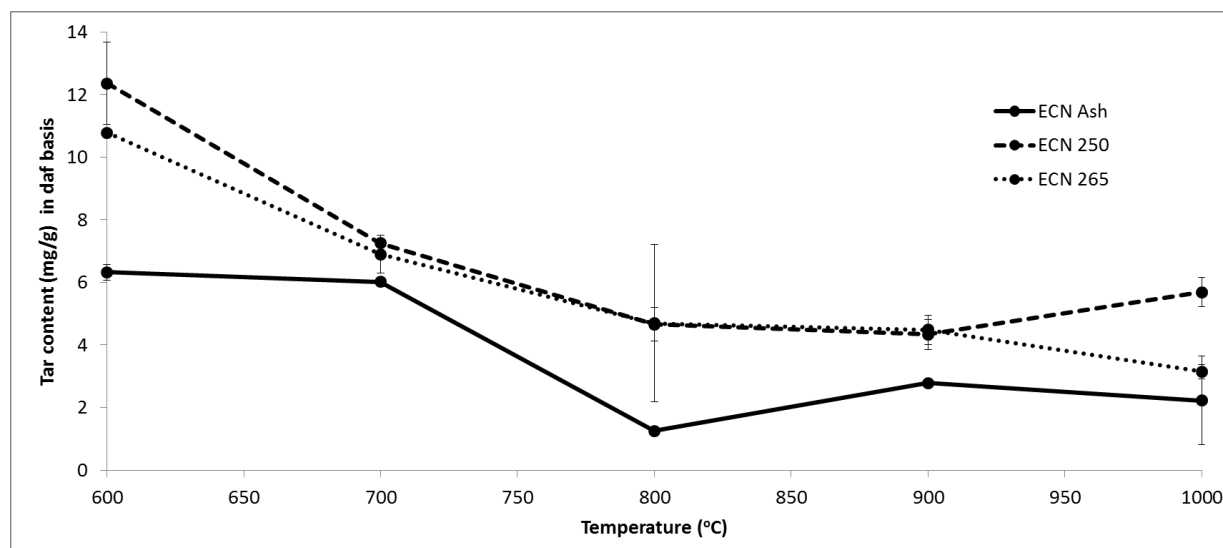


Figure 32: Total amount of identified tar compounds for the pyrolysis of untreated and torrefied ECN Ash

In the case of Torrrcoal, higher amounts of tars were identified for the torrefied (black) Torrrcoal at every temperature except 700°C. Nevertheless, the difference between the values at this temperature becomes less significant if we also consider the standard deviation. The biggest difference was noted at 800°C where Black Torrrcoal pyrolysis produced roughly 3.7mg/g more of identifiable tars. The same behaviour was noted for ECN Ash. At every temperature the amount of

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identifiable tars was higher for ECN 250 and 265 compared to the untreated material. At this case the biggest differences were presented at 600°C (6mg/g and 4.5mg/g more for ECN 250 and 265 respectively). Furthermore, the effect of torrefaction degree on the amounts of tars identified appears to be limited with the exception of 1000°C where ECN 250 pyrolysis produced roughly 2.5mg/g more than ECN 265 pyrolysis. This particular behaviour for both biomasses can be mainly attributed to the higher phenol yields for torrefied materials pyrolysis as it is going to be presented in the Chapter 3.3.2. In general, with the exception of ECN Ash pyrolysis at 1000°C phenols were the major tar species produced. Therefore, taking also into account the increase of light and heavy polyaromatic tars above 800°C the total amount of identified tars (phenol) decreases until 800°C before maintaining a more or less steady behaviour, when also PAHs are identified. More conclusions will be drawn by studying the individual tar evolution profiles in the following chapters.

3.3.2 Phenols

3.3.2.1 Effect of pyrolysis temperature on phenol production

As it can be derived from Figure 33, the amount of produced phenols is decreased with increasing pyrolysis temperature for treated and untreated Torriccoal. For white Torriccoal the biggest drop is noted from 700°C to 800°C. Above this temperature the phenol yield appears to be more or less stable. On the other hand black Torriccoal presents the biggest drop in phenol production from 600°C to 700°C. So, the peak in phenol production at 600°C is followed by two valleys at 700 – 800°C and 900 – 1000°C. At 1000°C the slight increase in the phenol yield compared to 900°C is minor, if the standard deviations are taken into account. In general, for white Torriccoal pyrolysis phenol yield decreased by approximately 86% from 600°C to 1000°C, while the corresponding value for black Torriccoal was lower (71.5%).

Regarding untreated and treated ECN Ash pyrolysis the same general trend can be derived for the relation between the phenols yield and the pyrolysis temperature. In the case of ECN Ash, phenol yield is almost the same at 600°C and 700°C before experiencing a significant decrease at 800°C. Its values are increased again at 900°C before dropping again at 1000°C. Nevertheless, in total the amount of produced phenols appears to stabilize above 800°C if we also consider the standard deviations. Moving over to ECN 250, the phenol yield dropped from 600°C to 700°C and from there to 800°C, with the first being the most significant reduction. Above 800°C the differences between the obtained values are not significant. For ECN 265, again the amount of produced phenol experiences the most significant amount of its total decrease between 600°C and 800°C. At higher temperature the yield continues to drop, but at a much lower rate. Finally, also in the case of this biomass species the untreated materials (ECN Ash) pyrolysis experienced the biggest decrease in phenol yield for increasing pyrolysis temperature from 600°C to 1000°C (roughly 89%). The corresponding values for the torrefied samples were 69% and 81% for ECN 250 and 265, respectively. However, the effect of torrefaction on the production of phenol is going to be discussed for both cases in the next section.

When comparing the two parent biomass species studied, it can be readily concluded that white Torriccoal produces a higher amount of phenol than ECN Ash at the entire pyrolysis temperature range. Nevertheless, the difference between the two declines as we move to higher temperatures. In total, this behaviour is consistent with the previous findings. As it was derived from the gravimetric char measurements, the higher char yield from the white Torriccoal pyrolysis is indicative of higher lignin content compared to ECN Ash. Further evidence suggesting higher lignin

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content for white Torrrcoal were also obtained from the examination of the liquid and gaseous yield. As it was mentioned earlier phenol and phenolic compounds in general, mainly originate from the lignin fraction of biomass. Therefore, the higher phenol production from white Torrrcoal further elaborates the previous conclusions. On the other hand, the conclusions derived from the comparison regarding the torrefied species are not that straightforward. Taking into account the standard deviation values and the closeness of the reported values, it can be argued that the differences between the torrefied species in terms of phenol production are negligible.

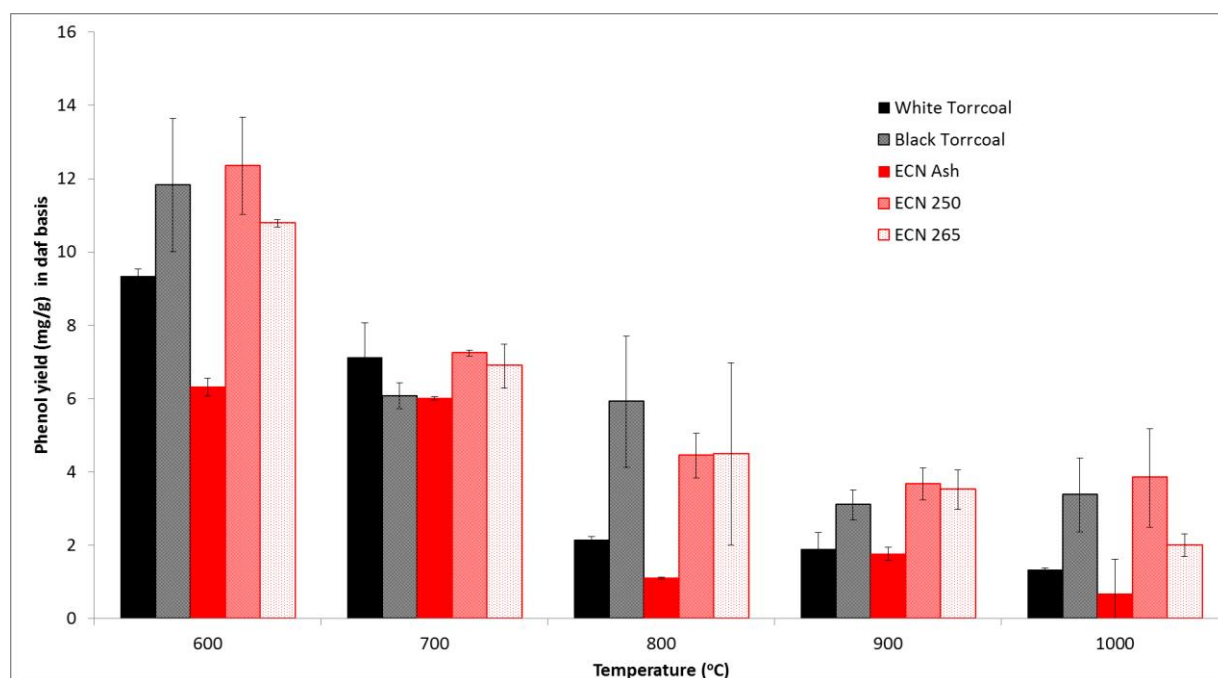


Figure 33: Phenol yield from the pyrolysis untreated and torrefied Torrrcoal and ECN Ash

It is useful at this point to investigate the data available from the literature regarding phenol production from pyrolysis of biomass materials. Despite the fact that biomass pyrolysis is a very well investigated process it proved to be difficult to create a large database of relevant findings. The main reason for this was the fact that the temperature range in which fast pyrolysis tests were performed in the present work (600°C – 1000°C) is higher than the temperatures often employed in the literature. This is anticipated, since as it was mentioned in Chapter 1, fast pyrolysis processes are most usually performed at temperatures around 500°C especially if the maximization of the liquid product is the goal. Nevertheless, in the following paragraphs, a sort summary of relevant studies from the literature is going to be presented. Not all of the following studies were performed using similar equipment to Pyroprobe. However their results can also serve as indicators for the trends in phenol formation for various temperatures.

Jiang, et al. [116] in their investigation of Alcell and Asian lignin, reported that the yield of phenol increased steadily with the pyrolysis temperature (from 400°C to 800°C) during experiments performed in a Pyroprobe yielding however significantly higher amounts compared to the present study despite the smaller (1 mg) sample size. One reason for that could be the higher holding time employed in this study (15s). It is also notable that the reported values for phenolic compounds decrease in total for an increase in temperature. According to the authors, the carbon – carbon bonds need a higher temperature to be broken down due to high bond dissociation energy.

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Furthermore, they argue that lignin in particular yields less liquid product compared to cellulose or whole biomass at lower temperatures.

Thangalazhy-Gopakumar, et al. [117], conducted pyrolysis experiments of pine wood chips and switchgrass in a Pyroprobe and found similar to the aforementioned results. Namely, they found that the concentration of all the compounds in the phenol group increased significantly with temperature (450 – 750°C), mostly between 500 and 650°C. An interesting observation of the authors was that because of the small biomass sample used (100 – 300µg), the amount of the basic constituents (cellulose, hemicellulose, lignin) present in each sample, can vary significantly leading to high uncertainty of the results.

A different trend was observed by Zhang, et al. [118] regarding the effect of temperature on phenol production. More specifically, in their paper it is noted that phenol production increased until a temperature of 800°C and then it was reduced until it was completely converted above 1000°C. The biomass used in this study was hinoki cypress sawdust and the experiments were conducted in an entrained drop – tube furnace with a feeding rate of 60 – 70g/h and a gas residence time of 3.5 – 4s.

Yu, et al. [119], performed pyrolysis experiments in a free – fall reactor with a gas residence time of roughly 1.5s using birch wood as a feedstock. The results also reported a decrease in phenol production as the pyrolysis temperature increased from 700 to 900°C. In this case the authors claim that the observed drop of the phenol to naphthalene ratio can be explained by the fact that aromatic compounds are formed from intermediates that are produced from phenolic compounds decomposition.

Similar observations were made by Brage, et al. [120] who conducted pyrolysis experiments of hardwood chips in a two – stage pyrolyzer. In particular the reactor had two separate heated zones, the one being the pyrolysis chamber operated at 700°C and the other being the cracking chamber which operated between 700°C and 900°C with the addition of steam. Despite the fact that the experimental conditions differ substantially from the ones employed in the present work, the investigation performed gives some information about the correlation between the pyrolysis temperature and the phenol yield. In particular the authors claim that with increasing temperature the amount of aromatics produced is increased at the expense of phenols.

Dufour, et al. in [121] made some important observations regarding phenol formation from the pyrolysis of 0.5 g of wood chips in a quartz tubular reactor which is similar to Pyroprobe. The gas residence time was between 0.5 and 0.7 s. The authors observed a decrease in phenol yield from 700°C to 1000°C. Moreover, they noted that between 800°C and 900°C phenol, along with indene and toluene, were almost completely converted to benzene and naphthalene. They claim that generally phenol is decomposed to form benzene, indene and naphthalene through cyclopentadienyl radicals and then to higher unsubstituted aromatic compounds. They also link phenol conversion to soot formation.

Another group of researchers (Branca, et al. [122]), conducted conventional pyrolysis experiments in a lab scale fixed – bed pyrolyzer, using 180g of beech wood as sample. By performing these experiments at temperatures between 327 and 627°C, they found out that the total amount of phenols group compounds produced increased along with temperature. This particular behaviour applies also for phenol. In their report it is argued that phenols, along with syringols and guaiacols are derived mainly from lignin degradation. Nevertheless, in contrast with the latter two, phenols yield increases with temperature, something that indicates that they are formed also from secondary degradation. Syringols and guaiacols originate from the primary decomposition of lignin.

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Demirbas [123], conducted beech and spruce wood pyrolysis in a fast pyrolysis reactor, similar to Pyroprobe, at temperature between 350 and 600°C. For both the biomasses studied an increase of the phenol yield along with the temperature was observed.

An experimental series performed with maple wood bark is also presented by Pakdel, et al. in [124] but the experimental parameters are not mentioned. However, in this work it was reported that the difference in the phenol yield does not vary greatly with temperature, despite an observed increase in phenolic yields at lower final temperatures. The authors elaborate on their findings by stating that phenolic compounds structures are preserved at lower temperatures, since some phenols are primary pyrolysis products, produced mostly by the cleavage of $\beta - O - 4$ aryl ether bonds in lignin. Furthermore, other operational parameters that influence the phenolic yield were studied in this work. To begin with, according to the results obtained from beech wood pyrolysis under vacuum conditions in a 1L batch reactor, faster heating rates lead to higher phenolic yield. Generally, secondary degradation reactions of phenolic compounds are prevented when primary vapours are quickly taken out from the hot chamber.

Finally, a similar study was performed by Henkel, et al. in [125] regarding the pyrolysis of invasive Chinese tallow tree in a low frequency inductively heated reactor. In this case a sample of 30g was used in the experiments. According to the results presented in their paper, those researchers claim that the phenolic yield, in terms of percentage of the liquid fraction obtained, increased for an increase in temperature from 500 to 550°C, before dropping largely at 600°C and continuing to increase from this temperature until 700°C.

The results of the aforementioned studies, along with some more are included in the literature table in Appendix I. Additionally, in Figure 34 some of the results are presented in comparison to the results obtained from the present study. Nevertheless, the reader should be aware that all the results are presented as a percentage of the initial mass sample, but the basis (as received, dry, dry ash free) is not common for all the results due to lack of sufficient data required for the conversion. The purpose of this graph is mainly to highlight the fact that the values obtained from the literature are similar to the values derived from this work in numerical terms. On the other hand, as it was made clear from the previous discussion, there is not a clear trend indicated from the literature regarding the evolution of phenol from biomass pyrolysis at temperatures higher than 600°C. In particular, some researchers have presented an increase in phenol production in the temperature range from 600° to 800°C [116-118, 125, 126]. However, there are also studies that support the trends derived from the present one [120, 121, 127] even partially (for the temperature range 800°C – 1000°C) [118].

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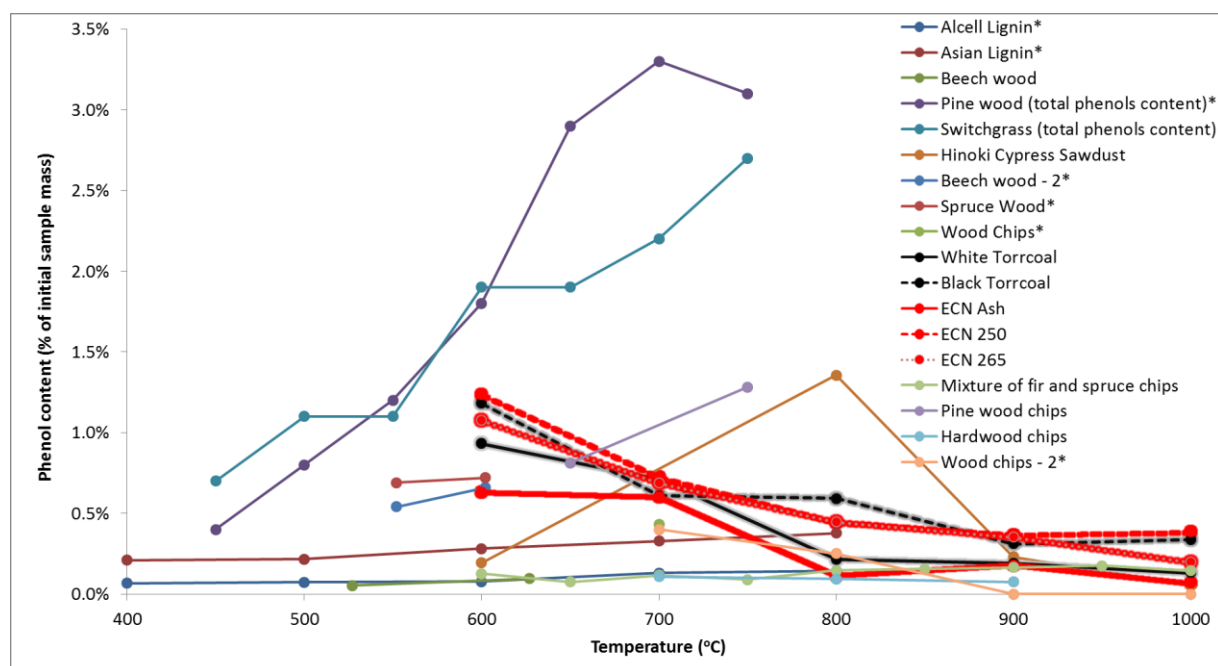


Figure 34: Phenol evolution temperature profile from the pyrolysis of various biomass species. The asterisk marked lines correspond to experiments performed in a Pyroprobe reactor or a very similar one in terms of basic operation (heating method, sample handling, etc).

3.3.2.2 Effect of torrefaction

As it can be observed by studying Figure 34, with the exception of Torrrcoal at 700°C torrefied biomass appears to produce a significantly higher amount of phenols compared to the untreated biomass. Furthermore, it is also apparent, that the difference on the phenol yield of treated and untreated material was higher above 800°C in both cases studied. What is interesting is that its trend was common for both the biomass materials studied. In particular the difference decreased from 600°C to 700°C before rising again majorly at 800°C. At 900°C it dropped again before increasing finally at 1000°C. It should also be mentioned, that despite the high values of standard deviations in some experimental points, the comparison between treated and untreated materials remains valid. The same cannot be said for the effect of the torrefaction degree. In absolute numbers it appears that the increase of torrefaction degree led to a decrease in the pyrolysis phenol yield, with the exception of 800°C where a 1% increase was noted. In particular a 13% and 48% decrease was noted at 600°C and 1000°C respectively, while at 700°C and 900°C the corresponding value was roughly 4.5%. However, in every case the reported difference between the two torrefied species (ECN 250 and 265) in terms of phenol production was lower than the sum of their standard deviations.

3.3.3 PAHs

The light polyaromatic species investigated in this thesis were naphthalene, anthracene, fluorene and phenanthrene. HPLC analysis for this particular species was performed for experiments conducted at 800°C and higher, since it was assessed that at lower temperatures their yields would be more or less insignificant and therefore undetectable. This decision was based also on data from the literature as it is going to be presented subsequently.

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Starting with Torrrcoal, for both treated and untreated materials the light polyaromatic tar fraction yield increased along with the pyrolysis temperature. The light polyaromatic content increased majorly at 900°C (roughly 2.5 times higher for white Torrrcoal and 3 times for black) compared to 800°C. The yield continued to increase at 1000°C but the increase was smaller (50% and 20% for white and black Torrrcoal respectively), considering also the standard deviation values. The same behaviour was noted for ECN Ash and ECN 250. The light polyaromatic yield increased from 800°C to 900°C by approximately 5.6 and 2.6 times respectively and 0.4 and 2.5 times from 900°C to 1000°C. For ECN 265 the light polyaromatic yield was quadrupled from 800°C to 900°C but it was slightly decreased by 9% from 900°C to 1000°C. The major increase in light polyaromatic yield above 800°C, along with particularly low concentrations noted at 800°C, justifies the decision of not analysing the samples obtained at 600°C and 700°C for PAHs in general as it is also going to become apparent by the presentation of the results for heavier polyaromatics. In general, it can be concluded, that light polyaromatics production experiences a steep increase for an increase in pyrolysis temperature from 800°C to 900°C. For 1000°C pyrolysis temperature the increase in their yield is significantly smaller or even negligible taking also the standard deviations into account.

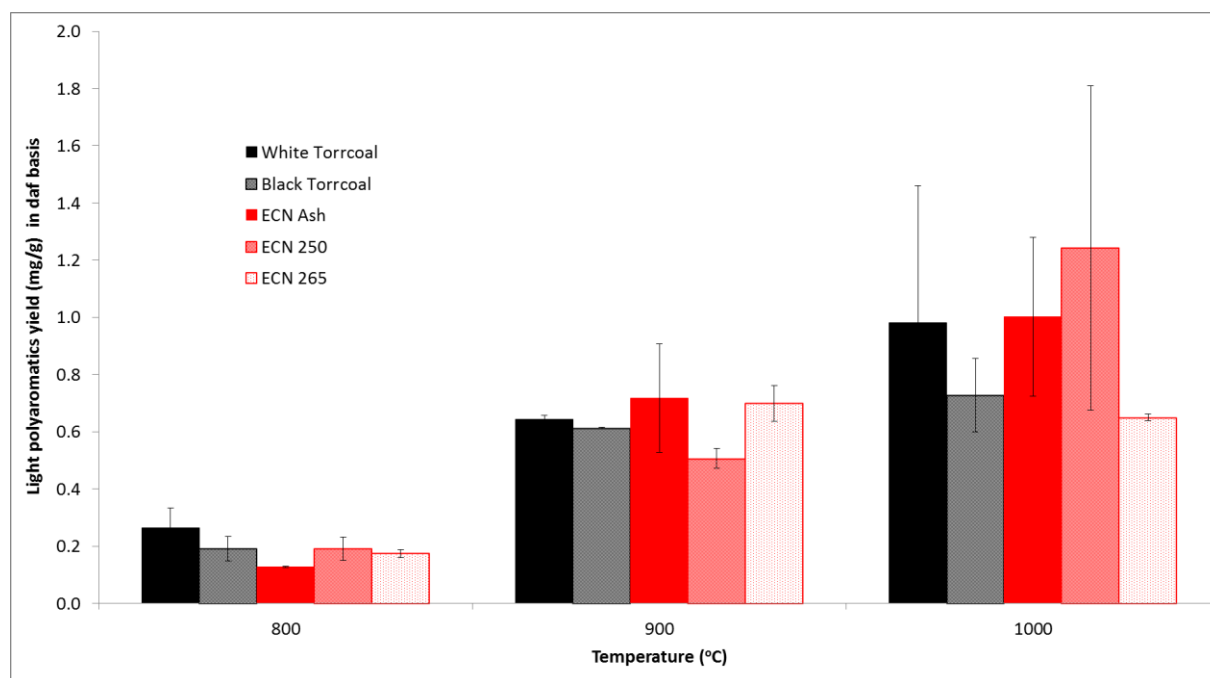


Figure 35: Light polyaromatics yield for the pyrolysis of untreated and torrefied Torrrcoal and ECN ash in the Pyroprobe at various temperatures

Regarding the effect of torrefaction on the light polyaromatic pyrolysis yield, for Torrrcoal, torrefaction appears to have led to a decrease in their yield which was more than 25% at 800°C and 1000°C and roughly 5% at 900°C. On the contrary, no specific trend could be observed for ECN Ash. For ECN 250, the amount of pyrolysis produced light aromatic tars increased after torrefaction in the case of pyrolysis at 800°C and 1000°C by 33% and 19%, respectively, while it decreased for 900°C. Moving over to ECN 265, after the initial increase in light aromatic yield for 800°C for the torrefied material, a decrease of 35 and 54% was noted for 900°C and 1000°C. Similarly, no clear trend was also apparent regarding the effect of the torrefaction degree on the light polyaromatic yield. More specifically, for a higher torrefaction degree (ECN 265) the production of light polyaromatic species was higher in the case of pyrolysis at 900°C by 38%, while it was lower for 800°C and 1000°C by 9%

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and 48%, respectively. This uncertainty described is strengthened by the high values of standard deviations especially at 1000°C. Therefore, if a conclusion has to be derived regarding the effect of torrefaction and its severity in light polyaromatic tars formation from pyrolysis, it is that they do not have a particular influence in their formation. Only in terms of percentage of identified tars it appears that the light polyaromatic yield is decreased upon torrefaction.

When it comes to differences in the light polyaromatic yield from the pyrolysis of the two biomass species studied, it can be easily concluded by studying Figure 35 that no major differences are present between the Torrcoal and ECN Ash, both torrefied and untreated. Again taking into consideration the standard deviation values it appears that the production of light polyaromatic species from the pyrolysis of each biomass is at the same levels. Perhaps, it will be more informing to compare the two biomasses in terms of individual compounds formed, as it is done in the following paragraphs.

Regarding the individual light polyaromatic species detected through the HPLC analysis, naphthalene was the major light polyaromatic and PAH in general species in almost every case. The only exception was noted in the case of ECN 265 pyrolysis at 1000°C (0.3 versus 0.14 mg/g in daf basis). Nevertheless, as it is going to be presented also in the chapter dedicated to naphthalene, this was the only case that a decrease in the naphthalene yield was presented from 900°C to 1000°C. Therefore, without neglecting the fact that phenanthrene values are high and comparable to the ones of naphthalene, there is a chance that naphthalene values were actually higher in this particular case. For Torrcoal pyrolysis the values of naphthalene yield were more than two times higher than phenanthrenes (0.6 versus 0.23 mg/g for white and 0.4 versus 0.175 mg/g for black Torrcoal). These two compounds were followed by anthracene and fluorene at this particular order. Every compounds detected concentration increased with the increase of the pyrolysis temperature. The same behaviour was also noted for treated and untreated ECN Ash, with the exception for ECN 265 that was mentioned earlier. For both treated and untreated ECN Ash the values of naphthalene were still higher, but much closer to the ones of phenanthrene compared to the case of Torrcoal. Furthermore, again the succession was repeated with anthracene and fluorene values following phenanthrene yield.

In this paragraph the yields of fluorene, phenanthrene and anthracene from the pyrolysis of Torrcoal and ECN Ash are compared. It should be mentioned that the comparison is performed separately for torrefied and untreated species. To begin with, fluorene yield was higher for both treated and untreated ECN Ash pyrolysis with the exception of ECN 250 at 800°C. For the untreated materials, phenanthrene yield was higher for ECN Ash pyrolysis at 900°C and 1000°C. Regarding the torrefied species the pyrolysis of ECN 265 produced higher amounts of phenanthrene at all the temperatures studied in contrast to ECN 250 pyrolysis that yielded higher amounts of phenanthrene than black Torrcoal only at 1000°C. Anthracene production had exactly the same behaviour as phenanthrene for both treated and untreated materials. Regarding the effect of torrefaction on the pyrolysis of the species studied, the same conclusions derived before for the light polyaromatics in general can be derived again. However, the high standard deviation values render any comparison at this level at least dubious. The values of the differences between the torrefied and untreated materials are not high enough to overcome the effect of the standard deviations. Of course, the same stands for the comparison of Torrcoal and ECN Ash performed before. Nevertheless, in this case the cumulative standard deviation values were lower. Consequently, the comparison still has validity.

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Moving over to the heavy polyaromatic tar species, it is also apparent from studying Figure 36, that their production becomes significant above 800°C for all biomass species studied, treated or untreated. For the pyrolysis of white Torrrcoal the amount of produced heavy polyaromatics was roughly 6 times higher for 900°C compared to the corresponding value at 800°C. At 1000°C, the increase was significantly smaller (roughly 37%). The reported increase was even higher for black Torrrcoal as the heavy polyaromatic tar yield became approximately 14 times higher at 900°C. Again the increase was reduced dramatically from 900°C to 1000°C (22%). It can be safely concluded that increasing the pyrolysis temperature from 900°C to 1000°C did not influence significantly the heavy polyaromatics production from white and black Torrrcoal. The results obtained from the pyrolysis of treated and untreated ECN Ash were similar. In the case of ECN Ash, the amount of heavy polyaromatics increased 20 times from 800°C to 900°C, while it was only doubled from 900°C to 1000°C. For ECN 250, the initial value of 0.02 mg/g of initial sample mass (daf basis) rose to 0.15 mg/g at 900°C and finally reached 0.6 mg/g at 1000°C. Finally, for ECN 265 the corresponding values were 0.02 mg/g, 0.26mg/g and 0.49 mg/g at 800°C, 900°C and 1000°C respectively. It is apparent from the results presented above, that the main part of the production of heavy polyaromatics from the pyrolysis of the biomass species studied is activated around 900°C. Until the pyrolysis temperature of 1000°C their yield keeps increasing but the rate of production is reduced significantly.

In contrast with the case of light polyaromatic species, there are significant differences in the amount of heavy polyaromatic tar species produced from the two biomass species studied. In particular, for pyrolysis at 900°C the production of this tar class is double for the untreated ECN Ash in comparison to the untreated Torrrcoal. At 1000°C the corresponding value for ECN Ash became 2.6 times higher than for white Torrrcoal. In regards to the torrefied materials, at 900°C black Torrrcoal and ECN 250 present similar values of produced heavy polyaromatics while ECN 265 exceeds them both by roughly 70%. Nevertheless, at 1000°C the corresponding values for ECN 250 and 265 are more than double than the one of black Torrrcoal.

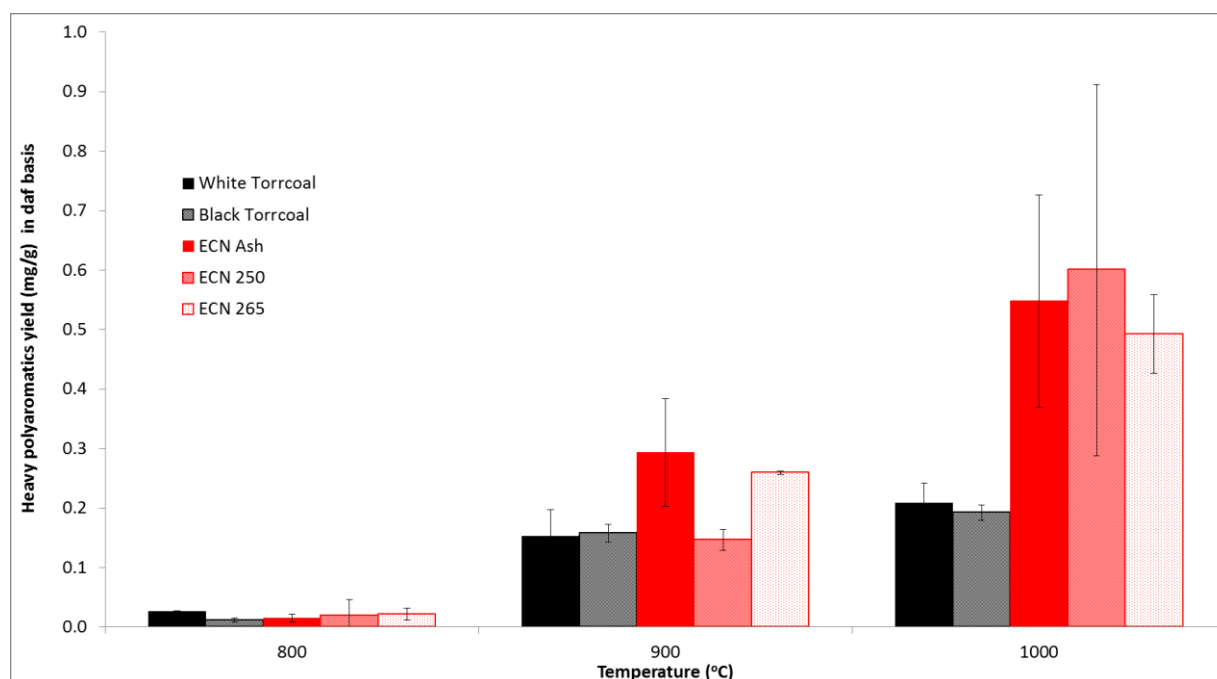


Figure 36: Heavy polyaromatics yield for the pyrolysis of untreated and torrefied Torrrcoal and ECN ash in the Pyroprobe at various temperatures

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Regarding the effect of torrefaction on the heavy polyaromatics yield from the pyrolysis of the treated and untreated materials, it appears that this process did not influence their production greatly in any way. As it can be observed in Figure 36, the obtained values for black and white Torrrcoal are very similar at 900°C and 1000°C. At 800°C the yield of white Torrrcoal pyrolysis is almost triple but the values are particularly low. For ECN Ash the values for 800°C and 1000°C are similar taking into consideration the standard deviation values in the latter temperature. At 900°C ECN Ash and ECN 265 had similar values (0.29 mg/g in daf basis and 0.26 mg/g respectively), while ECN 250 values were lower (0.15 mg/g). Nevertheless, the standard deviation especially in the case of ECN Ash at this particular temperature, leads more to the conclusion that the values of the three species are similar.

In terms of individual heavy polyaromatic tar class compounds, for both treated and untreated Torrrcoal pyrolysis, pyrene was the major one identified (0.09 and 0.075 mg/g daf basis respectively), followed closely by fluoranthene (0.08 and 0.06 mg/g daf basis). Among the rest heavy polyaromatic compounds benzo(a)anthracene and chrysene were identified at appreciable amounts for both cases. Benzo(b)fluoranthene for the white Torrrcoal and benzo(k)fluoranthene and benzo(a)pyrene for the black Torrrcoal were also identified but in very low concentrations. Moving over to treated ECN Ash pyrolysis, again pyrene and fluoranthene were the heavy polyaromatic species with the higher concentrations with the first being slightly higher (0.22 versus 0.21 mg/g and 0.18 versus 0.16 mg/g for ECN 250 and 265, respectively). For untreated ECN Ash pyrolysis fluoranthene was slightly higher than pyrene (0.174 versus 0.167 mg/g). Regarding the rest heavy polyaromatic compounds identified, again benzo(a)anthracene and chrysene and this time also benzo(a)pyrene were also detected at an appreciable extent. Other compounds identified at even lower concentrations were benzo(b)fluoranthene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno (1,2,3-cd)pyrene for ECN Ash, benzo(k)fluoranthene for ECN 250 and benzo(b)fluoranthene and indeno (1,2,3-cd)pyrene for ECN 265. Additionally, it has to be mentioned that for both Torrrcoal and ECN pyrolysis, treated and untreated, the individual compounds concentrations increased with the increase of the pyrolysis temperature. Finally, it should be noted that the results presented for all biomass species and mostly the comparisons, are meant to be indicative since the high values of the standard deviations in all cases do not allow us to draw solid conclusions.

3.3.3.1 Naphthalene

Before delving into the results of the present work regarding the naphthalene yield from the pyrolysis of the selected species, it is useful to present some literature data regarding its formation trend but also of PAHs in general. It should be mentioned that naphthalene was singled out from the other PAHs because firstly it was the majorly produced specie and secondly more data were available in the literature about its formation trends.

Regarding the effect of the increase of pyrolysis temperature on the evolution of naphthalene a study was conducted by Morf, et.al in [128]. The experimental setup was a laboratory scale fixed bed pyrolysis reactor and the biomass feed, namely wood chips, were fed in the reactor under a 1.6kg/h rate. According to this study, the amount of PAH and consequently naphthalene, is negligible until a temperature between 750 and 800°C. From there and on, a steep increase of their yield was reported until the final temperature of 1000°C. Furthermore, this group of researchers connected this increase in PAH production to the simultaneous increase they observed in the

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hydrogen yield. They claim these results are self – evident due to the fact that the formation and growth of naphthalene and other PAH are accompanied by hydrogen abstraction.

Zhang, et al. [118] performed pyrolysis experiments of hinoki cypress sawdust in an entrained drop – tube furnace employing a feed rate of 60 – 70 g/h. Under pyrolysis temperatures ranging from 800°C to 1200°C, the amount of naphthalene formed, presented an increase from 800 to 900°C before starting to drop until the temperature of 1200°C. The authors mention that naphthalene proved to be the most stable poly – aromatic compound among those detected, due to the fact that it was still detectable at 1200°C. Furthermore, since gasification experiments were also conducted in this study, it was reported that steam gasification stimulated the formation of naphthalene. This increase for aromatic species without substituent groups (benzene, naphthalene, anthracene, pyrene etc.) was accompanied by a decrease of aromatic species with specified substituent groups (styrene, xylene, phenol and methylnaphthalene). This behaviour suggests, according to the authors, that aromatic compounds without substituent groups partly originate from the decomposition of alkyl- or phenolic – OH substituted ones.

In another study, Yu, et al [119] conducted birch wood pyrolysis in a pressurized free – fall reactor under a constant feed rate of 1 kg/h. In their report they present an increase in PAH and naphthalene in particular, amounts as the pyrolysis temperature increased from 700 to 900°C. They also introduce the P/N ratio (phenol to naphthalene) which drops as a result of the increasing temperature and they claim that it is reactor specific.

Zhou et al. [129] observed a similar behaviour in the pyrolysis experiments they conducted with lignin in a fixed bed reactor. In particular they observed a steep increase in the production of naphthalene and PAHs in general above 700°C. In their conclusions they suggest that at higher temperatures the amount of PAHs increased more significantly. In general they also noted that with the increase of the temperature the percentage of 2-ring PAHs decreased in contrast to the percentage of 3- and 4-ring PAHs that showed the opposite behaviour.

Fassinou, et al. [126], conducted slow pyrolysis of pine wood chips in a two – stage gasifier. Despite the major differences between the process employed in this work and the present one, some trends that could apply to both can be extracted. Also in this case, naphthalene production was negligible at 650°C (0.9 mg/g) and with an increase of temperature at 750°C its value rose to 9.4mg/g. Furthermore, it was reported that by increasing the residence time, the naphthalene yield is decreased. Similar results, but regarding PAH evolution in general, were presented by Henkel et al. [125] for the pyrolysis of 30g of Chinese tallow wood in an inductively heated reactor. PAH production was zero until the temperature of 700°C.

An interesting observation was made by Mullen et al. [45] who conducted catalytic pyrolysis of several lignins. The authors observed a higher benzene and naphthalene yield from the pyrolysis of samples with a 1:1 lignin/cellulose mixture than from the pyrolysis of pure lignin samples. Therefore, they argue that cellulose is more selectively converted to unsubstituted aromatics than lignin.

The work of Jess [130] sheds some light on the mechanisms of aromatic hydrocarbons thermal reactions after their production from solid fuels pyrolysis. According to the author, the main condensed products of naphthalene pyrolysis are soot and soot precursors such as pyrene and fluoranthene. There are also organic products of naphthalene conversion which are mainly benzene, CH₄ and C₂ hydrocarbons. Naphthalene conversion starts at roughly 1000°C and is completed at 1300°C according to this study. However, as it was indicated by the previously presented studies, the

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production rate of naphthalene decreases before this temperature. Consequently it is likely that its conversion can be initiated at slightly lower temperatures.

Finally, Dufour et al. in a study that was mentioned also in Chapter 3.3.2 [121], investigated the formation of PAHs and naphthalene in particular in the temperature range between 700°C and 1000°C. The authors noted an almost three times increase in naphthalene yield from 700°C to 800°C and a reduction afterwards. As it was mentioned before, they attribute the reported increase mainly to phenol decomposition for the formation of naphthalene among else. However, the fewer conversions of unsubstituted aromatic compounds (benzene and PAH) between 900°C and 1000°C indicated that higher temperatures (above 1000°C) and/or higher than 1s residence times are required for significant thermal conversion of these compounds. Figure 37 contains the experimental results regarding naphthalene evolution from the pyrolysis of biomass species is presented compared to the results obtained from the present study. As it was mentioned for Figure 34, all the results are presented as a percentage of the initial mass sample, but the basis (as received, dry, dry ash free) is not common for all the results due to lack of sufficient data required for the conversion. The purpose of the graph is to roughly compare the values of naphthalene yield obtained from the conducted ECN Ash and Torrcoal experiments to the ones found in literature along with the temperature related trends. As it can be seen most studies are in agreement with the numerical results extracted from this study. Furthermore, most researchers agree with the increasing trend in naphthalene formation with increasing temperature. The values presented below and their sources are included in the literature table in Appendix I.

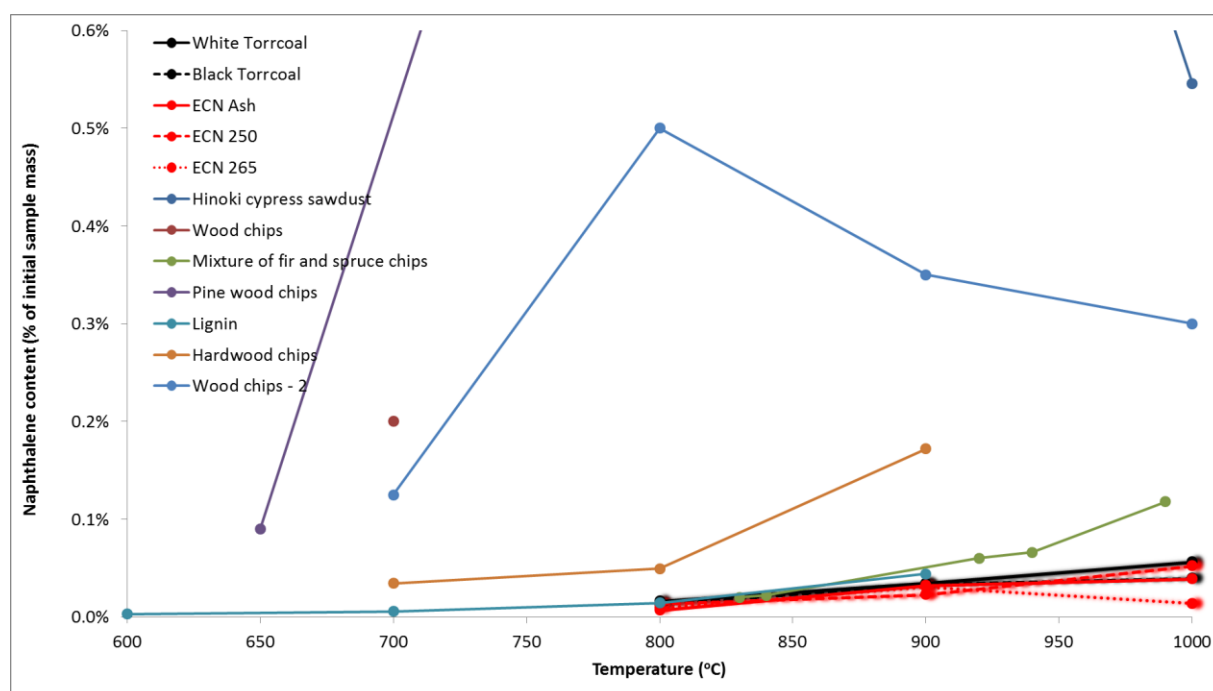


Figure 37: Naphthalene evolution temperature profile from the pyrolysis of various biomass species

3.3.3.1.1 Effect of pyrolysis temperature

By studying Figure 38, it can be immediately derived that the amount of produced naphthalene is increased significantly along with the increase of the pyrolysis temperature. In particular, for white Torricol its value is doubled from 800°C to 900°C and from 900°C to 1000°C it experiences a further increase of roughly 62%. For black Torricol the initial increase of roughly 250%

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is also followed by a smaller increase of 18%. A similar behaviour is noted for ECN Ash pyrolysis, as the naphthalene content at 900°C is almost 4.4 times higher than in 800°C, followed by a subsequent increase of 21% at 1000°C. For ECN 250, the naphthalene content at 900°C was by 62% higher than in 800°C. From 900°C to 1000°C the increase was even higher (roughly 2.3 times). A different behaviour was presented for ECN 265. After a big increase from 800°C to 900°C (3.2 times), from 900°C to 1000°C, the amount of produced naphthalene was decreased by roughly 66%. Generally, as it has been also apparent from the previously presented results, the investigation of the experimental results has been hindered by the high values of standard deviation in the HPLC analysis. In this case, the increase in naphthalene content from 800°C to 900°C is beyond doubt, even when the standard deviation values are considered. The issue arises at 1000°C, since for white and black Torrrcoal and ECN Ash the reported increase is small compared to the standard deviation values, which at 1000°C are particularly high. This is not the case though for ECN 250 and 265. ECN 250, even at the lower confidence bounds at 1000°C and the higher at 900°C, presents an increase in the naphthalene production. On the other hand ECN 265 pyrolysis appears to yield less naphthalene at 1000°C than in 900°C.

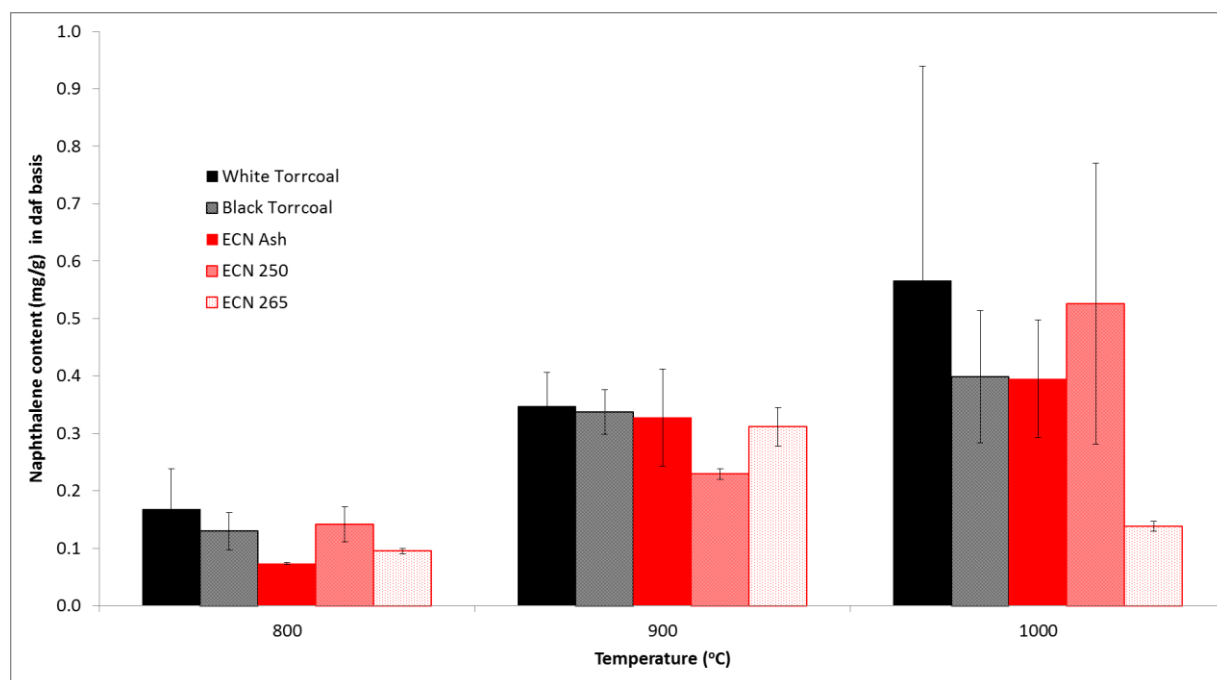


Figure 38: Naphthalene yield for the pyrolysis of untreated and torrefied Torrrcoal and ECN ash at various temperatures

3.3.3.1.2 Effect of torrefaction

By investigating the effect of torrefaction in terms of naphthalene formation for Torrrcoal pyrolysis, it can be concluded that this process led to a decrease of the naphthalene content at every temperature studied. The difference is 23% and 30% at 800°C and 1000°C and lower (3%) at 900°C, always in favour of white Torrrcoal. However, the high values of standard deviation introduce a significant uncertainty on these results. This uncertainty is strengthened by the corresponding results for ECN Ash torrefaction. At 800°C ECN 250 pyrolysis yields almost double naphthalene than ECN Ash, while ECN 265 values were also higher by roughly 30%. At this particular temperature the standard deviation values were also very low. At 900°C, ECN Ash production exceeds both 250 and 265 by 30% and 5%, respectively, with the standard deviation for ECN Ash being relatively high

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however. Finally, at 1000°C ECN 250 values rise above ECN Ash by roughly 33%, while ECN 265 values are reduced dramatically by 65% in comparison to the untreated material. Therefore, it is proven to be quite difficult to yield a conclusive result regarding the effect of torrefaction and torrefaction severity on naphthalene formation. Nevertheless, given the relatively small differences at 800°C and 900°C especially, and the standard deviation values, from the presented experimental series, it can be concluded that torrefaction does not have a particular effect on naphthalene formation from biomass pyrolysis.

3.3.3.1.3 Comparison between the biomass species

The same issues that were presented above are also presented when comparing the two biomass species studied. The standard deviation values and the small differences between the materials do not allow drawing solid conclusions. However, for the sake of completeness the results are going to be presented taking into account only the average values of the naphthalene yield. For the untreated materials, white Torricol pyrolysis yielded roughly 56% more naphthalene at 800°C. Its value was still higher than ECN Ash at 900°C, but very much reduced (6%), before increasing again at 30% at 1000°C. Moving over to the comparison of the torrefied materials, black Torricol pyrolysis yielded more naphthalene than ECN 265 at all temperatures studied (27%, 8% and 65% at 800°C, 900°C and 1000°C respectively). On the other hand ECN 250 pyrolysis produced more naphthalene than black Torricol at 800°C and 1000°C by 9% and 32% respectively. At 900°C the yield of black Torricol appears to be higher by 32%.

3.3.4 Discussion on tar compounds

A major contradiction arises by studying the literature regarding the production of phenolic compounds and phenol in particular from biomass pyrolysis at elevated temperatures. It is uncertain whether high pyrolysis temperatures lead to the destruction of phenol for the formation of polyaromatic species like naphthalene or if higher temperatures facilitate further lignin decomposition or secondary reactions for the production of phenol. The results of the present experimental investigation clearly indicate the first as it can also be observed in the following graph. Nevertheless, except from the temperature there are several other factors that influence the behaviour of phenol formation from biomass pyrolysis. To begin with, the very small particle size (smaller than 75µm) employed in this study, on the one hand accelerates heat transfer, but on the other hand creates an obstacle to the vapour removal due to the formation of a compact bed. This can lead to the decomposition of phenol before it can escape the reactor chamber and it can be a factor that differentiates the results of this and other relevant studies [131]. However, the most decisive factor on phenol formation except from the pyrolysis temperature, is the gas residence time as it is also suggested by the literature [54, 131]. Consequently, it becomes apparent, that under the present experimental conditions, cracking of phenol occurs, that does not allow the phenol yield to increase. This is consistent also with the gravimetric results, which show a reduction in the pyrolysis liquid yield for increasing temperatures for all biomass species studied. Furthermore, the stabilization of the liquid yield above 800°C is consistent with the phenol behaviour which constitutes by far the most important tar compound analysed. Additionally, as it was derived from the gas analysis the increasing values of the CO, CH₄ and H₂ yields are also indicative of secondary reactions. At this point, it should be reminded that stabilization in the yield of these gases from 900°C to 1000°C was noted for the Torricol species. The stabilization of phenol yield that was noted

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in this chapter is further indication that in the case of Torrrcoal less secondary reactions are taking place at higher temperatures at least in comparison with ECN Ash. Of course, the phenol yield of ECN ash (treated and untreated) is also stable and not all the oxygenated compounds produced from pyrolysis are accounted for. Nevertheless, the findings regarding treated and untreated Torrrcoal pyrolysis clearly support the above mentioned conclusion.

More specifically, the following cracking scheme for phenol can be adopted, as it was proposed by Cypres in [132]. The cracking mechanism can be regarded as a combination of dehydroxylation and dealkylation of higher phenols and secondary reactions between water and CH_3^* radicals. CO is the most abundant primary product from the inert gas cracking of phenol. The hydrogen necessary for these reactions has to be provided from the pyrolysed biomass. This can potentially explain the low hydrogen yields observed in the pyrolysis experiments. According to this scheme, which is also consistent with the scheme proposed by Yu [62] which was presented earlier, the primary mechanism of phenol cracking is the simultaneous formation of CO and cyclopentadiene. The second primary reaction from phenol cracking is the formation of dibenzofurane. The further cracking of cyclopentadiene leads to the formation of benzene, toluene, indene and naphthalene ($2\text{C}_5\text{H}_6 \longrightarrow \text{C}_{10}\text{H}_8 + 2\text{H}_2$), which was the only compound investigated in the present study among these. Furthermore, the stabilization of the phenol yield above 800°C that was observed earlier is consistent also with the increase of CO production that was derived from the GC analysis and the rapid increase of H_2 production rate [128].

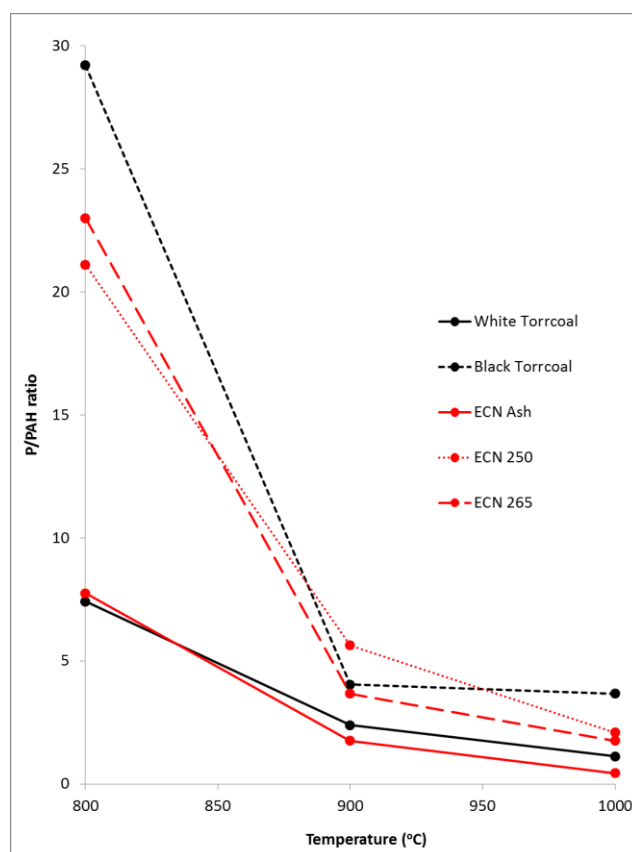


Figure 39: Phenol to PAH ratio of the investigated biomass species for increasing pyrolysis temperature

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Regarding the light polyaromatics formation from the pyrolysis experiments conducted in this work, it was found that their production rate increases mainly between 800°C and 900°C. At 1000°C their production increase was substantially lower. Naphthalene was the major light polyaromatic species formed, followed by phenanthrene, anthracene and fluorene in this particular order. The production of each light polyaromatic compound rose along the pyrolysis temperature. The exception in this trend noted for ECN 265 at 1000°C, is probably a result of experimental error. This conclusion is supported by the sudden increase in CO₂ production at this temperature which is mainly produced from primary devolatilization and was not expected at this point. Its value increased by 2% compared to 900°C. Furthermore, as it was presented earlier, the amount of produced phenol is more or less stable above 800°C for all the species studied. However, in this case there was also a notable decrease in its production. These three factors lead to the conclusion that something went wrong with the two experiments conducted at 1000°C for ECN 265. This behaviour can be caused by the presence of air in the pyrolysis chamber, due to a mistake in the nitrogen feeding process. However there are no further indications supporting this claim. The same trend presented for light polyaromatics was also presented for heavy polyaromatics, regarding the effect of temperature on their formation. Pyrene and fluoranthene were the major compounds identified, and the concentration of all the compounds increased along the pyrolysis temperature. At this point it should be mentioned that pyrene and fluoranthene are reportedly derived also from naphthalene pyrolysis at high temperatures (1000°C and above) [130]. This could explain the reduction in the naphthalene formation rate noted at this temperature. As it can be seen in Figure 40 the ratio of naphthalene to the sum of phenanthrene and pyrene plotted against the temperature presents almost linear behaviour for ECN Ash and ECN 250 with R values of 0.9887 and 0.9962, respectively. For ECN 265 this is not the case mainly due to the aforementioned issue at 1000°C since the values for 800°C and 900°C are similar to ECN Ash and 250. For treated and untreated Torricol the ratio is stable above 900°C, indicating once more the halt on secondary reactions noted before. Therefore a correlation between naphthalene and fluoranthene and pyrene is possible, but more compounds should be identified in order to further elaborate this finding. It is apparent that PAH formation rate in general was reduced above 900°C, as it is also obvious from Figure 39. As it was mentioned earlier in this chapter and also in Chapter 1.4.3, phenol is a PAH precursor. Nevertheless, BTEX compounds derived from the pyrolysis of cellulose and hemicellulose are also PAH precursors. The increase of the pyrolysis produced H₂ can be an indicator of phenol cracking as explained earlier, but also of hydrogen abstraction as part of the HACA sequence [128]. Therefore, it is fair to assume that both mechanisms contribute to PAH formation. From this discussion, it can be concluded that PAH are secondary pyrolysis products since they are produced at high temperatures from the decomposition of primary products such as phenol.

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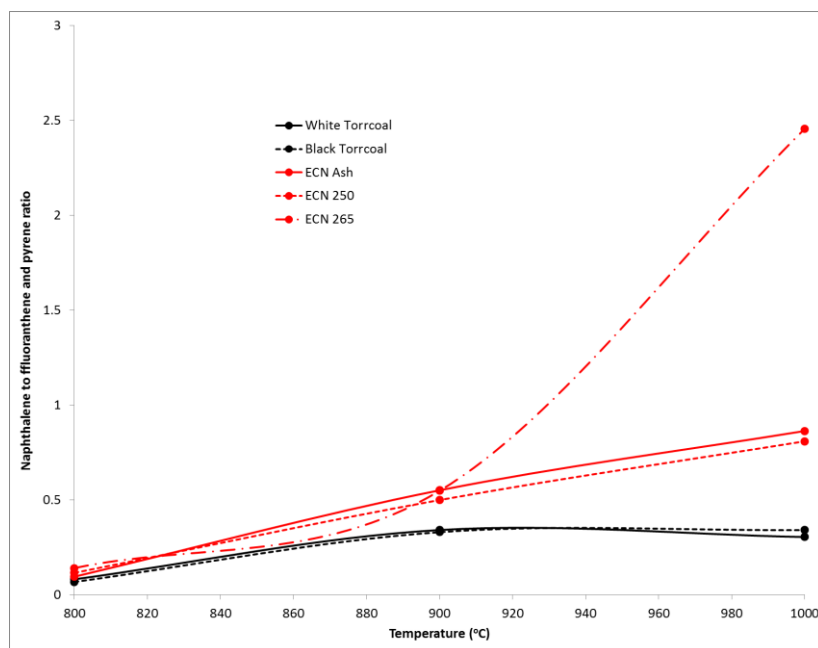


Figure 40: Naphthalene to fluoranthene and pyrene ratio versus temperature

From the experimental investigation conducted within this thesis project, it was concluded that torrefied biomass produces a higher phenol yield compared to the untreated material. Furthermore, the difference is enhanced for higher pyrolysis temperatures. Additionally, despite the fact that for both Torrc coal and ECN Ash the production of phenol was reduced for increasing pyrolysis temperatures, this reduction was significantly lower for torrefied biomass. This behaviour indicates that torrefaction favours the production of phenol from pyrolysis. As it was extensively discussed in earlier chapters, lignin is the major source of phenolic compounds among the biomass constituents. The cleavage of the methoxyl groups during torrefaction leads to an increase of the p-hydroxyphenol groups' formation that upon pyrolysis yields phenolic compounds. This is mainly due to the augmentation of the biomass lignin content through this particular process [133]. Therefore, the observed differences between treated and untreated materials can be explained through the changes occurring in biomass materials after the torrefaction process. It has also been reported in the literature that the torrefaction process promotes the production of phenol and phenolic compounds in general [74, 102, 106, 112, 134, 135]. The effect of the torrefaction degree depends on its effect on the biomass structure. Generally, increased torrefaction temperatures lead to higher lignin content and therefore to higher phenol yield. However, if severe charring occurs during the torrefaction process, due to either high torrefaction temperatures and/or residence times the phenolic yield decreases [106, 112, 133, 136]. Therefore the effect of the torrefaction degree on the pyrolysis phenol yield depends highly on the lignin structure for each particular biomass specie. In the present study, it appears that the increase of torrefaction severity does not promote phenol production from the pyrolysis of ECN Ash. However, this conclusion can be doubted due to the high error values of the HPLC analysis. On the other hand, torrefaction did not seem to influence the light polyaromatic yield of pyrolysis in terms of total production or at the individual species level. The same conclusion was derived also for heavy polyaromatics formation. This was fairly anticipated due to several reaction pathways towards PAH formation as they were described earlier. It appears that the loss in volatile content by torrefaction is balanced out by the relative gain in lignin content, at least for what PAH formation is concerned.

4. Conclusions and recommendations

In this chapter, a summary of the conclusions derived from this study is going to be presented, Moreover recommendations are given for further research.

- From the TGA analysis it was concluded that the amount of volatiles decreased while the amount of fixed carbon increased after torrefaction. On the other hand ash content of biomass was not affected by the process.
- The initial decomposition temperature during the TGA runs increased with torrefaction, indicating a higher thermal stability. Additionally, the maximum devolatilization rate increased with torrefaction while the corresponding temperature was unaltered. The devolatilization rate also increased above 400°C (lignin area) with torrefaction and the loss of hemicellulose was also apparent by the disappearance of the corresponding “shoulder” at lower temperatures.
- The energy content of the torrefied species was higher than the parent biomasses. The increase of the torrefaction severity this result also led to increased energy content in the case of ECN Ash.
- The mass balance closure for all the experiments conducted in the Pyroprobe was between 65% and 84%. These values are considered to be satisfactory given the difficulties in measuring all the pyrolysis products (pyrolytic water, higher hydrocarbon gases, etc.). The alteration of the Pyroprobe setup did not seem to affect the mass closure of the experiments. Only in the case of ECN Ash, it appeared that due to the reduced liquid content after torrefaction, mass balance closure percentages were lower at lower temperatures.
- Char yields decreased for higher pyrolysis temperatures for all biomasses. However, char production rate decreased dramatically above 800°C, attaining a steady behaviour in all cases except from Black Torrc coal where a small further decrease was noted.
- Torrefaction led to an increase of the char yield of the pyrolysis process. The increase of the torrefaction severity also led to an increased char yield but to a lower extent. For higher temperatures the differences between the heavily torrefied ECN Ash and black Torrc coal were particularly small indicating similar properties regarding char formation.
- The higher char yields and the lower liquid yields for both treated and untreated Torrc coal indicate higher lignin content for this biomass compared to ECN Ash.
- The liquid yield decreased with increasing pyrolysis temperature producing maximum values at 600°C for most cases and at 700°C for black Torrc coal and ECN 250. In the case of treated and untreated Torrc coal the liquid yield was more or less stable above 800°C.
- Torrefaction process led to a decrease of the liquid yield, as did the increase of the torrefaction severity.

4. Conclusions and recommendations

- Untreated ECN Ash pyrolysis produced a higher liquid yield than white Torriccoal. This was not the case for the torrefied samples since the liquid yield of Black Torriccoal and ECN 250 were similar and the yield of ECN 265 was lower. In general a higher amount of volatiles was produced by black Torriccoal pyrolysis than from ECN 265.
- The gas yield from treated and untreated Torriccoal pyrolysis increased along the pyrolysis temperature until maintaining a steady profile after 900°C. The same behaviour was noted for ECN 265, but for the rest species the gas yield continued to increase steadily until 1000°C.
- The differences in gas yields of torrefied and untreated species are not very significant and are only notable above 800°C.
- CO₂ production was only slightly decreased by the torrefaction process and its values were fairly similar for both biomass species. This leads to the conclusion that the parent biomass species have similar and probably low hemicellulose content. Furthermore, its yield was rather stable above 800°C.
- CO is the main produced gas above 800°C. Its values increased over the whole temperature range for every biomass with the exception of Torriccoal species at 1000°C. The corresponding values were slightly higher for ECN Ash. The differences noted between untreated and torrefied samples were negligible. The same goes for the torrefaction severity.
- CH₄ and H₂ values were significant above 700°C and 800°C, respectively, showing an increasing trend with the exception of Torriccoal species at 1000°C. However, the low production values render any comparison trivial.
- The stabilization of CO, H₂ and CH₄ yield noted at the 900°C – 1000°C range for the Torriccoal species is an indication of a halt in the secondary reactions. This conclusion was further elaborated by the findings of the tar analysis.
- Pyrolysis gas quality was higher for torrefied species (higher heating value). For both torrefied and untreated species ECN Ash produced the higher quality syngas.
- Generally, the experimental results were in good agreement with relevant literature data both in terms of trends and values.
- The amount of produced phenol decreased for increasing pyrolysis temperature until 800°C for all the biomass species studied. Above this temperature its yield was stable. White Torriccoal produced higher amounts of phenol compared to ECN Ash, despite the fact that above 800°C the difference was reduced. This was consistent with the conclusion derived regarding Torriccoals higher lignin content from the gravimetric results. The differences between the two different torrefied species were negligible.

4. Conclusions and recommendations

- Torrefied biomass pyrolysis produced a significantly higher amount of phenol compared to the untreated species. The effect of its severity though was negligible.
- PAH species yield increased steeply from 800°C to 900°C. The increase noted from 900°C to 1000°C was significantly smaller. Torrefaction and its severity did not have a particular influence in PAHs formation.
- Naphthalene was the major PAH produced in almost every case. Its production increased significantly from 800°C to 1000°C. Torrefaction did not affect its yield significantly. Also the comparisons between the biomass species were inconclusive.
- Phenanthrene, followed by anthracene and fluorene were the identified light polyaromatic species except naphthalene arranged with decreasing yields. Pyrene followed by fluoranthene was the major heavy polyaromatic species identified. Generally, the yield of light polyaromatics was higher than the yield of heavy polyaromatics at every temperature and for every biomass studied.
- A correlation between the naphthalene and the sum of fluoranthene and pyrene yields was noted especially in the cases of ECN Ash and ECN 250. It is possible that decomposition of naphthalene leads to the production of these two compounds.
- Tar analysis indicates that cracking of phenol takes place especially at higher temperatures for the formation mainly of naphthalene and CO.
- PAH are formed from phenol cracking and the HACA sequence. The latter is verified by the behaviour of H₂ at higher temperatures. The several pathways that are available towards PAH formation under pyrolysis conditions render their production values unaffected by the torrefaction process.

4.1 Recommendations

The following recommendations are meant to facilitate further research and enhance the scope of the present study.

- Analytical investigation and modelling of the heat transfer during the pyrolysis in the Pyroprobe reactor. Such an investigation was not found during the literature review.
- Conduction of experiments at higher flow rates in order to reduce the residence time of the product gases in the 300°C region. However, this can possibly result also to a reduction of the volatile yield in total or to char escape from the holder. Consequently the experimental conditions should be adjusted carefully.

4. Conclusions and recommendations

- Investigation of the effect of the biomass particle size.
- Investigation of the effect of longer than 10s pyrolysis times.
- Analysis of the char sample collected by the pyrolysis experiments conducted within this thesis (determination of pore size, structure, etc.).
- HPLC analysis for the identification of more compounds, especially heterocyclic and light aromatic tars, as well as benzene.
- Improvement of the tar sampling process. Some experiments with the use of ice around the impinger bottle have already been performed with pending results.
- Determination of the pyrolytic water with the use of a Karl – Fischer titration instrument.
- Determination of the structural biomass components (cellulose, hemicellulose and lignin).

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5. References

Appendix I – Literature tables

In this chapter, a table including the experimental results of similar studies is presented. Due to its size the included findings are reported and analysed on the previous chapters. Generally, the experiments in this table were conducted in similar apparatuses as the Pyroprobe reactor used in the present study mainly in terms of sample size. For each case the biomass feed, the pyrolysis temperature and the reactor type are mentioned.

Table 7: Literature review on biomass pyrolysis

Biomass type	Reactor type	Temperature	Char yield	Liquid yield	Gas yield	CO ₂	CO	CH ₄	H ₂	Reference
Wood residues^a	Heated foil reactor	600	35.40	21.30 ^c	19.10	10.30	7.80	1.20	-	[93]
		700	32.70	21.80 ^c	26.00	11.60	12.90	1.50	-	
		800	30.30	20.30 ^c	29.10	11.70	15.40	1.90	-	
		900	29.90	18.30 ^c	32.60	11.80	18.60	2.20	-	
		1000	32.30	16.60 ^c	32.40	11.60	18.60	2.20	-	
Reed residues^a	Heated foil reactor	700	18.50	31.10 ^c	27.00	11.10	14.20	1.40	-	[93]
		800	18.10	30.90 ^c	29.80	11.40	16.70	1.70	-	
		900	16.10	31.70 ^c	33.50	11.60	19.70	2.20	-	
		1000	14.20	32.20 ^c	35.10	11.80	20.90	2.40	-	
Douglas fir pellets^b	Microwave oven	480	53.42	19.48	27.1	-	-	-	-	[112]
Douglas fir pellets torrefied at 250 (20min)^b			33.76	32.23	34.02	-	-	-	-	
Douglas fir pellets torrefied at 275 (22min)^b			40.47	28.28	31.26	-	-	-	-	
Leucaena^b	TGA reactor	600	18	41.9	22.5	19	2.5	1	-	[100]
Leucaena torrefied at 250°C (30min)^b			18	25	18.5	15	2.5	1	-	
Hardwood^b	BFB reactor	500	10.3	71.1	19.7	-	-	-	-	[45]
Hardwood torrefied at 230°C (30min)^b			15.7	52.6	33.1	-	-	-	-	
Hardwood torrefied at 300°C (60min)^b			60.0	16.5	26.1	-	-	-	-	
Klason lignin^a	Pyroprobe	600	19.9	64.1 ^c	-	3.76	1.54	1.21	-	[94]
		700	17.2	55.3 ^c	-	6.19	5.75	1.86	-	
		800	14.9	50.4 ^c	-	6.98	9.29	2.47	-	
		900	14.4	43.1 ^c	-	7.55	14.9	2.39	-	
Municipal solid wastes^a	Pyroprobe	600	-	30.4 ^c	-	10.2	2	0.32	-	[108]
		700	-	29.5 ^c	-	13.2	3.2	0.67	-	
		800	-	30.6 ^c	-	14.9	5.3	1	-	
		900	-	22.6 ^c	-	17.7	8.7	1.5	-	
Kraft lignin^d	Pyroprobe	650	34	36.7 ^c	-	8.22	5.87	4.44	-	[101]
Switchgrass^d	Pyroprobe	600	11.08	66.43	22.50	18.11	3.24	1.11	-	[95]
		750	9.81	70.11	20.08	13.83	3.73	2.11	-	

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			900	9.81	72.58	18.61	11.22	3.91	2.83	-	
			1050	6.39	67.02	26.60	16.7	6.22	2.89	-	
Loblolly pine chips^a				9.7	67.2 ^c	23.1	-	-	-	-	
Loblolly pine chips torrefied at 270°C (2.5min)^a				22.2	17.4 ^c	23.3	-	-	-	-	
Loblolly pine chips torrefied at 300°C (2.5min)^a	Lab scale fluidized bed reactor	500		27	18.6 ^c	20.9	-	-	-	-	[74]
Loblolly pine chips torrefied at 330°C (2.5min)^a				43.3	15.6 ^c	23.2	-	-	-	-	
Pine chips^b				17.37	54.87 ^c	17	-	-	-	-	
Pine chips torrefied at 320°C (40min)^b	BFB reactor	520		23.28	22.72 ^c	11.83	-	-	-	-	[104]
Corn cob				21.14	57.2	21.66	-	-	-	-	
Corn cob torrefied at 250°C (20min)^b				24.57	55.15	20.28	-	-	-	-	
Corn cob torrefied at 275°C (20min)^b	Fluidized bed reactor	470		30.21	47.6	22.19	-	-	-	-	[106]
Corn cob torrefied at 300°C (20min)^b				38.19	40.74	21.07	-	-	-	-	
Coffee waste^e			600	23	42	-	24	6	2	-	
			700	20	33	-	27	11	4	-	
			825	18	22	-	29	17	5.5	-	
			900	17	17	-	32	19	6	-	
Brewer spent grains^e	TGA reactor		700	21	41	-	16	12.5	3	-	
			825	19	32	-	17.5	17.5	5.5	-	[83]
			900	18	30	-	18.5	19	6	-	
Fibreboard^e			600	23	47	-	15	10.5	2	-	
			700	22	35	-	16.5	18	3	-	
			825	20.5	25.5	-	18	24	6	-	
			900	18	25.5	-	19	25	6	-	
Sweet gum hardwood^b	Captive sample electrical screen heater reactor	1000		7	26	-	6.1	17	2.3		[84]
Mixture of waste wood shavings^b	Fluidized bed pyrolysis unit	550		17.1	66.2	15.2	6.86	6.71	0.69	0.023	[91]
Cellulose^b	Captive sample reactor	750		3.32	59.92 ^c	-	2.38	15.82	1.11	0.36	
		1000		3.91	49.12 ^c	-	3.36	22.57	2.62	1.18	[82]

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Legume straw ^b	Free – fall reactor	600	19	35	30	34 [†]	34 [†]	8 [†]	18 [†]	[96]
		700	12	18	72	13 [†]	42 [†]	21 [†]	21 [†]	
		800	11	19	79	15 [†]	38 [†]	17 [†]	28 [†]	
Apricot stone ^b		600	21	59	14	58 [†]	28 [†]	6 [†]	6 [†]	
		700	21	57	38	57 [†]	27 [†]	7 [†]	9 [†]	
		800	19	42	49	38 [†]	38 [†]	15 [†]	19 [†]	
Wheat straw ^b	Fixed bed reactor	600	25	18	33	-	-	-	-	[97]
		700	23	14	39	-	-	-	-	
		800	22.5	13.5	40	-	-	-	-	
Oat straw ^b		600	25	21	32	-	-	-	-	
		700	24	16	34	-	-	-	-	
		800	24	15	35	-	-	-	-	
Spruce chips ^e	Quartz tubular reactor	700	16	-	55	0.06 ^g	0.24 ^g	0.078 ^g	0.06 ^g	[98]
		800	14	-	65	0.06 ^g	0.32 ^g	0.105	0.1 ^g	
		900	13	-	64	0.055 ^g	0.325 ^g	0.11 ^g	0.15 ^g	
		1000	12	-	63	0.055 ^g	0.335 ^g	0.095 ^g	0.24 ^g	
Birch wood ^e	Free – fall reactor	700	-	-	76.3	17.8	41.9	10.4	0.9	[127]
		800	-	-	80.4	16.3	47.1	10.6	1.1	
		900	-	-	82.1	15.1	50.7	11	1.5	
Cotton cocoon shell ^e	Pyrolyzer	652	29.1	29.6	41.3	26.3 ^h	27.1 ^h	-	-	[110]
		702	28.7	27.1	44.2	17.3 ^h	33.4 ^h	-	-	
		752	27.9	22	50.1	14.8 ^h	29.5 ^h	-	-	
Tea factory waste ^e		652	32.8	25.4	41.8	24.9 ^h	28.3 ^h	-	-	
		702	32	24.5	43.5	19 ^h	27.5 ^h	-	-	
		752	31.1	23.2	45.7	17.3 ^h	27.4 ^h	-	-	
Olive husk ^e		652	25.8	34	40.2	19.3 ^h	16.3 ^h	-	-	
		702	22.4	33.7	43.9	13.4 ^h	24.2 ^h	-	-	
		752	22.8	32.6	44.6	14.1 ^h	22.7 ^h	-	-	
Corn stover ^a	Flash pyrolysis fluidized bed	600	27.7	29.4 ^c	13.4	8.64	3.82	0.42	0.07	[111]
		650	19	22 ^c	12.5	7.56	3.87	0.34	0.27	
Wheat straw ^a		600	17.5	42 ^c	21	-	-	-	-	
		650	14	31.5 ^c	27.5	-	-	-	-	
Aspen – Poplar bark ^b		600	19	31.5 ^c	35	11.25	5.2	0.5	-	
		650	17.5	25 ^c	45	11.55	7.4	0.8	-	
Safflower seed ^e	Fixed bed pyrolyzer	600	16.5	37	37.25	-	-	-	-	[137]
		700	16	33	40	-	-	-	-	
Holm – oak wood sawdust ^a	Wire – mesh reactor	600	21.9	43	35.1	-	-	-	-	[99]
		700	20.7	37.3	42	-	-	-	-	
		800	18.4	28.1	53.5	-	-	-	-	
		900	18.4	25	56.6	-	-	-	-	
Hazelnut shell ^e	Tubular reactor	627	34	33.75	37	-	-	-	-	[109]
		727	29.5	30	43	-	-	-	-	
		827	25	26	55	-	-	-	-	
		927	20	22.5	64	-	-	-	-	
Almond shell ^e		627	23.5	31.5	44	-	-	-	-	
		727	19.5	27.5	53	-	-	-	-	
		827	15	23.5	69	-	-	-	-	
		927	11.5	20	77	-	-	-	-	
Walnut shell ^e		627	36.5	36.5	25	-	-	-	-	
		727	34	32	34	-	-	-	-	
		827	30	28	45	-	-	-	-	
		927	25	23.75	57	-	-	-	-	
Sunflower shell ^e		627	17	28	54	-	-	-	-	
		727	13	24	62	-	-	-	-	
		827	9.5	20.5	70	-	-	-	-	
		927	6	16.5	77	-	-	-	-	

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^a Reported in wt% dry basis

^b Reported in wt%

^c Tar content

^d Unspecified percentage basis

^e Reported in wt% d.a.f.

^f Reported in mol%

^g Reported in Nm³ kg⁻¹ d.a.f.

^h Reported in % by volume

A further literature review was conducted for the formation of tar compounds through pyrolysis processes similar to the one conducted within this thesis. The results are presented in the following table.

Table 8: Tar compounds literature review table

Compound	Biomass	Quantity	Temperature	Type of pyrolysis	Sample size	Method	Source
Phenol	Alcell Lignin	0.066 (wt. % daf)	400	Pyroprobe	1 (mg)	PyGC – MS	[116]
		0.072 (wt. % daf)	500				
		0.076 (wt. % daf)	600				
		0.131 (wt. % daf)	700				
		0.142 (wt. % daf)	800				
	Asian Lignin	0.210 (wt. % daf)	400				
		0.216 (wt. % daf)	500				
		0.281 (wt. % daf)	600				
		0.329 (wt. % daf)	700				
		0.378 (wt. % daf)	800				
Benzene	beech wood	0.053 (wt. % d.b.)	527	lab scale fixed – bed pyrolyzer	180 (g)	GC - MS	[122]
		0.095 (wt. % d.b.)	627				
		0.0012 (wt. % d.b.)	527				
		0.001 (wt. % d.b.)	627				
Phenols	pine wood	0.4 ± 0.1 (wt. %)	450	Pyroprobe	100 (µg)	GC/5975MS	[117]
		0.8 ± 0.6 (wt. %)	500				
		1.2 ± 0.5 (wt. %)	550				

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		1.8 ± 1 (wt. %)	600				
		2.9 ± 1 (wt. %)	650				
		3.3 ± 1.1 (wt. %)	700				
		3.1 ± 1.3 (wt. %)	750				
		0.7 ± 0.3 (wt. %)	450				
		1.1 ± 0.4 (wt. %)	500				
		1.1 ± 0.1 (wt. %)	550				
		1.9 ± 0.5 (wt. %)	600				
		1.9 ± 0.7 (wt. %)	650				
		2.2 ± 0.5 (wt. %)	700				
		2.7 ± 1 (wt. %)	750				
	Toluene	0.01 ± 0.01 (wt. %)	450				
		0.03 ± 0.01 (wt. %)	500				
		0.05 ± 0.03 (wt. %)	550				
		0.05 ± 0.02 (wt. %)	600				
		0.05 ± 0.03 (wt. %)	650				
		0.09 ± 0.04 (wt. %)	700				
		0.13 ± 0.05 (wt. %)	750				
		0.02 ± 0.01 (wt. %)	450				
		0.03 ± 0.01 (wt. %)	500				
		0.01 ± 0.01 (wt. %)	550				
		0.09 ± 0.02 (wt. %)	600				
		0.1 ± 0.06 (wt. %)	650				
		0.2 ± 0.07 (wt. %)	700				
		0.2 ± 0.07 (wt. %)	750				
Benzene	ALM lignin	0.15 (% tot. p.a.)	500	Pyroprobe	0.5 (mg)	Perkin Elmer MS GOLD	[138]
	ETEK lignin	0.10 (%)					

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		tot. p.a.)								
Toluene	ALM lignin	0.63 (%) tot. p.a.)								
	ETEK lignin	0.13 (%) tot. p.a.)								
Ethylbenzene	ALM lignin	0.10 (%) tot. p.a.)								
	ETEK lignin	0 (%) tot. p.a.)								
Styrene	ALM lignin	0.39 (%) tot. p.a.)								
	ETEK lignin	3.22 (%) tot. p.a.)								
Phenol	ALM lignin	3.57 (%) tot. p.a.)								
	ETEK lignin	0.51 (%) tot. p.a.)								
		1.93 (g/kg)	600							
		13.55 (g/kg)	800							
		2.30 (g/kg)	900							
Benzene		0.52 (g/kg)	1000							
		1.87 (g/kg)	600							
		30.31 (g/kg)	800							
		34.66 (g/kg)	900							
		23.09 (g/kg)	1000							
Toluene		2.05 (g/kg)	600							
		7.21 (g/kg)	800							
		1.83 (g/kg)	900							
Styrene	hinoki cypress sawdust	0.38 (g/kg)	1000	Entrained drop-tube furnace	60 – 70 (g/h)	GC - MS	[118]			
		0.72 (g/kg)	600							
		4.20 (g/kg)	800							
		1.63 (g/kg)	900							
Indene	0.16 (g/kg)	1000								
	0.37 (g/kg)	600								
	5.4 (g/kg)	800								
Naphthalene	2.49 (g/kg)	900								
	10.25 (g/kg)	800								
	13.73 (g/kg)	900								
Fluorene	5.46 (g/kg)	1000								
	1.50 (g/kg)	800								
Anthracene	1.44 (g/kg)	900								
	3.22 (g/kg)	800								
	4.58 (g/kg)	900								
Pyrene	1.79 (g/kg)	1000								
	2.77 (g/kg)	800								
	4.38 (g/kg)	900								

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		3.18 (g/kg)	1000				
Chrysene		1.37 (g/kg)	900				
Phenol		9.3 (mole %)	700				
		4.8 (mole %)	800				
		2 (mole %)	900				
Benzene		29.2 (mole %)	700				
		55 (mole %)	800				
		62.5 (mole %)	900				
Toluene		15 (mole %)	700				
		9.5 (mole %)	800				
		5.2 (mole %)	900				
Indene		4.4 (mole %)	700				
		3.6 (mole %)	800				
		2.5 (mole %)	900				
Naphthalene	birch wood	8 (mole %)	700	Pressurized free – fall reactor	1 kg/h	GC	[119]
		12 (mole %)	800				
		13.7 (mole %)	900				
Fluorene		0.6 (mole %)	700				
		0.3 (mole %)	800				
		0.4 (mole %)	900				
Phenanthrene		1.3 (mole %)	700				
		0.8 (mole %)	800				
		1.2 (mole %)	900				
Anthracene		0.4 (mole %)	700				
		0.2 (mole %)	800				
		0.3 (mole %)	900				
Fluoranthene		0.5 (mole %)	700				
		0.7 (mole %)	800				

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		0.6 (mole %)	900				
Pyrene		0.7 (mole %)	700				
		0.7 (mole %)	800				
		0.5 (mole %)	900				
Phenol	beech wood - 2	0.54 (wt. % d.b.)	552	Fast pyrolysis reactor	unknown	GC	[123]
		0.66 (wt. % d.b.)	602				
	spruce wood	0.69 (wt. % d.b.)	552				
		0.72 (wt. % d.b.)	602				
Benzene		9.6 (g/kg d.b.)					
		5.8 (g/kg d.b.)					
Toluene		3.8 (g/kg d.b.)					
		3.6 (g/kg d.b.)					
Phenol		4.3 (g/kg d.b.)					
		3.8 (g/kg d.b.)					
Indene	wood chips	2.1 (g/kg d.b.)	700	Quartz tubular reactor (similar to Pyroprobe)	0.5 (g)	GC – MS (Impingers / SPA)	[139]
		2 (g/kg d.b.)					
Naphthalene		1.8 (g/kg d.b.)					
		2 (g/kg d.b.)					
Acenaphthalene		1.9 (g/kg d.b.)					
		1.9 (g/kg d.b.)					
Phenanthrene		0.5 (g/kg d.b.)					
		0.7 (g/kg d.b.)					
Phenol	oak	3.14 (% tot. p.a.)	400				
	pine	2.24 (% tot. p.a.)	400				
	bamboo	4.99 (% tot. p.a.)	800				

Appendix I – Literature tables

Naphthalene	oak	3.43 (% tot. p.a.)	400	Low frequency induction heater	30 g	GC – MS	[125]
	bamboo	5.97 (% tot. p.a.)	800				
Fluorene	oak	1.32 (% tot. p.a.)	400				
	pine	1.06 (% tot. p.a.)	400				
	bamboo	1.58 (% tot. p.a.)	800				
Phenanthrene	oak	2.55 (% tot. p.a.)	400				
	pine	2.15 (% tot. p.a.)	400				
	bamboo	6.00 (% tot. p.a.)	800				
Fluoranthene	oak	0.83 (% tot. p.a.)	400				
	pine	0.87 (% tot. p.a.)	400				
	bamboo	3.07 (% tot. p.a.)	800				
Pyrene	oak	0.67 (% tot. p.a.)	400				
	pine	0.97 (% tot. p.a.)	400				
	bamboo	4.21 (% tot. p.a.)	800				
Phenols	chinese tallow wood	38.18 (% liquid yield)	600				
		51.1 (% liquid yield)	650				
		79.60 (% liquid yield)	700				
Phenol	Mixture of fir and spruce chips	0.125 (% d.b)	600	Fixed bed reactor	1.6 kg/h	GC - MS	[128]
		0.075 (% d.b)	650				
		0.115 (% d.b)	700				
		0.09 (% d.b)	750				
		0.1455 (% d.b)	800				
		0.155 (% d.b)	850				
		0.165 (% d.b)	900				
		0.175 (% d.b)	950				

Appendix I – Literature tables

		0.145 (% d.b)	1000				
		0.02 (% d.b)	830				
		0.022 (% d.b)	840				
		0.06 (% d.b)	920				
		0.066 (% d.b)	940				
		0.118 (% d.b)	990				
Phenol	Pine wood chips	8.12 (mg/g)	650	Pyrolyzer cylinder (part of a two stage gasifier)	15kg/h		[126]
		12.81 (mg/g)	750				
		0.90 (mg/g)	650				
Naphthalene		9.37 (mg/g)	750				
Naphthalene	Lignin	30 (µg/g)	600	Fixed bed reactor	1g	Varian 3380 GC	[129]
		55 (µg/g)	700				
		145 (µg/g)	800				
		440 (µg/g)	900				
Phenol		1.069(g/kg d.b.)	700				
		0.941 (g/kg d.b.)	800				
		0.753 (g/kg d.b.)	900				
		0.345 (g/kg d.b.)	700				
Naphthalene		0.494 (g/kg d.b.)	800				
		1.722 (g/kg d.b.)	900				
Fluorene	Hardwood chips	0.119 (g/kg d.b.)	700	Fixed bed reactor	0.2kg/min	GC - MS	[120]
		0.149 (g/kg d.b.)	800				
		0.276 (g/kg d.b.)	900				
		0.065 (g/kg d.b.)	700				
Phenanthrene		0.1 (g/kg d.b.)	800				
		0.368 (g/kg d.b.)	900				
Anthracene		0.017 (g/kg d.b.)	700				
		0.042 (g/kg d.b.)	800				

Appendix I – Literature tables

		0.107 (g/kg d.b.)	900				
		0.049 (g/kg d.b.)	700				
		0.038 (g/kg d.b.)	800				
		0.140 (g/kg d.b.)	900				
Pyrene							
		4 (g/kg d.b.)	700				
		2.5 (g/kg d.b.)	800				
		0 (g/kg d.b.)	900				
		0 (g/kg d.b.)	1000				
Phenol							
		1.25 (g/kg d.b.)	700				
		5 (g/kg d.b.)	800				
Naphthalene	Wood chips - 2	3.5 (g/kg d.b.)	900	Quartz tubular reactor (similar to Pyroprobe)	0.5 (g)	GC – MS (Impingers/SPA)	[121]
		3 (g/kg d.b.)	1000				
		0.5 (g/kg d.b.)	700				
		1.5 (g/kg d.b.)	800				
Phenanthrene		1.25 (g/kg d.b.)	900				
		1 (g/kg d.b.)	1000				

Appendix II – Gravimetric and GC results

To begin with, the figures depicting the mass balance closures for black Torrc coal, ECN 250 and 265 are presented here.

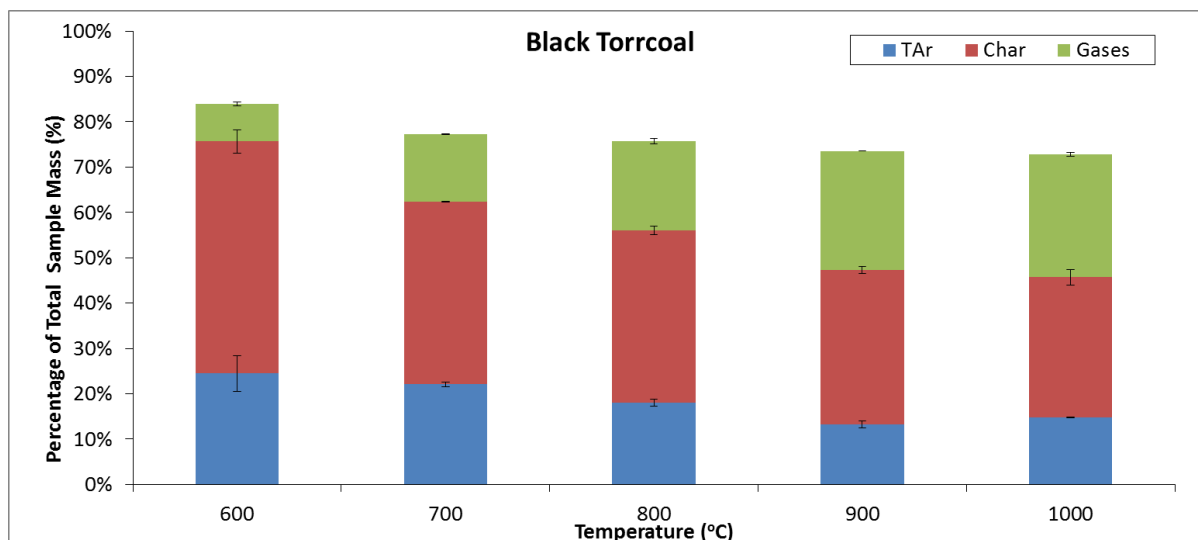


Figure 41: Mass balance of torrefied (black) Torrc coal pyrolysis (d.a.f. basis)

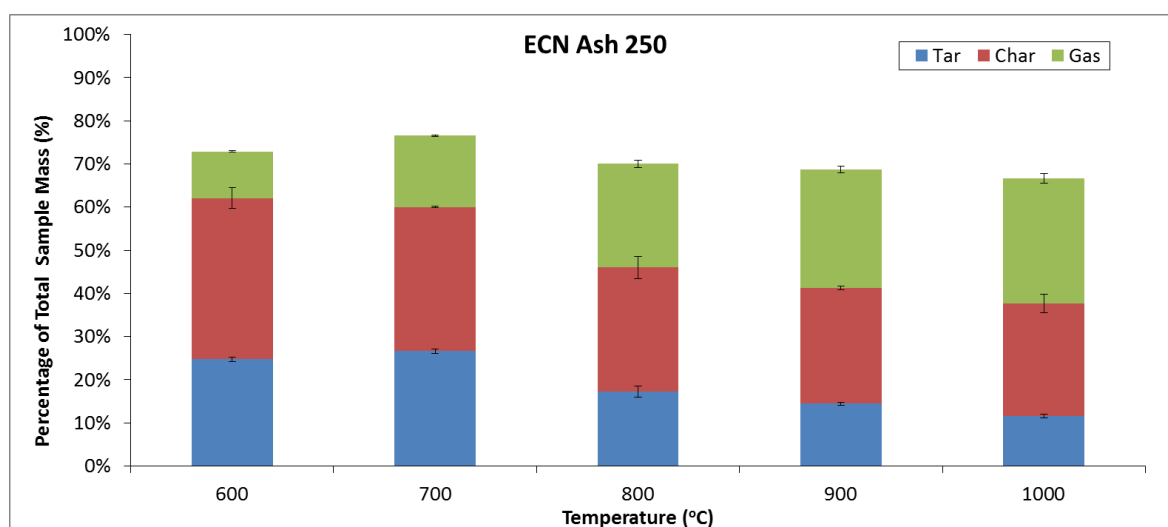


Figure 42: Mass balance for the pyrolysis of ECN ash torrefied at 250°C (d.a.f. basis)

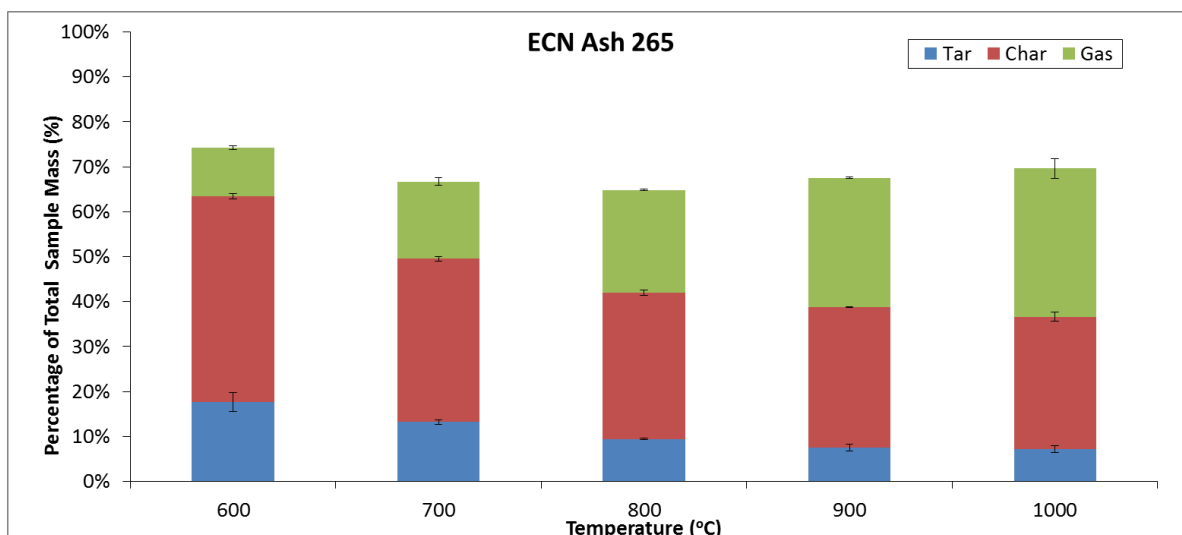


Figure 43: Mass balance for the pyrolysis of ECN ash torrefied at 265°C (d.a.f. basis)

In the following tables the gravimetric and GC results from the pyrolysis experiments conducted within this thesis are presented.

Table 9: Gravimetric and GC results of the treated and untreated Torrc coal experiments

Temperature (°C)	White Torrc coal		Black Torrc coal	
	Yield (d.a.f. basis)	Standard deviation	Yield (d.a.f. basis)	Standard deviation
Mass Closure				
600	74.93%	0.01%	83.92%	6.09%
700	78.61%	1.21%	76.63%	1.54%
800	73.00%	2.82%	75.76%	0.45%
900	73.90%	0.30%	73.98%	0.57%
1000	77.20%	0.96%	72.78%	1.32%
Tar				
600	29.78%	1.14%	24.49%	3.97%
700	32.75%	3.13%	22.06%	0.59%
800	25.15%	3.00%	18.01%	0.83%
900	20.74%	2.97%	13.17%	0.76%
1000	24.20%	1.69%	14.81%	0.08%
Char				
600	34.61%	0.33%	51.19%	2.60%
700	30.52%	4.34%	40.28%	0.04%
800	24.16%	1.23%	38.03%	0.98%
900	25.26%	1.75%	34.21%	0.78%
1000	25.63%	1.67%	30.91%	1.69%
Gas				
600	10.54%	0.82%	8.24%	0.48%
700	15.33%	2.43%	14.90%	0.04%
800	23.70%	1.41%	19.72%	0.61%
900	27.90%	1.52%	26.21%	0.02%
1000	27.36%	2.40%	27.06%	0.45%

CO₂ yield				
600	7.19%	0.52%	5.29%	0.42%
700	8.64%	1.23%	7.19%	0.02%
800	10.11%	0.61%	8.06%	0.11%
900	10.90%	0.20%	9.29%	0.19%
1000	10.68%	1.52%	9.48%	0.25%
CH₄ yield				
600	0.18%	0.05%	0.18%	0.01%
700	0.75%	0.28%	1.10%	0.03%
800	1.96%	0.16%	1.82%	0.21%
900	2.72%	0.18%	2.98%	0.02%
1000	2.72%	0.29%	3.15%	0.03%
CO yield				
600	3.17%	0.25%	2.76%	0.07%
700	5.90%	0.91%	6.57%	0.10%
800	11.44%	0.61%	9.71%	0.50%
900	13.96%	1.51%	13.60%	0.13%
1000	13.64%	0.49%	14.06%	0.17%
H₂ yield				
600	0.01%	0.00%	0.01%	0.00%
700	0.04%	0.01%	0.04%	0.00%
800	0.18%	0.03%	0.12%	0.02%
900	0.33%	0.03%	0.34%	0.03%
1000	0.32%	0.10%	0.37%	0.00%

Table 10: Gravimetric and GC results of the treated and untreated Torrc coal experiments

Temperature (°C)	ECN Ash		ECN 250		ECN 265	
	Yield (d.a.f. basis)	Standard deviation	Yield (d.a.f. basis)	Standard deviation	Yield (d.a.f. basis)	Standard deviation
Mass Closure						
600	80.58%	1.55%	72.89%	3.10%	74.22%	1.89%
700	76.78%	1.33%	76.52%	0.14%	66.72%	0.13%
800	72.71%	1.93%	70.02%	2.95%	64.86%	0.87%
900	73.07%	2.70%	68.74%	0.87%	67.54%	0.90%
1000	66.09%	0.34%	66.68%	3.72%	69.60%	4.05%
Tar						
600	42.97%	0.32%	24.71%	0.57%	17.66%	2.12%
700	37.93%	0.03%	26.61%	0.50%	13.24%	0.49%
800	30.52%	1.15%	17.23%	1.23%	9.43%	0.13%
900	24.61%	1.24%	14.44%	0.39%	7.46%	0.75%
1000	15.72%	1.37%	11.62%	0.46%	7.17%	0.80%
Char						
600	25.05%	1.89%	37.33%	2.42%	45.73%	0.60%
700	21.45%	1.56%	33.39%	0.18%	36.29%	0.46%
800	16.43%	0.23%	28.77%	2.58%	32.51%	0.59%

Appendix II – Gravimetric and GC results

900	16.12%	2.28%	26.84%	0.46%	31.28%	0.06%
1000	14.23%	0.11%	25.98%	2.16%	29.43%	1.01%
Gas						
600	12.56%	0.01%	10.84%	0.11%	10.82%	0.37%
700	17.40%	0.19%	16.51%	0.18%	17.20%	0.82%
800	25.76%	0.54%	24.02%	0.86%	22.93%	0.14%
900	32.34%	0.83%	27.46%	0.80%	28.80%	0.21%
1000	36.13%	1.15%	29.08%	1.11%	32.99%	2.24%
CO₂ yield						
600	7.94%	0.20%	6.21%	0.03%	6.23%	0.22%
700	8.43%	0.18%	7.10%	0.09%	7.52%	0.45%
800	9.09%	0.35%	7.85%	0.11%	7.84%	0.04%
900	10.45%	0.34%	8.56%	0.05%	8.68%	0.06%
1000	10.76%	0.14%	8.47%	0.09%	10.65%	0.73%
CH₄ yield						
600	0.24%	0.04%	0.41%	0.05%	0.41%	0.04%
700	0.91%	0.10%	1.27%	0.03%	1.46%	0.10%
800	2.22%	0.02%	2.52%	0.13%	2.51%	0.01%
900	3.31%	0.13%	3.18%	0.13%	3.56%	0.03%
1000	3.88%	0.24%	3.50%	0.15%	4.02%	0.15%
CO yield						
600	4.38%	0.17%	4.21%	0.09%	4.18%	0.11%
700	8.01%	0.27%	8.10%	0.12%	8.18%	0.27%
800	14.26%	0.18%	13.46%	0.60%	12.42%	0.20%
900	18.19%	0.29%	15.36%	0.68%	16.07%	0.12%
1000	20.88%	1.00%	16.61%	0.94%	17.64%	1.18%
H₂ yield						
600	0.01%	0.00%	0.01%	0.00%	0.01%	0.00%
700	0.05%	0.00%	0.05%	0.00%	0.05%	0.00%
800	0.19%	0.00%	0.19%	0.01%	0.16%	0.00%
900	0.39%	0.06%	0.36%	0.03%	0.49%	0.00%
1000	0.61%	0.03%	0.50%	0.07%	0.69%	0.19%

Appendix III – Tar analysis results

In this chapter the results from the HPLC analysis of the pyrolysis liquid samples is presented. Due to size, the table has been divided into three smaller ones.

Table 11: HPLC results of the pyrolysis liquid of treated and untreated Torrc coal

	Biomass sample	Black Torrc coal					White Torrc coal				
	Temperature	600	700	800	900	1000	600	700	800	900	1000
Phenol	Quantity mg/g (daf)	11.829	6.074	5.918	3.108	3.375	9.347	7.122	2.155	1.902	1.329
	Standard deviation	1.817	0.354	1.795	0.404	1.004	0.194	0.948	0.092	0.451	0.061
Naphthalene	Quantity mg/g (daf)			0.130	0.337	0.398			0.168	0.348	0.565
	Standard deviation			0.032	0.039	0.115			0.071	0.059	0.374
Fluorene	Quantity mg/g (daf)			0.013	0.053	0.063			0.008	0.041	0.070
	Standard deviation			0.004	0.010	0.003			0.004	0.012	0.030
Phenanthrene	Quantity mg/g (daf)			0.029	0.145	0.175			0.048	0.165	0.226
	Standard deviation			0.004	0.021	0.007			0.000	0.043	0.046
Anthracene	Quantity mg/g (daf)			0.019	0.077	0.091			0.041	0.089	0.119
	Standard deviation			0.002	0.011	0.002			0.001	0.018	0.028
Fluoranthene	Quantity mg/g (daf)			0.000	0.050	0.061			0.000	0.052	0.077
	Standard deviation			0.000	0.008	0.001			0.000	0.025	0.009
Pyrene	Quantity mg/g (daf)			0.009	0.061	0.075			0.014	0.067	0.095
	Standard deviation			0.000	0.008	0.002			0.001	0.022	0.012
Benzo(a)anthracene	Quantity mg/g (daf)			0.003	0.022	0.026			0.008	0.020	0.026
	Standard deviation			0.004	0.003	0.001			0.001	0.001	0.004
Chrysene	Quantity mg/g (daf)			0.000	0.019	0.019			0.002	0.014	0.011
	Standard deviation			0.000	0.003	0.004			0.003	0.001	0.008
Benzo(k)fluoranthene	Quantity mg/g (daf)			0.000	0.002	0.004					
	Standard deviation			0.000	0.003	0.005					
Benzo(b)fluoranthene	Quantity mg/g (daf)								0.003	0.000	0.000
	Standard deviation								0.004	0.000	0.000
Benzo(a)pyrene	Quantity mg/g (daf)			0.000	0.004	0.008					
	Standard deviation			0.000	0.005	0.011					
Dibenzo(a,h)anthracene	Quantity mg/g (daf)										
	Standard deviation										
Benzo(g,h,i)perylene	Quantity mg/g (daf)										
	Standard deviation										
Indeno (1,2,3-cd)pyrene	Quantity mg/g (daf)										
	Standard deviation										
Total	Quantity mg/g (daf)	11.829	6.074	6.121	3.878	4.295	9.347	7.122	2.445	2.698	2.519
	Standard deviation	1.817	0.354	1.833	0.386	1.145	0.194	0.948	0.022	0.511	0.451

Table 12: HPLC results of the pyrolysis liquid of untreated ECN Ash

	Biomass sample	ECN Ash
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Appendix III – Tar analysis results

	Temperature	600	700	800	900	1000
Phenol	Quantity mg/g (daf)	6.319	6.011	1.110	1.772	0.675
	Standard deviation	0.247	0.047	0.023	0.180	0.955
Naphthalene	Quantity mg/g (daf)			0.074	0.327	0.395
	Standard deviation			0.002	0.085	0.102
Fluorene	Quantity mg/g (daf)			0.010	0.076	0.121
	Standard deviation			0.001	0.022	0.031
Phenanthrene	Quantity mg/g (daf)			0.026	0.204	0.324
	Standard deviation			0.001	0.055	0.100
Anthracene	Quantity mg/g (daf)			0.019	0.110	0.162
	Standard deviation			0.001	0.029	0.045
Fluoranthene	Quantity mg/g (daf)			0.000	0.097	0.174
	Standard deviation			0.000	0.025	0.038
Pyrene	Quantity mg/g (daf)			0.007	0.083	0.167
	Standard deviation			0.003	0.027	0.068
Benzo(a)anthracene	Quantity mg/g (daf)			0.005	0.033	0.064
	Standard deviation			0.000	0.010	0.020
Chrysene	Quantity mg/g (daf)			0.003	0.027	0.048
	Standard deviation			0.004	0.009	0.016
Benzo(k)fluoranthene	Quantity mg/g (daf)					
	Standard deviation					
Benzo(b)fluoranthene	Quantity mg/g (daf)			0.000	0.006	0.008
	Standard deviation			0.000	0.001	0.011
Benzo(a)pyrene	Quantity mg/g (daf)			0.000	0.026	0.055
	Standard deviation			0.000	0.010	0.022
Dibenzo(a,h)anthracene	Quantity mg/g (daf)			0.000	0.007	0.009
	Standard deviation			0.000	0.003	0.002
Benzo(g,h,i)perylene	Quantity mg/g (daf)			0.000	0.005	0.016
	Standard deviation			0.000	0.003	0.010
Indeno (1,2,3-cd)pyrene	Quantity mg/g (daf)			0.000	0.009	0.009
	Standard deviation			0.000	0.003	0.012
Total	Quantity mg/g (daf)	6.319	6.011	1.253	2.784	2.225
	Standard deviation	0.247	0.047	0.019	0.100	1.412

Table 13: HPLC results of the pyrolysis liquid of untreated ECN Ash

	Biomass sample	ECN 250					ECN 265				
		600	700	800	900	1000	600	700	800	900	1000
Phenol	Quantity mg/g (daf)	12.357	7.243	4.447	3.677	3.845	10.783	6.896	4.492	3.519	2.004
	Standard deviation	1.319	0.080	0.603	0.438	1.343	0.102	0.603	2.487	0.535	0.309
Naphthalene	Quantity mg/g (daf)			0.141	0.229	0.526			0.095	0.312	0.138
	Standard deviation			0.031	0.009	0.244			0.005	0.034	0.009
Fluorene	Quantity mg/g (daf)			0.011	0.057	0.139			0.017	0.076	0.080
	Standard deviation			0.015	0.004	0.063			0.001	0.007	0.001

Appendix III – Tar analysis results

Phenanthrene	Quantity mg/g (daf)			0.024	0.143	0.387			0.037	0.202	0.296
	Standard deviation			0.035	0.014	0.178			0.005	0.015	0.020
Anthracene	Quantity mg/g (daf)			0.015	0.077	0.191			0.025	0.109	0.136
	Standard deviation			0.021	0.007	0.081			0.003	0.007	0.002
Fluoranthene	Quantity mg/g (daf)			0.007	0.055	0.210			0.004	0.082	0.158
	Standard deviation			0.010	0.006	0.115			0.005	0.003	0.018
Pyrene	Quantity mg/g (daf)			0.009	0.059	0.216			0.010	0.088	0.182
	Standard deviation			0.013	0.006	0.123			0.001	0.004	0.038
Benzo(a)anthracene	Quantity mg/g (daf)			0.003	0.017	0.061			0.006	0.033	0.041
	Standard deviation			0.004	0.003	0.022			0.001	0.001	0.001
Chrysene	Quantity mg/g (daf)			0.000	0.015	0.089			0.002	0.028	0.042
	Standard deviation			0.000	0.001	0.039			0.003	0.002	0.002
Benzo(k)fluoranthene	Quantity mg/g (daf)			0.000	0.000	0.010					
	Standard deviation			0.000	0.000	0.006					
Benzo(b)fluoranthene	Quantity mg/g (daf)								0.000	0.007	0.022
	Standard deviation								0.000	0.000	0.003
Benzo(a)pyrene	Quantity mg/g (daf)			0.000	0.000	0.015			0.000	0.021	0.040
	Standard deviation			0.000	0.000	0.007			0.000	0.001	0.005
Dibenzo(a,h)anthracene	Quantity mg/g (daf)										
	Standard deviation										
Benzo(g,h,i)perylene	Quantity mg/g (daf)										
	Standard deviation										
Indeno (1,2,3-cd)pyrene	Quantity mg/g (daf)								0.000	0.000	0.008
	Standard deviation								0.000	0.000	0.002
Total	Quantity mg/g (daf)	12.357	7.243	4.658	4.330	5.688	10.783	6.896	4.687	4.478	3.146
	Standard deviation	1.319	0.080	0.535	0.490	0.464	0.102	0.603	2.512	0.470	0.232

Appendix IV – Pyroprobe protocol

1. PYROLYSIS EXPERIMENT

Prior to conducting the experiment, the biomass sample should be ground and sieved to, at least, 0.2mm size. Furthermore, for a more thorough analysis of the results, the conduction of TGA experiments for sample characterization is suggested.

In order to avoid contamination of the various removable parts (especially the holder and the trap) the user is requested to use plastic gloves during the entire experimental procedure.

The experimental procedure described below is of an instructive character. The user should modify it as he/she sees fit, as long as the basic guidelines are followed.

1. Firstly, the sample holder should be cleaned. This is done by searing it with the use of a torch and then with pressurized air or nitrogen. **In order to avoid accidents, the user should wait until the sample holder cools down after its searing.**
2. Again, with the use of the torch, the wool should be seared in order to remove contaminants.
3. The sample holder, apart from the biomass sample, will contain to pieces of quartz wool on each side, in order to prevent the sample from escaping. So, the next step is to insert the first piece of wool on one side of the holder. It would be the best if the inserted glass wool is one piece. 4! Try to keep the wool intact as it can break easily and subsequently contaminate the sample. This can affect a future analysis of the extracted char.
4. The sample holder together with the inserted piece of wool should be weighed.
5. Roughly 30mg of sample should be inserted in the holder and subsequently weighed. The sample mass must be large enough if permanent gases are to be samples and analysed.
6. The user should try not to compress the inserted sample. After inserting the sample, the walls of the holder have to be cleaned with a paper tissue for the inside walls and pressurized air for the outside ones.
7. Insert the second piece of wool in the sample holder and clean it with pressurized air or nitrogen.

Try not to waste wool!

8. Weigh the full sample holder.
9. Turn on Pyroprobe, from back switch.
10. On the PC press communications tab and then connect.
11. Measure the nitrogen flow which has to be higher than 15ml/min and lower than 20ml/min. This measurement is performed with the use of a test tube filled with soaped water. **Make sure there is no air flow for pyrolysis experiments.** The user should also keep in mind that in order to measure the flow the probe has to be tightly closed.
12. Prepare the trap.
 - a) Clean the condenser assembly with isopropanol (IPA).
 - b) Dry the condenser with pressurized air or nitrogen. **The user should make sure that there is no IPA left in the last part of the assembly (where the gas extraction takes place).**
 - c) Insert 2ml of IPA in the condenser.

- d) Weigh the empty trap. **The user should keep in mind that the trap should be always weighed standing, in a vertical position. Furthermore, due to initial vibration after its placement, it might take the scale a while to reach to the right weight value. The trap should be weighed with the same orientation before and after the experiment.**
- e) Insert trap and tighten the screws carefully. The filter of the trap should be on the outside and exactly on the Pyroprobe orifice.
- f) Connect the condenser to the trap
- 13. Unscrew the probe and insert the sample holder. **The holder should not be in contact with the wick on the bottom and the probe coils should not be in contact with each other.** Subsequently, screw the probe tightly.
- 14. Make sure that the syringe for the gas sampling works properly. This is done by connecting it to the nitrogen outflow from Pyroprobe.
- 15. On the PC, go to the Pyroprobe tab and select the heating rate and the final temperature according to test parameters. Furthermore, adjust if needed the parameters on the Accessory tab. Then save and subsequently load the current method.

The pyrolysis temperature set in Pyroprobe is different from the actual temperature in which pyrolysis takes place. The corresponding values are included in Chapter 1. Additionally the holding time set in Pyroprobe does not correspond to the interval on which the sample is heated at the pyrolysis temperature. Instead it includes the time needed to achieve the specified temperature. The time that needs to be set for 10s of holding time is also presented also in Chapter 1.

- 16. Before initiating the experiment it should be made sure that every component is tightly closed (e.g. probe, gas sampler, etc.).
- 17. Press RUN.

If the experiment is proceeding smoothly, bubbles should appear in the condenser. Furthermore, during and a little bit after pyrolysis the user might notice smoke in the vial.

- 18. Before the temperature of the accessory reaches 300°C, the syringe is inserted. **The syringe should not contain any air, but pushing it out should be done with care in order for it not to get stuck.**
- 19. During the test, there might be a smell of “burning”. The smell should not be strong as this would mean that there is a leakage.
- 20. Wait until the test is over. **Then, first separate the condenser from the trap immediately in order to avoid IPA back-flow into the trap and afterwards remove the syringe and put its lid on also immediately.**
- 21. Note the volume of the gases collected in the syringe, as it will be used for the gas products determination.
- 22. Measure the weight of the trap. **The trap should be weighed as fast as possible after the completion of the experiment in order to prevent major losses of very volatile tar compounds.** For the same reason, the part of the trap that contains the filter should be placed at the bottom of the balance.
- 23. Wait for the accessory to cool down at 50°C in order to remove the sample holder safely.
- 24. Tar collection:
 - a) Insert 3ml of IPA in a testing tube and add the 2ml of IPA that were already in the condenser.
 - b) Insert the trap into the testing tube.

- c) Stir the tube carefully. **Make sure that the bottom part of the trap is at the side of the testing tube where the IPA is, so the trapped tars are removed as efficiently as possible.**
- d) Leave it in a standing position for at least 30 minutes. Longer residence time in the IPA solution can improve tar analysis and the subsequent trap cleaning.
25. When the temperature falls below 50°C, open the probe and retrieve the sample holder using tweezers.
26. Weigh the sample holder, in order to measure the amount of reacted biomass.
27. Carefully remove the wool and the char from the sample holder. The char must be stored. **Stored char should not contain traces of wool if possible.**
28. Resume tar collection:
 - a) Empty the tar solution through a paper filter into a clean testing vessel. Make sure that the part of the solution that is in the trap is also collected.
 - b) Collect the tar solution (with a pipet) into a small vial and seal it.
29. Clean all used vessels with acetone.
30. The trap should be cleaned with IPA both on the inside and on the outside. Carefully, clear any remaining tars from the bottom part of the trap. Also, by pushing gently IPA through the filter, the user should try to remove from it any particles that might be stuck there. **After cleaning the trap should be dried immediately using pressurized nitrogen. In order for it to be completely dried, the trap should also be inserted into the Pyroprobe, this time with the filter facing the inside of the Pyroprobe and left there for some minutes. An oven set at temperatures around 150°C can also be used for this purpose.**
31. Measure the nitrogen flow again. If a big deviation from the former value is observed, it probably means that there is a blockage of the device and cleaning should be performed before the conduction of more experiments.

2. Gas Analysis

Gas analysis is performed manually in a Micro GC using the Galaxie software.

1. Insert the syringe into the Micro-GC reception.
2. Press quick start.
3. Change name (i.e. save the results with the selected name)
4. Change identifier (i.e. 1,2,3,4 because there will be multiple injections).
5. Press start.
6. When a distinctive sound is heard from the Micro GC (i.e. the mGC is injecting) press the syringe slightly in order to push out an amount of gas sample. Keep pressing repeatedly until the sound goes off. **Be very careful not to remove the reception tube due to the gas-pushing; it should be held firmly while pushing.**
7. Repeat the process above at least 3-4 times. Every time keep the same name and change the identifier. The last run gives the final values for the gas analysis.
8. In order to view the results go to File: open chromatogram: file name (on the left side of the screen).