

## 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 CO<sub>2</sub> and CO, and light condensable species, such as H<sub>2</sub>O, 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, CO<sub>2</sub> 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

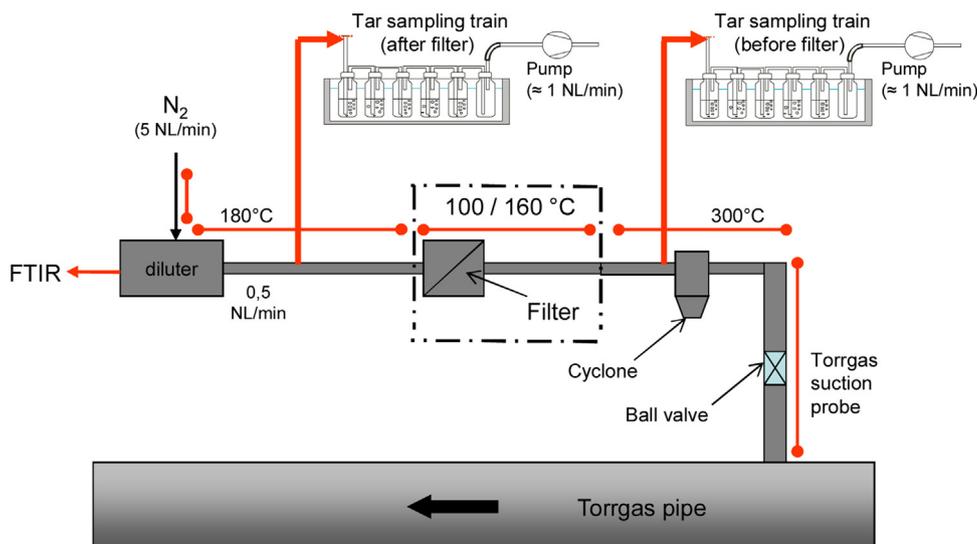
The detected tar compounds by GC–MS–FID were classified based on their structure in 3 different groups:

- 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  $\alpha$  and  $\beta$  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.

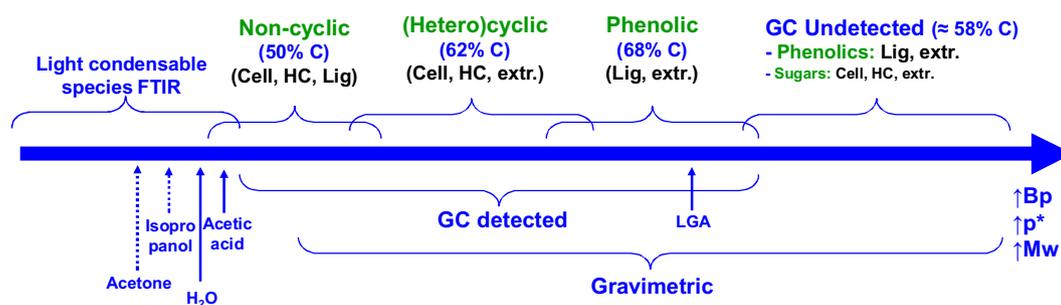
The product composition of the torrgas is detailed in Table 4. Volatiles species are classified in permanent gases, light condensable species and gravimetric tars. Light condensable species are water and several oxygenated species with carbonyl and/or alcohol functional groups that have been detected 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.

**Table 2**  
Composition in mass percentage of the GC detected fraction of the gravimetric tars.

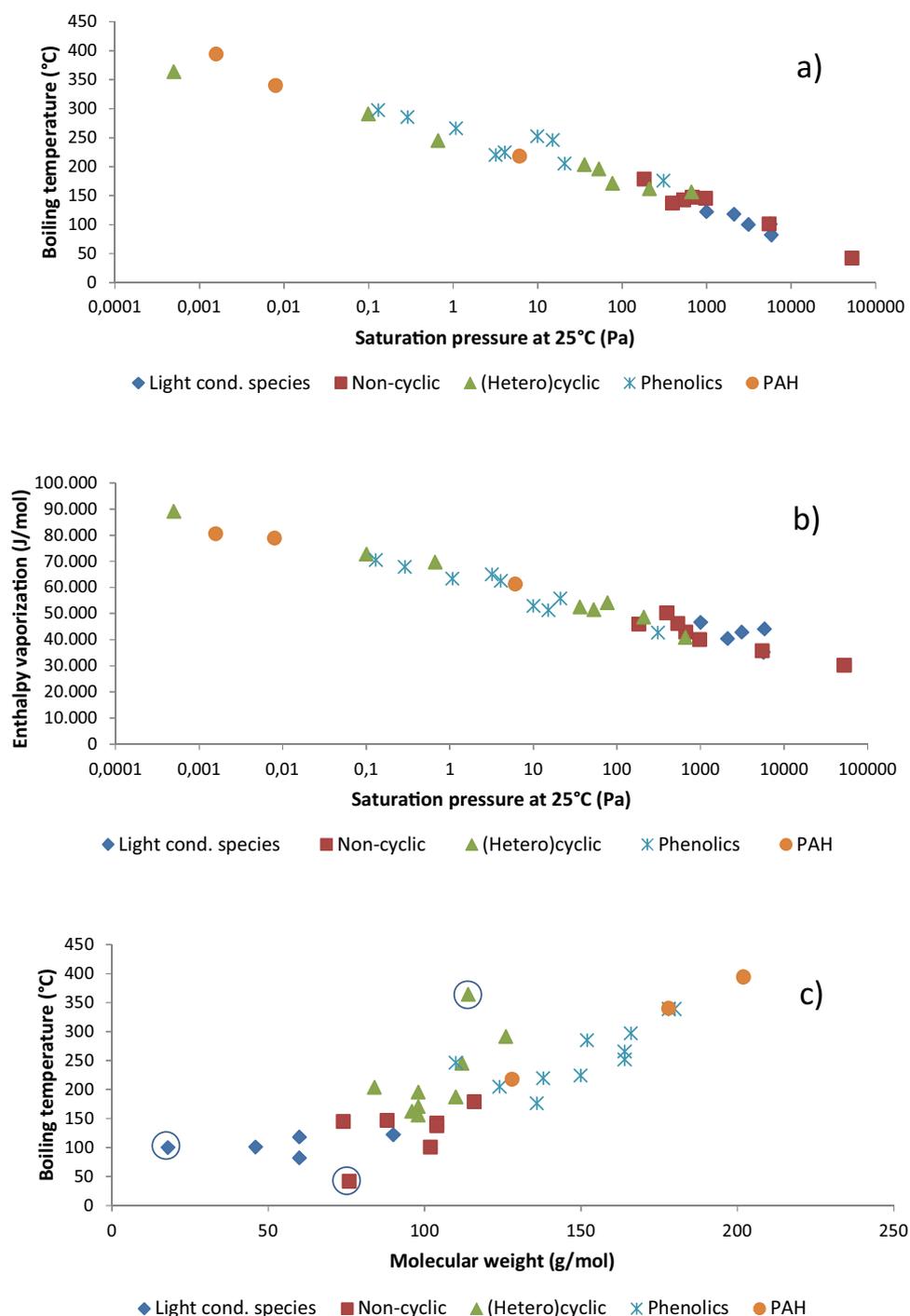
Name	Mw (g/mol)	% mass	Group
Hydroxyacetone	74	4.55 ± 1.87	Non-cyclic
Dimethoxymethane	76	1.65 ± 0.18	Non-cyclic
4-Hydroxy-2-butanone	88	4.59 ± 0.26	Non-cyclic
Propyl nitrite	89	2.17 ± 0.17	Non-cyclic
Methyl glycolate	90	0.48 ± 0.07	Non-cyclic
Methoxyethylvinylether	102	0.97 ± 0.05	Non-cyclic
2-oxo-propionic acid methyl ester	102	0.87 ± 0.05	Non-cyclic
Acetoxyacetone	116	1.73 ± 0.09	Non-cyclic
1,3-Dioxol-2-one	74	1.09 ± 0.08	(Hetero) cyclic
2-(5H)-Furanone	84	2.50 ± 0.04	(Hetero) cyclic
Furfural	96	13.67 ± 1.62	(Hetero) cyclic
Furfuryl alcohol	98	5.30 ± 0.51	(Hetero) cyclic
2-Hydroxy-2-cyclopentenone	98	1.54 ± 0.10	(Hetero) cyclic
5-Methyl-2-furfural	110	1.91 ± 0.09	(Hetero) cyclic
Methylhydantoin	114	1.82 ± 0.10	(Hetero) cyclic
2-(1-Hydroxyethyl)-tetrahydrofuran	116	0.57 ± 0.05	(Hetero) cyclic
Furandicarboxaldehyde	124	1.23 ± 0.25	(Hetero) cyclic
Ethylcyclohexanone	126	1.14 ± 0.32	(Hetero) cyclic
HMF	126	7.35 ± 0.64	(Hetero) cyclic
Maltol	126	2.03 ± 0.05	(Hetero) cyclic
Limonene	136	1.92 ± 0.15	(Hetero) cyclic
alpha-Pinene	136	0.74 ± 0.04	(Hetero) cyclic
beta-Pinene	136	1.26 ± 0.17	(Hetero) cyclic
Homofuraneol	142	0.82 ± 0.10	(Hetero) cyclic
Acetoxymethylfurfural	168	1.01 ± 0.14	(Hetero) cyclic
Catechol	110	1.93 ± 0.09	Phenolics
2-Methoxyphenol (Guaiacol)	124	2.24 ± 0.06	Phenolics
Creosol	138	1.50 ± 0.03	Phenolics
Methoxy-vinyl-phenol	150	1.84 ± 0.25	Phenolics
Vanillin	152	3.51 ± 0.16	Phenolics
Ethylmethoxyphenol	152	0.49 ± 0.04	Phenolics
Eugenol	164	0.80 ± 0.14	Phenolics
cis-Isoeugenol	164	0.56 ± 0.07	Phenolics
trans-Isoeugenol	164	4.82 ± n0.39	Phenolics
Acetovanillone	166	0.86 ± 0.21	Phenolics
5-Propylguaiaacol	166	1.57 ± 0.35	Phenolics
3-(p-Hydroxy-m-methoxyphenyl)-2-propenal	178	7.17 ± 0.23	Phenolics
Guaiacyl acetone	180	1.89 ± 0.06	Phenolics
Homovanillic acid	182	2.37 ± 0.11	Phenolics

**Fig. 2.** Classification of condensable species. Bp: boiling point, p\*: saturation pressure, Mw: molecular weight, C: carbon content in percentage of mass, Cell: cellulose, HC: hemicellulose, Lig: lignin, extr: extractives, LGA: levoglucosan.

The groups of condensable products are depicted in Fig. 2, from lower to higher boiling point. Acetic acid is defined as the boundary between the light condensable species, detected by FTIR (including acetic acid and formic acid), and the non-cyclic tars, detected by GC.

Not all gravimetric tars are identified and quantified by GC–MS–FID. The detected fraction corresponds to approximately 40% of the total gravimetric tars. Heavy tars with a high boiling point could not be detected. These compounds do not evaporate into the GC column and are trapped in the quartz wool to protect the separation column and the detector. Their measured carbon content is presented in Section 4.3.

The compounds that can be present in the not detected GC fraction are most probably phenolic or sugar compounds. Lignin decomposition produces pyrolytic lignin [17,18], composed of phenolic compounds with more than one aromatic ring, therefore with a higher boiling point than the GC detected phenolic compounds, which have one ring. This is the most probable source. Another possible source of the not detected GC fraction is extractives. Hydrophilic extractives are mainly composed of phenolic compounds, such as lignans, and sugars can also be present [16]. Sugars are known to have a high boiling point. Lipophilic extractive compounds could also be present.



**Fig. 3.** Correlations between saturation pressure at 25 °C and boiling temperature at 1 atm. (a) and enthalpy of vaporization (b) and between molecular weight and boiling temperature at 1 atm. (c).

Cellulose and hemicellulose also produce sugars during pyrolysis. However, the sugar compound levoglucosan (LGA) has been detected in low quantities in previous batch fixed bed torrefaction experiments with 75 g of spruce chips [8], but it was not detected in this study. The higher retention time of the torrgas in the reactor employed for this study may enhance the secondary decomposition of LGA [19].

The torrgas composition presented in this study is compared to the one obtained in the lab-scale experiments [8] in Table 4. It should be noted that a uniform temperature was not obtained inside the bed during the lab-scale experiments. Target

temperatures of 250 and 285 °C were set at the middle of the bed. The main difference between the two studies is the presence of LGA in the lab-scale experiments.

#### 4. Condensation model and experiments

##### 4.1. Condensation properties

Boiling point temperatures, saturation pressures and molecular weights of several compounds have been searched in available online databanks [20–23] and are plotted in Fig. 3. The 33 employed

**Table 3**  
Elemental composition and molecular weight of the GC detected gravimetric tars groups. SD: standard deviation.

	Phenolics	(Hetero) cyclic	Non-cyclic	Total GC
% C	68.2 ± 0.1	61.8 ± 0.2	50.2 ± 0.1	61.8 ± 0.2
% H	6.4 ± 0.1	5.6 ± 0.1	8.5 ± 0.1	6.4 ± 0.1
% O	25.5 ± 0.1	31.6 ± 0.4	39.3 ± 0.3	31.0 ± 0.3
% N	0.0	1.0 ± 0.1	1.9 ± 0.3	0.8 ± 0.1
% mass	34.1 ± 0.9	47.3 ± 1.3	18.6 ± 1.6	100
Mw (g/mol)	159.9 ± 0.8	107.0 ± 0.3	86.7 ± 2.7	114.9 ± 1.5
SD Mw (g/mol)	32.2 ± 2.1	19.0 ± 0.2	29.9 ± 1.4	39.5 ± 1.5

compounds are listed in Table A1 and identified with their CAS number (Registry Number from American Chemical Society). The compounds belong to the groups: light condensable species, non-cyclic, (hetero) cyclic, phenolic and polycyclic aromatic hydrocarbons (PAH). Compounds from all groups have been detected by GC or FT-IR in the torrgas, with the exception of PAHs.

When plotting the saturation pressure ( $p^*$ , in Pa) at 25 °C in a logarithmic scale, there is a linear correlation with the boiling point at atmospheric pressure ( $B_p$ , in °C) and with the enthalpy of vaporization ( $L$ , in J/mol) (see Fig. 3, top and middle). The correlations are shown in Eq. (1) and (2):

$$B_p = -17.99 \log_{10}(p^*) + 257.94 (r^2 = 0.96) \quad (1)$$

$$L = -3073 \log_{10}(p^*) + 64416 (r^2 = 0.96) \quad (2)$$

There is also a correlation between the molecular weight ( $M_w$ , in g/mol) and the boiling temperature (see Fig. 3, bottom). The bigger the molecule, the higher is the boiling point. The correlation, without the outliers marked with a circle in the figure (dimethoxymethane, methylhydantoin and H<sub>2</sub>O), is shown in Eq. (3). The previous compounds show a different behaviour than

other species in the torrgas due to their different functional groups present in their structure: dimethoxymethane does not have a carbonyl or alcoholic group, as most of the light condensable species, water is known as a compound with unique properties and methylhydantoin (C<sub>4</sub>H<sub>6</sub>O<sub>2</sub>N<sub>2</sub>) has very high nitrogen content.

$$B_p = 1.8413 M_w - 13.459 (r^2 = 0.80) \quad (3)$$

The boiling point, saturation pressures and heat of vaporization of the compounds of one group are in a similar range, so the proposed classification of tars in the selected groups is reasonable. The group of PAH was selected to check that the correlations are also valid in the range of low saturation pressures, which is the range where the not GC detected compounds should be present.

In order to apply the condensation model, each tar group (phenolics, heterocyclic, non-cyclic) is sub-divided into two groups with the same percentage of mass and the following molecular weight: Mean ± (std. dev.)/2 (see Table 5 and Table 3). The boiling points and saturation pressures at 25 °C are then estimated based on the previously presented correlations (Eq. (1) and Eq. (3)). The heat of vaporization ( $L$ ) is additionally calculated with the Clausius–Clapeyron equation (Eq. (4)). The input data for this equation are the boiling point temperature ( $T_1 = B_p$  in K) at atmospheric pressure ( $P_1$ ) and the saturation pressure ( $P_2$ ) at temperature  $T_2$  (298 K, 25 °C). For each group, it has also been checked that the enthalpy of vaporization obtained from the Clausius–Clapeyron equation is similar (deviations on average of  $2.2 \pm 1.3\%$  for all groups) to the one obtained with the correlation presented in Eq. (2).

$$\ln \left( \frac{p_2}{p_1} \right) = \frac{L}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \quad (4)$$

**Table 4**  
Composition of the products of spruce torrefaction in% mass.

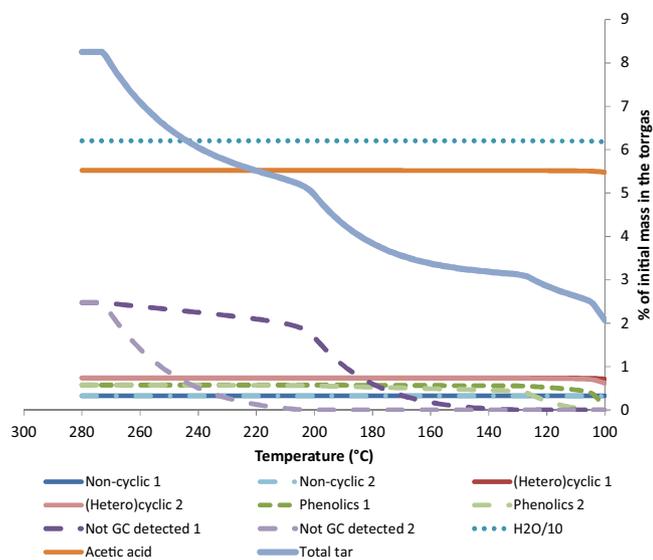
	This study	Spruce 250 °C lab-scale [8]	Spruce 285 °C lab-scale [8]
Total permanent gases	20.25 ± 0.53	25.7	26.8
Total light condensable species	69.69 ± 1.34	61.00	55.65
Total gravimetric tars	10.04 ± 0.53	13.30	17.54
Phenolics (GC)	1.39 ± 0.09	2.00	2.56
(Hetero) cyclics (GC)	1.93 ± 0.05	2.51	2.86
Non-cyclic (GC)	0.76 ± 0.07	2.64	3.57
LGA (GC)	0	1.33	2.19
Not GC detected	5.97 ± 0.39	4.83	6.37

**Table 5**  
Properties of the groups for the condensation model.

	$p^*$ (25 °C, 1 atm)	Bp (°C, 1 atm)	$\Delta h$ vap (kJ/mol)	Mw (g/mol)	% mass
H <sub>2</sub> O	3111	100	42.96	18	62.03
Acetic acid	2095	118	40.44	60	5.52
Non-cyclic 1	2200	117	40.31	72	0.330
Non-cyclic 2	105	177	50.48	102	0.330
Cyclic 1	170	167	49.13	97	0.742
Cyclic 2	28	197	55.55	115	0.742
Phenolic 1	1.7	247	63.89	142	0.577
Phenolic 2	0.06	307	73.15	174	0.577
Not GC detected 1	0.0018	392	80.19	220	2.475
Not GC detected 2	4.00E-06	482	98.13	270	2.475

**Table 6**  
Condensation experiments and comparison to the model.

	Spruce tars 150 °C	Spruce tars 120 °C	Spruce tars 105 °C
Temperature range in the filter (°C)	145–160	115–125	100–110
% mass of tars in torrgas after filter (not condensed), measured	31.3	28.8	22.0 ± 1.2
% mass of tars in torrgas after filter (not condensed), corrected	34.0	31.5	25.0 ± 1.2
% mass of not condensed tars predicted by model	39.4–42.3	33.5–37.0	25.6–32.1



**Fig. 4.** Equilibrium model for condensation. Torrgas from spruce torrefaction at 280 °C with the mass composition: 62.03% H<sub>2</sub>O, 5.52% acetic acid and 8.25% gravimetric tars.

**Table 7**  
Condensation of the different groups of tars at two temperatures as predicted by the model.

Group	% initial mass	% condensed at 110 °C	% condensed at 150 °C
Non-cyclic 1	4.0	0.00	0.00
Non-cyclic 2	4.0	1.24	0.28
Cyclic 1	9.0	0.89	0.21
Cyclic 2	9.0	2.71	0.51
Phenolic 1	7.0	17.52	2.63
Phenolic 2	7.0	89.49	19.28
Not GC detected 1	30.0	100.00	94.07
Not GC detected 2	30.0	100.00	100.00
Total tar		67.9	59.8

The molecular weight of the not GC detected fraction is unknown and assumptions should be made in order to define an appropriate molecular weight. It was assumed that, as previously discussed, the not GC detected fraction consists of compounds with a higher boiling point and, therefore, molecular weight, than the phenolic, (hetero) cyclic and non-cyclic compounds, as they did not evaporate during the GC detection. The maximum temperature of the experiments, 280 °C, represents the upper limit for the possible condensation of the not GC detected fraction at the specific torrgas composition. The molecular weights of the two not GC detected tar fractions have been fitted in a way so that a smooth trend in the condensation behaviour has been obtained, with the two boiling point limits mentioned above, i.e., higher than for the other groups and low enough so that no condensation takes place at temperatures over 280 °C (see Fig. 4).

The properties of the groups are summarized in Table 5. Condensation is considered for tar, H<sub>2</sub>O and acetic acid, but not for the other compounds as they will not condense at the considered conditions. The employed torrgas composition is also shown in the table. The torrgas composition differs to the one presented in Table 4 due to the extra addition of water vapour downstream.

#### 4.2. Condensation model

The equilibrium model calculates, from a defined torrgas composition, the amount of tar that condenses at a defined temperature if equilibrium is reached. For the calculations at each temperature,

the partial pressures of the components are employed. The calculations start at 280 °C. The condensation model determines first at each temperature if there is saturation or not, based on the Raoult law and assuming an ideal mixture [24]. The saturation pressure of a mixture ( $p^*$ ) is the sum of the saturation pressures of each component ( $p_i^*$ ) multiplied by the gas mol fractions ( $X_i$ ), as shown in Eq. (5). The saturation pressures of each component at the defined temperature are calculated with the Clausius–Clapeyron equation (Eq. 4). Condensation occurs if Eq. (6) is satisfied, being  $p_i$  the partial pressure of each component.

$$p^* = \sum_{i=1}^n (p_i^* X_i) \quad (5)$$

$$\sum_{i=1}^n \left( \frac{p_i}{p_i^*} \right) > 1 \quad (6)$$

If there is condensation, the composition of the condensed phase is determined for each species by Eq. (7). The amount of condensation are determined by Eq. (8).  $\Delta p$  (in Pa) represents the difference between the current vapour pressure and the saturation pressure. Therefore, in case of saturation, it represents the amount of vapours that has to be condensed to reach again equilibrium.

$$X_{i,cond.} = \frac{p_i}{p_i^*} \quad (7)$$

$$\Delta p = \left[ \sum_{i=1}^n \left( \frac{p_i}{p_i^*} \right) - 1 \right] / \sum_{i=1}^n \left( \frac{X_i}{p_i^*} \right) \quad (8)$$

The new partial pressures of the components in the gas phase are calculated by subtracting the amount that condensed from the initial amount. The calculations are done assuming ambient atmospheric pressure and that a low volume fraction condenses. Therefore, it can be assumed that the total pressure is almost kept constant. The calculation continues with the next temperature (step of –1 °C), employing as an input the obtained partial pressures from the previous calculation step.

#### 4.3. Application of the model

Tar condensation has been calculated at different temperatures, ranging from 280 to 100 °C, employing the equilibrium model described in the previous sub-section. The employed torrgas composition was shown in Table 5 and the results are shown in Fig. 4. The heavy not GC detected compounds condense at high temperatures (above 150 °C). The phenolics condense at temperatures slightly higher than 100 °C. The cyclic and non-cyclic compounds almost do not condense at temperatures higher than 100 °C. The same is valid for H<sub>2</sub>O and acetic acid.

Experiments were carried out, as described in Section 2, to check the condensation behaviour in equilibrium at different temperatures and to validate the model developed. The low temperature experiment has been repeated 2 times showing a good reproducibility of the results. The experimental results for the percentage of mass of tar in the torrgas after the filter are presented in Table 6 in two ways: the experimentally measured value and a corrected one. The experimentally measured value is obtained by the relation of the amount of gravimetric tars determined before and after the filter, according to the gravimetric method. The correction was done assuming that the group non-cyclic 1 completely evaporates during the determination of the gravimetrics, and that this group does not condense in the filter, as predicted by the model for the set temperatures (see Table 7). The assumption that this group evaporates is reasonable, as it has a similar vapour pressure as acetic acid (see Table 5), that should also evaporate. The boiling points at 150 mbar of acetic acid and non-cyclic 1 are 66 and 65 °C, respectively, and

**Table 8**  
Elemental composition of the condensed tars and the tars before and after the filter.

		C (% mass d.b.)	H (% mass d.b.)	N (% mass d.b.)
Spruce tars 150 °C	Before filter (torrgas)	59.8	6.8	0.18
	After filter (not condensed)	60.3	6.5	0.26
	Filter (condensed)	58.4	6.7	0.16
Spruce tars 105 °C	Before filter (torrgas)	60.1	6.9	0.16
	After filter (not condensed)	60.5	6.5	0.19
	Filter (condensed)	58.6	6.7	0.16

the gravimetric tars are dried at that pressure and a temperature of 55 °C. Therefore, the mass of the group non-cyclic 1 was added to the measured amount of gravimetric tars before and after the filter in the correction.

There is a reasonable agreement between the equilibrium model and the experimental values. In general, the model over-predicts the measured amount of tar that does not condense. With the proposed correction, the predictions of the model improve and are very similar to the experimental results. The condensation model can be considered as validated.

It can be seen in Table 7 that at temperatures around 150 °C the not GC detected fraction will almost completely condense, while the other groups are almost not condensed. When the temperature is decreased to 110 °C, most of the phenolic compounds will condense also.

The elemental composition of the condensed tars and the tars before and after the filter are shown in Table 8 for two experiments. The condensed tars, that correspond mainly to the not GC detected fraction, have very similar carbon, hydrogen and oxygen contents than the total tars. The not condensed tars have a slightly higher carbon content and a slightly lower hydrogen content. Some differences appear in the nitrogen content. The nitrogen content of the not condensed fraction is higher than the one of the total tar. According to this results, the not GC detected fraction should have a carbon content of approximately 58%. Therefore, the assumption that it is mainly composed of pyrolytic lignin (carbon content of  $\approx 66\%$  mass, [18]) with some contribution from sugars (carbon content of  $\approx 45\%$  mass) is reasonable.

## 5. Conclusions

The gravimetric tars produced during torrefaction of spruce at 280 °C have been characterized and their condensation behaviour has been investigated. The detected tar compounds have been classified, based on their structure, in three groups: phenolics, (hetero) cyclic (mainly furans) and non-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 order to study the condensation behaviour, a filter with a variable temperature has been designed and the tar content before and after the filter was measured. 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 condenses in

equilibrium at a defined temperature. The model is based on the presented classification of tar compounds in groups, according to their structure, and it is able to predict the experimental results with reasonable accuracy.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jaap.2016.02.020>.

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