



Characterization and condensation behaviour of gravimetric tars produced during spruce torrefaction



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ABSTRACT

The gravimetric tars produced during torrefaction of spruce at 280 °C account for approximately 10% of the mass in the torrgas. These tars are characterized in this study and their condensation behaviour at different temperatures is experimentally investigated and modelled. The identified tar compounds have been classified, based on their structure, in phenolics, (hetero)cyclic (mainly furans) and not cyclic (mainly carbonyls). The heavy tars compounds, with a high boiling point, have not been identified, but it is inferred that they are mainly composed of pyrolytic lignin with some amounts of sugars. In the designed condensation system, between 65 and 75% of the gravimetric tars have condensed at temperatures between 160 and 100 °C. A tar condensation model was developed to calculate the amount of tars that condense in equilibrium at a defined temperature. The model classifies the tar compounds in groups, according to their structure, and it is able to predict the experimental results with reasonable accuracy.

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1. Introduction

Torrefaction is a biomass pre-treatment process conducted at low temperatures, ranging from 220 to 350 °C, which improves the biomass storage and transportation properties. Torrefaction and its applications were reviewed by Van der Stelt et al. [1] and Tumuluru et al. [2]. Biomass loses mass and gets enriched in carbon due to volatiles and water release during this process. The main components in the torrgas are permanent gases, such as CO₂ and CO, and light condensable species, such as H₂O, acetic acid and methanol [3–5]. Heavy condensable species, such as phenolic compounds, are also produced during torrefaction [6]. However, this fraction of the volatiles is often disregarded, despite accounting for approximately 10% of the mass in the torrgas produced from wood torrefaction [7,8]. The analysis of the torrefaction products of agricultural residues [9] and sewage sludge [10] has also shown that heavy condensable species are generated from these feedstocks. Moreover, detailed models have been presented for the prediction of the product composition from biomass torrefaction [11,12]. In this study the gravimetric tars produced during torrefaction of

spruce are analyzed and their condensation behaviour at different temperatures is experimentally investigated and modelled. To the knowledge of the authors, tar condensation has so far been investigated only for the volatiles of pyrolysis [13,14], but not yet for the tars of a torrgas. The employed experimental setup is described in Section 2, the characterization of gravimetric tars is shown in Section 3 and the condensation experiments and model are described in Section 4. Finally, the conclusions are exposed.

2. Experimental setup

Torrefaction of spruce chips has been conducted in a cylindrical and indirectly heated rotating drum reactor. The experiments have been conducted at an approximated temperature in the reactor of 280 °C with an average retention time of 35 min at atmospheric pressure. The averaged particle size of the spruce chips was 6 mm and the yield of torrefied biomass was 75% (w.b.). The input flow of wet biomass ranged from 500 to 670 kg/h. The chemical composition of spruce and torrefied spruce is shown in Table 1.

The torrgas has been extracted downstream the reactor. All torrgas pipes of the setup were heated indirectly to a temperature of 300 °C. The concentrations of permanent gases (CO, CO₂ and light hydrocarbons) and light condensable species (water vapour, formaldehyde, acetic acid, acetaldehyde, methanol, ethanol,

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Table 1
Elemental analysis, ash and moisture content. Values obtained for 3 samples of untreated and torrefied spruce chips.

	Spruce chips	Torrefied spruce chips
C (% mass d.b.)	49.7 ± 0.1	54.3 ± 0.4
H (% mass d.b.)	6.2 ± 0.1	5.8 ± 0.1
O (% mass d.b.)	43.7 ± 0.1	39.3 ± 0.3
N (% mass d.b.)	0.06 ± 0.01	0.06 ± 0.01
Ash (% mass d.b.)	0.4 ± 0.1	0.6 ± 0.1
Moisture (% mass w.b.)	5.4 ± 1.8	–

lactic acid, formic acid and propanal) of the torrgas were measured by Fourier transform infrared spectroscopy (FT-IR, Gasmeter DX-4000), after a dilution with a factor 10 to 1. The tars were sampled in impinger bottles (filled with isopropanol) during the measurements and analysed afterwards in the laboratory. The tar content of the torrgas has been measured using a gravimetric method according to the tar protocol (CEN/TS 15439), that is, the samples are dried in a vacuum drier (150 mbar absolute pressure) at 55 °C until all solvent as well as light condensable species are evaporated and the remaining tars are weighted. In addition, the gravimetric tars have been characterized by gas chromatography (GC) coupled to mass spectrometry (MS) to identify the compounds and a flame ionization detector (FID) to quantify them (Agilent 6890 N Network GC System). 10.0 ml of sample from the impinger bottles were extracted with 10.0 ml of dichloromethane (extraction step repeated 3 times), drying afterwards the sample with sodium sulphate and analysing the resulting dichloromethane phase by GC–MS–FID. The injector temperature was 240 °C. The FID was calibrated for the 18 most relevant compounds. For the other detected compounds, the calibration values from compounds with a similar structure were employed.

Moreover, a tar filtration set up to catch condensed tars at variable filter temperatures was designed and has been installed in the torrgas measurement setup. The experimental setup is depicted in Fig. 1. The filter consists on an impinger bottle filled with glass wool and raschig rings. 3 experiments have been conducted with average filter temperatures of 150, 120 and 105 °C. The gravimetric tar content before and after the filter was measured as previously explained. The elemental composition of the condensed tars and the tars before and after the filter (C, H, N) has been measured using an elemental analyser (Vario EL III Elementar).

3. Characterization of gravimetric tars

The detected tar compounds by GC–MS–FID were classified based on their structure in 3 different groups:

- Phenolic compounds: aromatic compounds linked with hydroxyl and other O-containing groups, such as guaiacols.
- (Hetero) cyclic compounds: cyclic compounds, mainly heterocyclics, such as furans (e.g. furfural).
- Non-cyclic compounds: compounds with carbonyl and/or alcoholic groups, such as hydroxyacetone.

As opposite to pyrolysis, no tar compounds without oxygen, such as polycyclic aromatic hydrocarbons (PAH), have been found. The composition of the GC detected gravimetric tars is shown in Table 2. The total percentage of mass and the averaged elemental composition and molecular weight of the three groups is shown in Table 3. The characterization has been repeated 3 times showing a good reproducibility of the results. The carbon content and molecular weight of the different groups differ. Phenolics have the highest carbon content and molecular weight. Non-cyclic compounds have the lowest values for these properties.

The phenolic group is mainly composed of guaiacols, therefore, they have mainly a lignin origin. Guaiacols are the main products of pyrolysis of softwood lignin [15]. Another possible source is hydrophilic extractives, which are mainly composed of phenolic compounds, such as lignans [16]. The (hetero) cyclic group is mainly composed of furans, which are produced from cellulose and hemicellulose. Terpenes, which are lipophilic extractives, such as α and β Pinen or limonene, were also detected by GC and are included in the cyclic group. Non-cyclic compounds with a carbonyl structure can be produced by cellulose, hemicellulose and lignin. Non-cyclic lipophilic extractives, such as fats and fatty acids as well as waxes, have not been detected.

The product composition of the torrgas is detailed in Table 4. Volatiles species are classified in permanent gases, light condensable species and gravimetric tars. Light condensable species are water and several oxygenated species with carbonyl and/or alcohol functional groups that have been detected by FT-IR (see Section 2). The boiling points of these species range between –19 °C for formaldehyde or 21 °C for acetaldehyde to 118 and 122 °C of acetic acid and lactic acid, respectively.

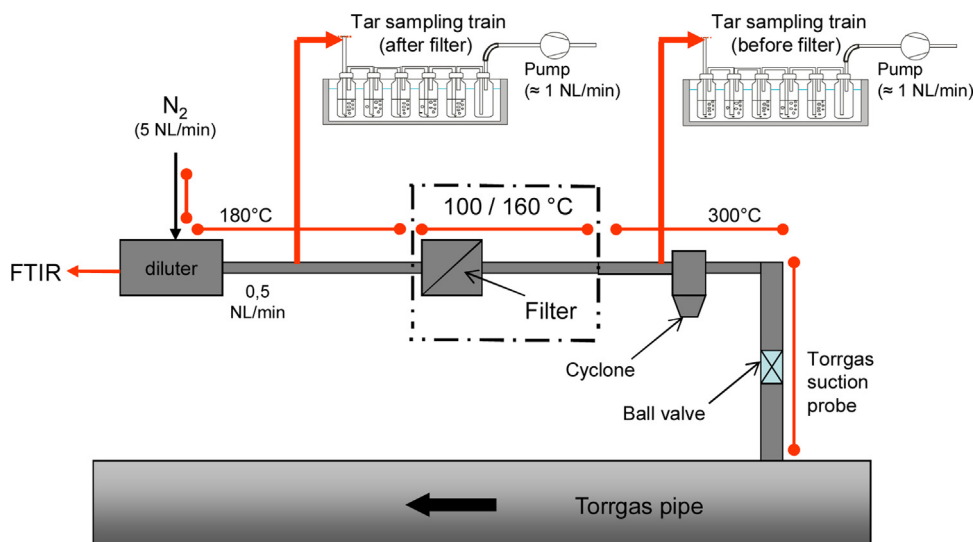


Fig. 1. Experimental setup for tar condensation.

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