



Characterization of the effect of pyrolysis in torrefied wood chips

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Abstract. The pyrolysis behavior of torrefied wood produced in Portugal was investigated. Torrefaction is the thermochemical upgrading of biomass at approximately 300°C in an atmosphere free of oxidizing agents to increase fuel density and to improve fuel quality, decreasing moisture and increasing heating value. Torrefied woodchips were pyrolysed at pressurized conditions in an inert atmosphere at 600°C. All the condensable liquids were sampled for analyses. All pyrolysis hydrocarbon liquids were analysed using simulated distillation (simdis) and gas chromatography mass spectrometry (GCMS). Torrefied wood hydrocarbon liquid showed higher concentrations of aliphatic aldehydes liquid. A decrease in all the other molecular components was observed for the torrefied wood hydrocarbon liquid. The main organic components in the torrefied wood pyrolysis water fractions were acids, alcohols and aliphatic oxygenates. Torrefied wood pyrolysis water exhibited a significantly lower acid concentration when compared to nontorrefied wood pyrolysis water. The biomass chars (prepared at 600°C) were analysed using proximate analyses and carbon dioxide char reactivity. Proximate analyses showed that volatile matter was still present in the torrefied wood, but was almost completely devolatilized after pyrolysis.

Key words

Pyrolysis, Pyrolysis compounds, Chemical composition, Torrefaction.

1. Introduction

Biomass residues and waste are abundant potential feedstock for pyrolysis, gasification or combustion processes and seem to be an attractive alternative raw material to current fossil fuel resources [1]. Pyrolysis is an attractive technology that converts biomass directly into liquid products [2]. However, during pyrolysis can be produced as well gaseous and solid products, depending on the residence time of the raw materials in the reactor chamber, and to the temperature choc to which raw materials are submitted. Torrefaction can be suggested as a method of biomass pre-treatment and can be defined as the thermochemical conversion of biomass at approximately 300°C in an inert atmosphere [3].

During biomass torrefaction, almost all moisture and a fraction of the light volatiles are removed to form a solid, dry material known as torrefied biomass [4]. The aim of torrefaction is to change the properties of biomass to obtain a better fuel quality with higher energy density, more homogeneous composition, lower hygroscopicity and elimination of biological activity [5].

In this study, torrefied biomass was produced at YGE – Yser Green Energy SA (Portugal) and characterized at Sasol Technology, Research and Development (South Africa). The experimental methods (pyrolysis and analytical methodologies) were previously established using a selection of South African biomass species.

2. Materials and Methods

2.1. Biomass samples

Wood chips were torrefied at approximately 260-280°C at YGE – Yser Green Energy SA in Portugal and subjected for characterization and pyrolysis studies to Sasol Technology, Research and Development in South Africa.

2.2. Fischer-tar Assay

The Fischer-tar Assay is a standard laboratory test for determining the yield of tar, water, char and gas (by difference) for a given coal (SANS 647: 1974)) [6]. The method entails the controlled heating of a defined quantity of material (50g) in an aluminum retort to a final temperature of 520°C. The heating program used is given in Table 1. During this test, biomass is converted to char with release of volatile matter [7]. All condensable material (tar and water) is collected in a round bottom flask submerged in ice. The water content of the condensable product is determined via a Dean and Stark distillation. The gas percentage is obtained by difference.

2.3. Termogravimetric analysis (TGA)

2.3.1. TGA proximate analysis

All thermogravimetric analyses were conducted in a nitrogen atmosphere with a flow of 150 ml/min.

Samples were heated from room temperature to 110°C with a heating rate of 50°C per minute. The samples were kept at 110°C for three minutes. Mass loss at this temperature was assigned to moisture.

Samples were then heated from 110°C to 900°C with a heating rate of 50°C per minute. The samples were kept at 900°C for seven minutes. Mass loss at this temperature was assigned as volatile matter. This volatile matter includes liquid hydrocarbons, gas and pyrolytic water. The TGA atmosphere was then changed to oxygen (150 ml/min) and kept for 20 minutes. The mass loss due to combustion was assigned as fixed carbon. The remaining residue was recorded as the amount of ash in the sample.

2.3.2. TGA mass loss

All thermogravimetric mass loss analyses were conducted in a nitrogen atmosphere with a flow of 150 ml/min. Samples were devolatilized from room temperature to 900°C at a heating rate of 10°C per minute. The samples were kept at 900°C for seven minutes.

2.3.3. TGA carbon dioxide char reactivity

Prior to char reactivity analyses, a standard proximate analysis was conducted to determine the amount of fixed carbon for a given sample. A sample containing 5mg of fixed carbon was heated in an inert atmosphere to 1200°C with a heating rate of 50°C per minute. The char was then allowed to cool down to 1000°C. When the temperature and mass were stabilized, the inert gas was replaced with carbon dioxide.

The Boudouard reaction [8] was allowed to continue until no further mass loss was observed. The calculation of the carbon dioxide char reactivity at 60% burn-off is discussed in literature [9]–[12].

2.3.4. Pyrolysis experiments

The standard KoekebakkerTM setup was used for biomass pyrolysis [13].

All experiments were conducted at atmospheric pressure in a nitrogen atmosphere. The KoekebakkerTM was loaded with approximately 150 to 400g of biomass prior to pyrolysis. During the pyrolysis experiments, two hydrocarbon liquid fractions were collected: condensed oil and additional oil.

A condenser connected to a chiller was connected to the outlet of the reactor. The condenser was connected to a two-neck round-bottom flask immersed in an acetone/ice bath.

Connected to the round-bottom flask were four solvent traps in series (three traps filled with solvent and a final empty trap). With one exception, all the solvent traps were immersed in ice/acetone baths.

Table 1. Heating	program used	for	Fischer-tar	Assay.
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Time from start (minutes)	Temperature (°C)
10	220
20	310
30	380
40	440
50	480
60	505
70	520
80	520

The solvent traps were filled with acetone for both quantity and quality experiments. All involved gases were captured in a bag after the solvent traps. All pyrolysis experiments were conducted at 600° C with a heating rate of ~10°C per minute.

2.3.5. Determination of water content in the liquid hydrocarbon

Toluene was added to the liquid product in the roundbottom flask and Dean-Stark distilled to quantitatively determine the amount of water. The condenser and all pipes were washed with acetone. All acetone fractions (solvent traps and acetone from washed pipes) were added together. The acetone was removed from the hydrocarbon liquid by distillation.

2.3.6. Determination of liquid hydrocarbon quality

Chloroform was added to the condensate in the roundbottom flask and transferred to a separation funnel. The organic phase was removed from the water phase. The condenser and all pipes were washed with acetone. Solvents were removed by distillation.

2.4. Characterization of liquid hydrocarbons

2.4.1. Simulated distillation (simdis)

Simulated distillation was conducted on a hightemperature GC-FID fitted with an ARX 2887 Restek column (10m x 0.53mm x 0.53 μ m). Approximately a 0.2 μ L sample was injected into the GC column per analysis. The GC oven program started with an initial temperature of 40°C, then heated at 15°C per minute to 540°C and hold at that temperature for 10 minutes.

2.4.2. Gas chromatography mass spectrometry (GCMS)

All oil samples were analyzed using a GC-FID (quantification) and a GCMS (peak identification) fitted with HP-FFAP column (50m x 0.2mm x 0.33 μ m). The HP-FFAP column is a high polarity column suited for the analyses of organic acids, free fatty acids and phenols. Approximately 1 μ L of sample was injected into GC column with a split of 200 (if samples were too diluted a split of a 100 was used). The GC oven program was as follows: initial temperature of 60°C held for 5 minutes, heating at 6°C per minute to 240°C and hold for 30 minutes (until all compounds were eluted). Gas flow through the column was 1.2ml per minute (helium in GCMS and hydrogen in GC-FID).

2.4.3. Two-dimensional gas chromatography mass spectrometry

Two-dimensional gas chromatography mass spectrometry (hereafter GCxGCxMS) was conducted on a Leco GCxGC TOF fitted with a Restek Stabilwax column ($60m \ge 0.25mm \ge 0.25\mu m$) and Restek RTXi5 column ($2m \ge 0.1mm \ge 0.1\mu m$). Approximately $0.5\mu L$ of sample was injected into the GC column with a split of 400. Helium gas flow through the column was 1.3ml per minute. The GC oven program for column 1 was as follows: initial temperature of 40°C held for 1 minute, heating at 2°C per minute to 230°C. The GC oven program for column 2 was as follows: initial temperature of 65°C held for 1 minute and heating at 2°C per minute to 255°C.

3. Results and discussion

3.1. Characterization of biomass

3.1.1. Proximate analyses

Biomass samples were air-dried and crushed to $<150\mu m$ for proximate analyses and the results are presented in Table 2. During torrefaction, all moisture and light volatiles are removed from the biomass.

3.1.2. Thermochemical behavior (TGA devolatilization)

The combined devolatilization profiles (thermograms) are presented in Figure 1. The individual devolatilization profiles are presented in Figure 2. The first derivative of the mass loss curve was determined to observe the thermal behavior of these biomass samples (Figure 3).

The thermograms in Figures 2 and 3 exhibited an initial mass loss ending at 110°C. This mass loss was assigned as moisture associated with the sample. The un-torrefied wood thermogram showed a rapid devolatilization starting at approximately 230°C and ending at approximately 370°C (fast pyrolysis zone). A slow mass loss was still observed after 370°C for this biomass sample (slow pyrolysis zone).

The first derivative of the mass loss curve showed that there were two thermal events occurring during fast pyrolysis (between 230°C to 370°C). These events could be attributed to the decomposition of hemicellulose and cellulose polymers in the biomass samples [14].

Table 2. Proximate analyses results for torrefied biomass.

	Air-dry	Ι	Dry basi	s	Dry, a	ish-free
	basis				ba	asis
Sample	%	%	%	%	%	% FC
_	Moisture	VM	FC	Ash	VM	
Torrefied	4.4	62.4	36.4	1.2	63.2	36.8
wood						

VM – Volatile matter; FC – Fixed carbon



Figure 1. Devolatilization profiles (thermograms) of torrefied and normal wood.



Figure 2. Individual devolatilization profiles (thermograms) of normal wood (left) and torrefied wood (right).

The first event was associated with hemicellulose decomposition that typically occurs at relatively low temperatures (~200°C) [15]. The second thermal event was associated with cellulose decomposition (typical decomposition temperature of 315 to 400°C) [16].

The slow pyrolysis observed was associated with the slow decomposition of lignin (from 370 to 900°C) [17].

The torrefied wood thermogram showed a rapid devolatilization starting at approximately 300°C due mainly to hemicellulose degradation.

The fast pyrolysis zone was observed between 300°C and 380°C (assigned to the decomposition of remnant cellulose). A slightly slower mass loss was still observed after 380°C up to 900°C (assigned to the decomposition of remnant lignin).

3.1.3. Pyrolysis of biomass (product quality and quantity) 3.1.3.1. Pyrolysis yields

Results from Fischer-tar Assay for yields torrefied biomass are summarized in Table 3. Results of pyrolysis products are shown in Table 4.

As mentioned above, in the section Pyrolysis experiments, water and oil condensates, consist of all the oil condensed in the ice-acetone cooled round-bottom flask. Additional oil consists of oil isolated from the four solvent traps and oil washed from the condenser and pipes.

The torrefied wood still yields a significant amount of water during pyrolysis. This is pyrolytic water formed from the thermal decomposition of the oxygen functionality present in the molecular structure of biomass.

3.1.3.2. Pyrolysis gas characterization

Pyrolysis gas was collected during the pyrolysis experiments (bag samples) and analyzed using gas chromatography. All experiments were conducted in a nitrogen atmosphere. Therefore data were normalized to a nitrogen-free basis. The gas compositions of the various pyrolysis experiments are shown in Table 5.

The torrefied wood pyrolysis gas composition differed significantly in comparison to usual normal wood. Torrefied wood pyrolysis yielded significantly high amounts of hydrogen ($\sim 20\%$) and methane ($\sim 22\%$).

Table 3. Fischer-tar Assay for torrefied biomass.

Product	Torrefied wood
% Char	44.7
% Tar	16.2
% Water	20.4
% Gas	18.7
Total	100.0
0/ C · 1 /	11 1.00

% Gas is determined by difference

Table 4. Quantitative pyrolysis results for torrefied biomass.

Sample	Torrefied wood
% Char	43.2 (0.12)
% Hydrocarbon liquid	14.0 (0.98)
% Water	20.3 (1.06)
% Gas	22.6 (0.20)
Total	100.0

% Gas is determined by difference. Standard deviation is shown in parentheses.

Carbon dioxide and carbon monoxide are formed from the thermal decomposition of the oxygen remaining in the molecular structure of biomass. Torrefaction removed a significant amount of oxygen atoms or radicals from the molecular structure of biomass. Therefore less oxygen was available for the formation of carbon monoxide and carbon dioxide.

3.2. Characterization of biomass liquid hydrocarbons

As aforementioned, two types of hydrocarbon liquids were collected during the pyrolysis experiments: condensed oil and additional oil. These two hydrocarbon liquid fractions were mixed together to form a homogeneous hydrocarbon sample for analysis.

3.2.1. Simulated distillation of biomass liquid hydrocarbons

Simulated distillations (simdis) [18] were conducted to determine the boiling point distributions of all the biomass liquid hydrocarbons (Figure 3).

The weight average boiling points (WABP) of the simulated distillation curves were calculated (Equation 1) for comparison. Results are summarized in Table 6.

$$WABP = \frac{T_{10wt\%} + T_{30wt\%} + T_{50wt\%} + T_{70wt\%} + T_{90wt\%}}{5}$$
(1)

From these simulated distillations, was concluded that torrefied wood hydrocarbon liquid and normal wood hydrocarbons liquids had similar boiling point distribution, with torrefied wood liquid being slightly smaller.



Figure 3. Simulated distillation results for torrefied wood and normal wood.

Table 5. Pyrolysis gas composition of torrefied wood.

	Torrefied wood
Other (C2+)	2.3
Oxygen/Argon	2.9
Carbon dioxide	22.5
Carbon monoxide	30.1
Methane	22.0
Hydrogen	20.1

Table 6. Weight average boiling points from simulated distillation curves.

Sample	Torrefied wood
WABP (°C)	216.5

3.2.2. Gas chromatography mass spectrometry of biomass liquid hydrocarbons

The GCMS profiles of the hydrocarbon liquids consisted of various types of oxygenates (oxygen containing organic compounds).

To simplify the chromatographic data, the compounds were grouped according to specific molecular families. These families included: aliphatic hydrocarbons, acids, aliphatic esters, aliphatic aldehydes and ketones, aliphatic alcohols, alkylbenzenes, alkylphenols, furans (with polyfunctional oxygen), linear and cyclic aliphatic oxygenates (polyfunctional oxygen), aromatic oxygenates (polyfunctional oxygen) and nitrogen/sulphur containing compounds.

The percentage of each molecular family for each biomass sample was determined and is summarized in Table 7.

The torrefied wood hydrocarbon GCMS chromatogram was less complex when compared to normal wood. The wood chromatogram consisted of 125 normal compounds, whereas the torrefied wood chromatogram consisted of 56 compounds (excluding the unknown peaks). This decrease in hydrocarbon complexity was expected since torrefaction removes most of the light hydrocarbons and acids from the solid biomass. Torrefied wood hydrocarbon liquid showed higher concentrations of aliphatic aldehydes, ketones and alkylphenol when compared to normal wood hydrocarbon liquid. A decrease in all the other components was observed for the torrefied wood hydrocarbon liquid when compared to the normal wood sample. The main advantage of torrefaction was the decrease in the acid concentrations when compared to normal wood.

3.2.3. GSMS analytical results for pyrolysis water fraction of torrefied biomass

The pyrolysis water and oil were separated using a separation funnel after each pyrolysis experiment. The water fractions were collected and analyzed using GCMS. The organic compounds present in the water phase fraction are summarized in Table 8.

Table 7. GCMS analytical results for composition of the various

hydrocarbon liquid fraction in torrefied biomass		
Molecular component	Torrefied	
	wood	
Aliphatic	0.57	
Acids	2.24	
Aliphatic ester	0.00	
Aliphatic aldehydes and ketones	33.32	
Aliphatic alcohol	0.00	
Alkylbenzenes	2.07	
Alkylphenol	35.83	
Furan	0.70	
Furan (polyfunctional oxygen)	5.90	
Linear and cyclic aliphatic	6.61	
oxygenates (polyfunctional		
oxygen)		
Aromatic oxygenates	12.25	
(polyfunctional oxygen)		
Nitrogen and sulphur containing	0.51	
compounds		
Total	100.0	

The amount of unknown compounds observed in the GC chromatograms was 22.9% for torrefied biomass.

Note that the quantification of the amount of organics in the water was not conducted due to water added during the separation step to distinguish between the two phases (this was due to discoloration of the water phase).

The main organic components in both normal wood and torrefied wood pyrolysis water fractions were acids, alcohols and aliphatic oxygenates. The remaining organic compounds consisted of various types of oxygenates. Torrefied wood pyrolysis water exhibited a significantly lower acid concentration when compared to normal wood pyrolysis water.

Proximate analyses of the normal wood chars showed that volatile matter was still present. This was expected when evaluating the devolatilization profiles of the normal wood sample. Although devolatilization stops at approximately 370°C there was still slow mass loss up to 900°C.

The carbon dioxide gasification reactivity of the fixed carbon at 50% burn-off was determined using the pyrolysis biomass chars. The results are summarized in Table 9.

3.2.4. Pyrolysis char proximate analysis and reactivity Results of char proximate analysis are summarized in Table 10.

Table 8. GCMS composition results of organic compounds for the pyrolysis water faction in torrefied biomass

Component	Torrefied wood
Acids	27.31
Aliphatic hydrocarbons	1.39
Aliphatic alcohol	21.41
Aliphatic aldehydes and ketones	9.05
Alkylphenols	7.26
Aromatic oxygenates	3.50
Aliphatic oxygenates	25.84
Furan oxygenates	4.23
Nitrogen heteroatoms	0.00
Total	100.0

Data was normalized to 100% organic composition.

Table 9. Carbon dioxide reactivity of biomass chars (TGA)

Sample	TGA CO2 char reactivity
Normal wood	10.5
Torrefied wood	17.1

Table 10. Proximate analysis of biomass chars (600°C chars).

	Dry, ash-free basis			
Sample	% VM	% FC		
Normal wood	18.7	81.3		
Torrefied wood	5.9	94.1		

3. Conclusions

The pyrolysis behavior of torrefied wood was investigated. Torrefaction is the thermochemical upgrading of biomass at approximately 200 to 320°C (inert atmosphere) to increase the fuel quality. Torrefied wood was pyrolysed at atmospheric pressure (nitrogen atmosphere) at 600°C. All the condensable liquids (water and oil) were sampled for detailed analyses. The pyrolysis behavior of torrefied wood was compared to normal wood pyrolysis. Comparison between normal wood and torrefied wood samples:

- Proximate analyses showed that normal wood and torrefied wood were significantly different in composition. Normal wood had a higher volatile matter content compared to torrefied wood, as expected.
- Thermogravimetric analyses (devolatilization showed rapid profiles) of normal wood devolatilization starting at ±230°C and ending at $\pm 370^{\circ}$ C (fast pyrolysis zone). A slow mass loss was still observed after 370°C (slow pyrolysis zone). The torrefied wood thermogram showed a rapid devolatilization starting at approximately 300°C. The fast pyrolysis zone was observed between 300°C and 380°C. A slightly slower mass loss was still observed after 380°C up to 900°C. The mass loss in terrified biomass TGA was lower than that of normal biomass, as expected, due torrefaction changes.
- The normal wood sample exhibited the highest hydrocarbon liquid yield, followed by the torrefied sample.
- The torrefied wood pyrolysis gas composition differed significantly in comparison to normal wood sample. Torrefied wood pyrolysis yielded significantly higher amounts of hydrogen and methane and significantly lower amounts of carbon dioxide.
- Torrefied and normal woody biomass hydrocarbon liquid fractions were similar in boiling temperature distribution, with torrefied wood liquid being slightly smaller. The torrefied wood hydrocarbon GCMS chromatogram was less complex when compared to the normal wood sample, reflecting a significant difference between the two woody biomasses. Torrefied wood hydrocarbon liquid exhibited higher concentrations of aliphatic aldehydes and ketones and alkylphenol when compared to the wood hydrocarbon liquid. A decrease in all the other molecular components was observed for the torrefied wood hydrocarbon liquid. The GCMS analyses showed that normal biomass hydrocarbon liquids consisted predominantly of various types of oxygenates containing organic compounds). (oxygen Α significant decrease in the acid concentration was also observed for the torrefied woody biomass hydrocarbon liquid.
- The main organic components in both normal wood and torrefied wood pyrolysis water fractions were acids, alcohols and aliphatic oxygenates. The remaining organic compounds consisted of various types of oxygenates. Torrefied wood pyrolysis water exhibited a significantly lower acid concentration when compared to the normal wood pyrolysis water.
- The biomass chars were analyzed using proximate analyses and carbon dioxide char reactivity. Proximate analyses showed that volatile matter was still present in the normal wood chars. Torrefied wood, however, was almost completely devolatilized after pyrolysis.

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