

Supercritical extraction of biomass as an effective pretreatment step for the char yield control in pyrolysis



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ARTICLE INFO

Article history:

Received 23 November 2020

Received in revised form

22 January 2021

Accepted 24 January 2021

Available online 1 February 2021

Keywords:

Supercritical extraction

Char yield

Scots pine

Heating rate

Fluidisation

ABSTRACT

This work demonstrates that the coupling of supercritical carbon dioxide extraction with pyrolysis is an effective method for the removal of extractives from forestry residues and generation of solid char with different properties from the remaining solid wood fractions. Extraction of the needles and stumps shows greater yields of resin acids, terpenes, steroids and other derivatives than that of pinewood bark, cones and branches. The char yields of both non-treated and scCO₂ extracted wood fractions varied from approximately 17.5 to 38.5 wt. % on dry basis at fast heating rates. The catalytic effect of extractives is significant on the yields and morphology of solid chars in fast pyrolysis and less pronounced at slow heating rates. These results are promising as they show that both the composition and location of extractives inclusions in the interior of wood particle can affect the morphology of char samples. Moreover, the impact of alkali metals on the wood devolatilization appears to be less compared to the lignocellulosic composition in slow pyrolysis. These results demonstrate that supercritical carbon dioxide extraction can be integrated in biorefinery as a pretreatment step to control the properties of pyrolysis products by varying the heating rate.

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1. Introduction

The transportation sector relies almost exclusively on liquid hydrocarbons as the energy source [1]. One reason to use liquid hydrocarbons is their high volumetric energy density and convenience of use. Both ethanol and bio-diesel are bio-based alternatives to fossil fuels. However, these are typically first generation biofuels, whose feedstocks (including corn and palm oil) can also be utilized for food applications. With the growing interest in the production of second generation bio-fuels from waste cellulosic biomass, methanol and hydrogen produced from biomass through gasification are attractive alternatives for use in road transportation. Moreover, the utilization of biomass for transportation involves an efficient use of land and can contribute to a decrease of

the dependency on fossil fuels for transportation [2]. Biomass gasification offers high conversion efficiency and the possibility to handle different lignocellulosic materials to a wide variety of applications such as heat, electricity, chemicals and transport fuels [3]. Fast pyrolysis at high temperatures and at high heating rates is the initial step of suspension biomass firing or biomass gasification depending on the reaction atmosphere. One of the major challenges in biomass gasification is the formation of tars which condense and thus, cause the clogging of filters and reduction of the energy content of the product gas [4,5].

The removal of extractives from the wood prior to pretreatment provides a valuable feedstock for the chemical and energy sectors [6]. Supercritical carbon dioxide extraction (SFE) significantly reduces the risks associated with off-gassing and oxygen depletion during fuel storage [7], while the extracted fatty acids can be utilized as primary feedstocks for chemicals and biorefinery applications [8]. Supercritical carbon dioxide extraction can remove over half of the fatty and resin acids from wood [9]. Like other supercritical carbon

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dioxide processes, extraction of forest residues is carried out at low temperatures and pressures [10,11]. Utilization of the forest residues is constrained and frequently prevented by economic, technical and ecological challenges which are related to the anisotropic properties of wood [12]. The physical and chemical properties of lignocellulosic materials depend on structural (e.g. knots and grain deviation) and environmental (e.g. moisture and temperature) interactions during the tree growth [13]. The properties of wood vary among trees in longitudinal and radial directions [14]. The differences in physical and chemical properties of wood affect soot and tar formation and therefore, the gasification efficiency [15]. Previous studies speculate about the catalytic effect of extractives on the product yields and composition [16–21]. The extractives can favour the formation of gaseous and solid (char) products (at the expense of liquids) due to the prolonged residence times of vapours [18]. A recent study on the slow pyrolysis of lignin demonstrates that the remaining extractives in the organosolv lignin do not affect the thermal stability of lignin; to a limited extent, however, they influence the formation of released products during HSGC-MS heating [22]. Another study shows that the extraction of needles can lead to greater yields of steroids and terpenes, while the pyrolysis of scCO₂ pretreated branches formed porous soot particles with a less ordered nanostructure in fast pyrolysis [9]. ScCO₂ extraction of branches followed by pyrolysis leads to the formation of soot particles with a ring graphitic structure. This indicates the influence of the extractives type on soot nanostructure and overall, the impact of lignocellulosic composition on soot morphology. No previous work has looked into the effect of supercritical CO₂ extraction on the morphology of solid char under fast pyrolysis conditions and therefore it is desired to relate the reactions during fast pyrolysis with the chemical properties of the feedstock.

The purpose of the present study is to develop a fundamental understanding of the composition of non-treated and scCO₂ extraction biomass fractions and how this leads to the formation of solid char during fast pyrolysis. Importantly, the use of supercritical carbon dioxide extraction avoids the use of potentially toxic, hazardous, or flammable organic solvents. In this study, the impact of supercritical carbon dioxide extraction on the morphology of the solid char from high-temperature fast pyrolysis is investigated using SEM. Laboratory-scale fast pyrolysis experiments are carried out in a wire mesh reactor (WMR) to determine solid char yields, whereas the impact of slow heating rate on the wood devolatilization is investigated using a thermogravimetric analyser (TGA).

2. Materials and methods

Scots pine trees with an average of 147 year old were harvested from a forest stand in northern Sweden. Fractions from the harvested trees were green needles, branches without needles, cones from the whole crown, bark from the basal log with a mean cross-sectional diameter of 210 mm and bark from the second log with a diameter of 100 mm. In addition, Scots pine stump heartwood without bark from parts above the ground level was obtained. Wood fractions were processed on a hammer mill (MAFA EU-4B manufacturer) with an operating speed of 60 Hz. Then, biomass samples were divided into four equal (100 mg) fractions using a micro-riffler PT100 (Retsch Technology, Germany).

scCO₂ extraction was performed on different pinewood fractions. Solid residues were collected after extraction, dried at room temperature, and weighed for the calculation of yields. Pyrolysis was carried out on the non-treated wood fractions and samples after scCO₂ extraction using the WMR. The impact of the heating rate on the devolatilization of wood fractions was studied in the WMR and TGA. The structural characteristics of the solid char were obtained using scanning electron microscopy (SEM).

2.1. Supercritical CO₂ extraction

The scCO₂ extractions were conducted using a supercritical extractor SFE 500 (Thar Technologies, USA). Supercritical fluid grade carbon dioxide (99.99%, dip-tube liquefied CO₂ cylinder obtained from BOC) was used in the extractions. The CO₂ supplied from a cylinder as a liquid was maintained in this state through a cooling unit (−2 °C) to avoid cavitation in the high pressure pump, as shown in Fig. 1.

Evaluation was made by determination of the extracts' weight in the different experiments. Approximately 180 g of biomass was placed into the 500 mL extraction vessel. The reaction vessel was heated to the required temperature and was equilibrated for 5 min. An internal pump was used in order to obtain the required pressure. The system was run in dynamic mode, where the carbon dioxide containing the extractives was flowed into the collection vessel. A flow rate of 40 g min^{−1} of liquid CO₂ was applied and the extraction was carried out for 2 h. On completion the system was depressurized over a period of 60 min. Extractives from the supercritical extraction were collected in a fractional separator, samples were then stored in a fridge at 4 °C prior to analysis.

2.2. Wire mesh reactor

A wire mesh reactor (WMR) was used in the pyrolysis of feedstocks under high temperature and high heating rate conditions, as described previously [23]. The experiments were performed at T = 1000 °C and heating rate of 800 °C s^{−1} under 1 atm of nitrogen in quiescent conditions. The high heating rate and short residence times obtained with the wire mesh reactor simulate the conditions in entrained-flow gasifiers [24]. The sample mass of 5 ± 0.5 mg for each experiment was selected to achieve one monolayer of particles within a mesh bag based on the previous studies [25]. The experiments were performed as follows: (1) the sample was weighed and gently spread on the bottom mesh; (2) the glass chamber was placed onto the reactor, and the control volume vacuumed to a pressure of 5 mbar; (3) nitrogen was introduced into the control volume until atmospheric pressure was reached; (4) the heating rate and temperature conditions were selected based on prior knowledge of the voltage and current of the welding machine; (5) the trigger was done using a LabVIEW interface, and the heat source was kept on, and the mesh was heated to the specified plateau temperature and for the specified holding time; (6) upon completion of the experiment the mesh was allowed to cool down under inert atmosphere until reaching room temperature; (7) upon reaching room temperature, the glass chamber was removed, the mesh and sample weighed to obtain the values of the char yields, and the char was collected for further analysis. The char yield (Y_s) was defined as a non-devolatilized solid fraction of the reacted biomass, remaining on the mesh after an experiment.

$$Y_s [\text{wt. \%}] = \frac{m_{\text{mesh+char}} - m_{\text{mesh}}}{m_{\text{mesh+biomass}} - m_{\text{mesh}}} \cdot 100 \quad (1)$$

The char yield measurements were performed at least in triplicate and the results are the arithmetic mean of all measured yields. The error bars represent the 98% confidence interval limits, and the error was calculated to be within ± 4 wt. % for all samples and conditions. The inaccuracy during measurement of char yields was mainly due to weighing errors.

2.3. Thermogravimetric analysis

The thermal decomposition of the raw wood fractions and extracted samples was determined using a thermogravimetric

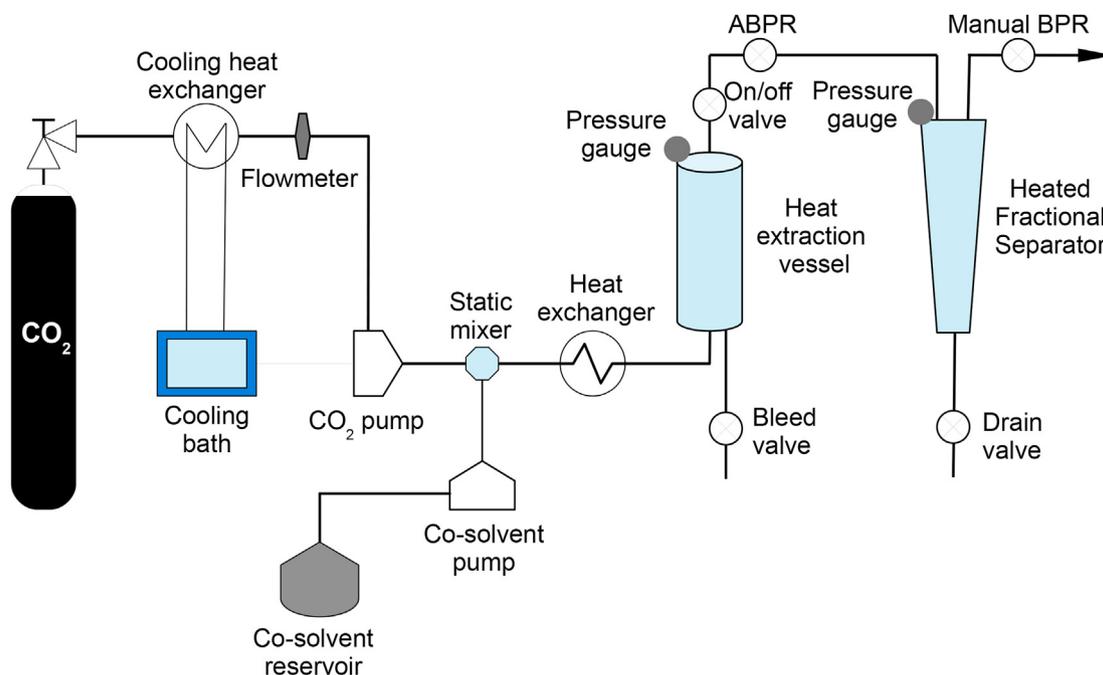


Fig. 1. scCO_2 extraction of wood fractions schematic.

instrument Q5000IR (TA Instruments, USA) by loading 20 mg of sample in Al_2O_3 crucible. The wood fractions were firstly heated up to 105°C and kept for 10 min isothermally for drying. The dried samples were subsequently heated up to 550°C at a constant heating rate of $20^\circ\text{C min}^{-1}$.

2.4. SEM

The morphology of char samples from fast pyrolysis was characterized using Scanning Electron Microscopy (SEM). Samples were placed on a carbon tape and coated with Au/Pd before analysis. Imaging was performed using a 400F instrument (FEI Quanta, USA) under high vacuum.

3. Results and discussion

3.1. Biomass characterization

Compositional analyses of non-treated and extracted tree fractions namely, bark from large diameter logs, bark from small diameter logs, needles, branches, cones and stumps of Scots pine wood are shown in Tables 1 and 2. The fractions were milled on a hammer mill (MAFA EU-4B manufacturer) and sieved to particle size fractions of 0.05–0.2 mm. The ash compositional analysis was determined for the non-treated Scots pinewood fractions. Previous results showed that the ash content of non-treated bark and bark after scCO_2 extraction remains unchanged, and thus, no differences in the ash composition are expected in other wood fractions, confirming the previous results of Philpot [26,27]. Importantly, supercritical carbon dioxide pretreatment is not only effective at the removal of lipophilic extractives but also removes water from within the structure. The resulting drying of biomass negates the loss in calorific value from removal of the extractives. In addition, the removal of water by supercritical carbon dioxide may lead to internal changes in the hydrogen bonding, and may also influence any pyrolysis processes. This emphasized the effect of the

extraction type on the calorific value and thermal stability of the feedstocks. The compositional analysis of biomass (cellulose, hemicellulose, acid-soluble lignin, acid-insoluble lignin, protein and extractives) was conducted according to NREL technical reports [28–30] and Thammasouk et al. [31], and shown in Table 3 for non-treated wood fractions and samples after scCO_2 extraction.

3.2. Optimisation of the supercritical CO_2 extraction

Seven extractions were carried out at various pressures (200, 300 and 400 bar) and temperatures (40°C , 50°C and 60°C). The conditions chosen (300 bar and 50°C) for the scCO_2 extraction of the needles was based on optimisation studies in the literature [32]. Due to the vast differences in structural composition between the bark and the needles, a 2x2 factorial experimental design was conducted on the Scots pine bark in order to identify the optimal conditions leading to the highest extraction rates.

Since the chemical composition of the branches and cones is similar to that of the bark, the optimal conditions obtained for the bark were also implemented in the scCO_2 extraction of these biomass components. The effect of temperature (T) and pressure (P) (independent factors) on yields of the crude extract (wt. %, db) (dependent factor) was investigated. Seven experiments were carried out: (i) Low T, Low P (ii) Low T, High P (iii) High T, High P (iv) High T, Low P (v) Mid-point: repeated three times to increase the accuracy of the model.

From Table 4 and Fig. 2 it can be seen that the optimal conditions leading to the highest amount of lipids extracted were 300 bar and 50°C . Rather than extreme conditions, this indicates that there is a specific temperature and pressure that leads to optimal extraction. Since pressure and temperature are related to the density of CO_2 , it can be concluded that there is a specific density of CO_2 that needs to be incorporated in order to maximise the crude extract yields. This contrasts with the needles, whereby the temperature was found to have a more significant effect on the extraction yield than the pressure or density.

Table 1
Proximate, ultimate and ash analyses of non-treated Scots pinewood fractions.

| Fuel | Needles | Bark | | Branches | Cones | Stumps |
|---|---------|--------------------|--------------------|----------|-------|--------|
| | | small \odot pine | large \odot pine | | | |
| Proximate and ultimate analysis (% on dry basis) | | | | | | |
| Moisture ^a | 6.5 | 7.6 | 9 | 7.3 | 8.2 | 7.3 |
| Ash (550 °C) | 2.2 | 2.3 | 0.6 | 0.8 | 0.6 | 0.2 |
| Volatiles | 80.8 | 77.4 | 71.6 | 80.6 | 78.5 | 87.9 |
| HHV ^b | 22.4 | 20.2 | 21.8 | 21.7 | 20.3 | 23.1 |
| LHV ^b | 21 | 18.9 | 20.6 | 20.4 | 19.1 | 21.8 |
| C | 53.7 | 50.7 | 54.7 | 53.5 | 52 | 55.7 |
| H | 6.5 | 5.9 | 5.5 | 6.2 | 5.7 | 6.3 |
| O | 36.1 | 40.5 | 38.8 | 39.0 | 41.3 | 37.7 |
| N | 1.3 | 0.6 | 0.3 | 0.4 | 0.4 | 0.1 |
| S | 0.1 | 0.04 | 0.02 | 0.03 | 0.02 | < 0.01 |
| Ash compositional analysis (mg kg ⁻¹ on dry basis) | | | | | | |
| Cl | 0.02 | 0.01 | < 0.01 | < 0.01 | 0.01 | 0.01 |
| Al | 250 | 550 | 250 | 150 | 150 | 40 |
| Ca | 2450 | 4700 | 1200 | 1300 | 250 | 500 |
| Fe | 70 | 60 | 60 | 60 | 20 | 30 |
| K | 5600 | 3500 | 800 | 2000 | 2000 | 200 |
| Mg | 750 | 900 | 200 | 400 | 350 | 100 |
| Na | 25 | 10 | 10 | < 10 | < 10 | < 10 |
| P | 1500 | 750 | 150 | 400 | 350 | < 10 |
| Si | 400 | 150 | 350 | 400 | 350 | 150 |
| Ti | 4 | 1 | 2 | 6 | 7 | 1 |

^a wt. % (as received).

^b in MJ kg⁻¹.

Table 2
Proximate, ultimate and ash analyses of wood fractions after scCO₂ extraction.

| Fuel | Needles | Bark | | Branches | Cones | Stumps |
|--|---------|--------------------|--------------------|----------|-------|--------|
| | | small \odot pine | large \odot pine | | | |
| Proximate and ultimate analysis (% on dry basis) | | | | | | |
| Moisture ^a | 5.6 | 7.4 | 8 | 6.8 | 7.5 | 5.7 |
| Ash (550 °C) | 2.3 | 2.3 | 0.5 | 1 | 0.5 | 0.1 |
| Volatiles | 78.8 | 76.7 | 70.9 | 79.9 | 78.3 | 86.5 |
| HHV ^b | 21.3 | 19.5 | 21.3 | 20.9 | 20 | 21.2 |
| LHV ^b | 20 | 18.2 | 20.1 | 19.6 | 18.8 | 19.8 |
| C | 51.8 | 49.5 | 54.5 | 51.4 | 51.1 | 52.3 |
| H | 6.3 | 5.6 | 5.4 | 5.9 | 5.5 | 6 |
| O | 38.2 | 42 | 39.4 | 41.2 | 42.6 | 41.5 |
| N | 1.4 | 0.6 | 0.2 | 0.5 | 0.3 | 0.1 |
| S | 0.1 | 0.05 | 0.02 | 0.04 | 0.02 | 0.02 |

^a wt. % (as received).

^b in MJ kg⁻¹.

Table 3
Composition of non-treated scots pinewood fractions and extractives yield after scCO₂ extraction, calculated in percentage based on dry basis (wt. %).

| Biomass | Cellulose | Hemi-cellulose | Lignin | | Extractives (raw wood) | Extractives (after scCO ₂ extraction) |
|---------------------------|-----------|----------------|----------------|--------------|------------------------|--|
| | | | acid insoluble | acid soluble | | |
| Needles | 23.4 | 15.1 | 26.5 | 0.5 | 12.1 | 7.9 |
| Bark (small \odot pine) | 27.6 | 20.3 | 19.5 | 0.8 | 5.3 | 3.4 |
| Bark (large \odot pine) | 19.5 | 15.1 | 46 | 0.5 | 3.9 | 2 |
| Branches | 25.3 | 19.4 | 28 | 1 | 8 | 4.4 |
| Cones | 35.8 | 22.5 | 24.3 | 0.8 | 4.1 | 1.5 |
| Stumps | 35.4 | 18.5 | 26.3 | 0.4 | 13 | 8.6 |

3.3. Yields of extractives

Fig. 3 illustrates the total amounts of extractives. Total amounts of extractives varied between 4.1 and 13% of dry substances. The largest amounts of extractives (13 wt. %, db) were determined in Scots pine stumps and needles, whereas the extractives content was significantly lower in pine cones and bark (about 5 wt. %, db), corresponding to the results of Matisons et al. [33,34].

It is well known that the proportion and composition of extractives varies considerably depending on the part of the tree being

analyzed [35]. The extraction of stumps led to significantly greater yields of resin, fatty acids and other extractives, as compared to the extraction of branches, bark, cones and needles. Previous studies showed that pinewood stumps mainly contains fatty and resin acids, sterols and neutral diterpenes, phenolic stilbenes, flavonoid pinocembrin and lignan [36]. The extraction of needles led to greater yields of steroids and derivatives. Previous studies have demonstrated that needles contained the highest amounts of free sterols, which was a reflection of the increased membrane production at this stage of plant development, while in mature needles the free and

Table 4
Optimisation of supercritical extraction of lipids from Scots Pine bark: extraction conditions and yields (wt. %, db).

| Experiment | Temperature °C | Pressure bar | Extraction yield wt. %, db |
|------------|----------------|--------------|----------------------------|
| 1 | 40 | 200 | 2.2 |
| 2 | 60 | 200 | 2.2 |
| 3 | 40 | 400 | 2.2 |
| 4 | 50 | 300 | 2.3 |
| 5 | 50 | 300 | 2.3 |
| 6 | 50 | 300 | 2.3 |
| 7 | 60 | 400 | 2.2 |

esterified sterols were in even proportions [37,38]. The major compositional difference of pinewood needles to other wood fractions was the high content of terpenes, which were represented by monoterpenes, numerous sesquiterpenes, diterpenoids and their derivatives, as reported previously [39].

The extraction of bark from small diameter pinewood gave greater yields of fatty acids than the extraction of large diameter pinewood. This was related to the heartwood content that changed with the annual tree growth leading to the differences in the logs' diameters and numbers of annual rings [40,41]. Moreover, the present findings showed that bark, cones and branches gave lower

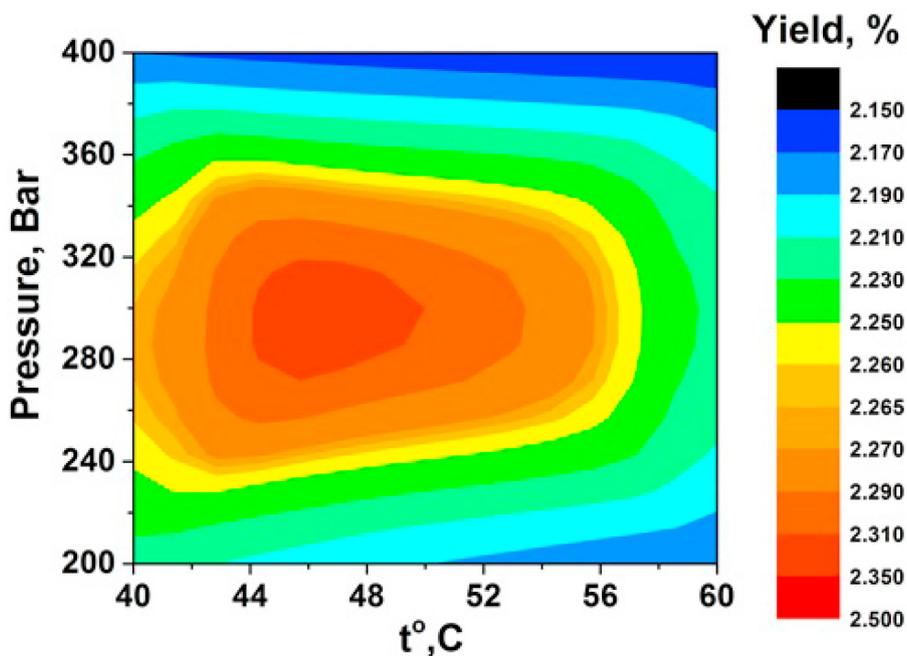


Fig. 2. 2-D plot showing the effect of varying pressure and temperature on yields of the crude wax (wt. %, db) from Scots Pine bark.

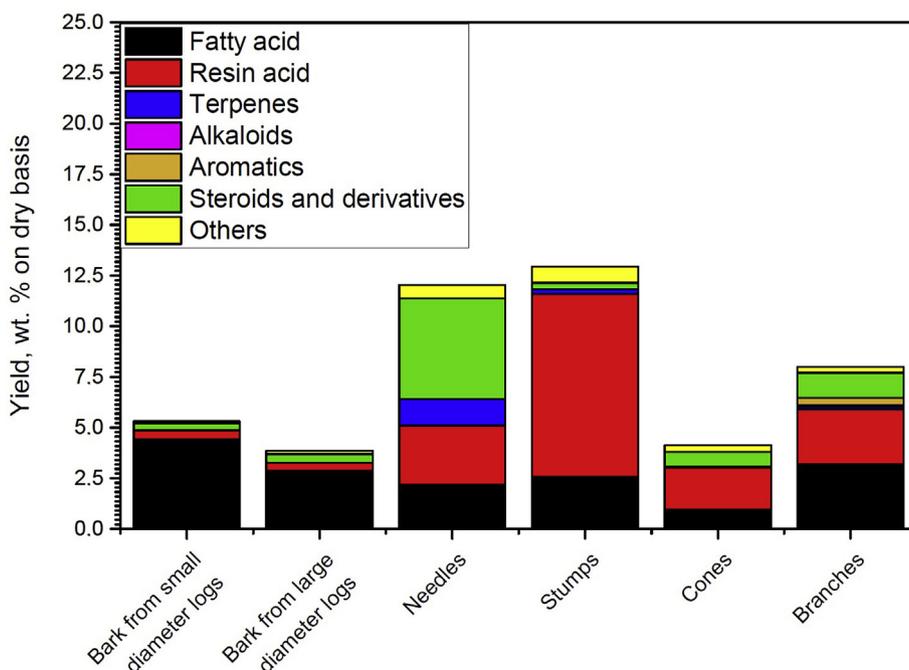


Fig. 3. Yields of non-treated wood fraction extractives. The yields were determined using a Soxhlet apparatus.

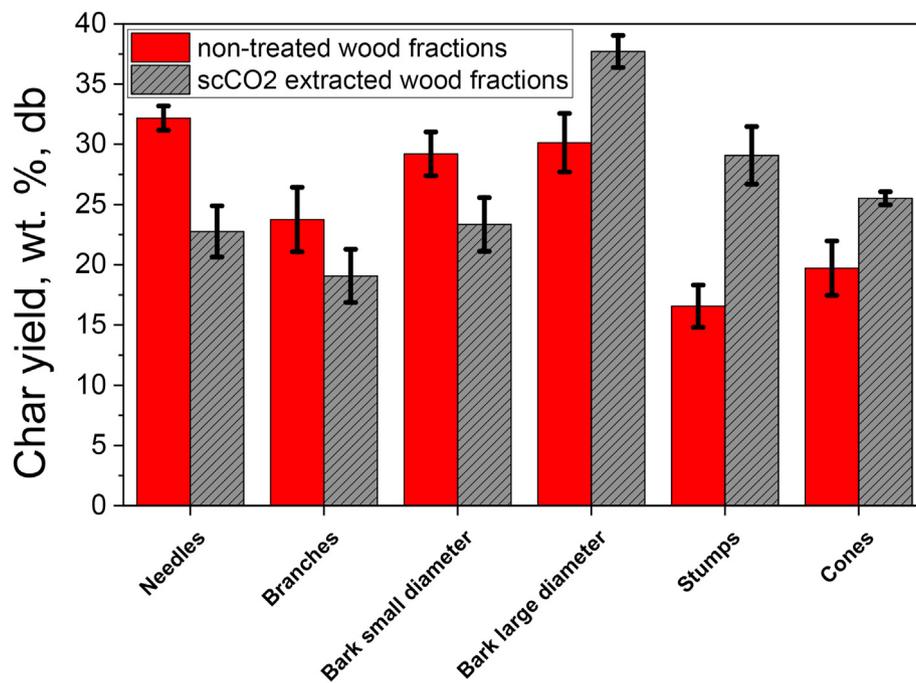


Fig. 4. Char yield of needles, branches, bark from small and large diameter pinewood, stumps and cones and samples after scCO₂ extraction from pyrolysis at 1000°C (shown in wt. % db).

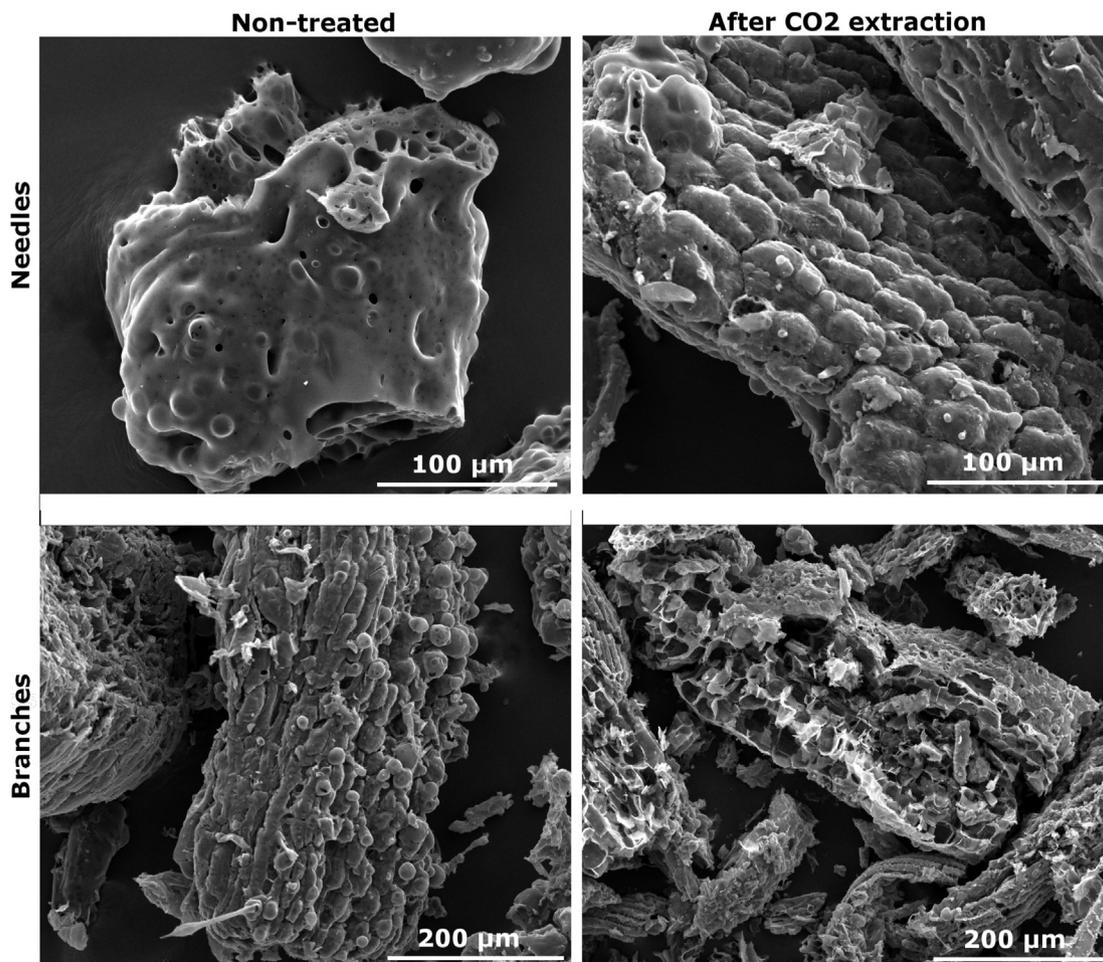


Fig. 5. SEM images of chars from non-treated needles and branches and scCO₂ extracted feedstocks reacted at 1000°C in the wire mesh reactor.

proportions of extractives including sterols than needles and stumps. Branches and especially branch whorls are known to form resins, as a result of wound healing, which contribute to the yields of fatty and resin acids [42]. The bark from large diameter pine-wood has more annual rings and the outer part of the bark is greater than the inner part of the bark [43]. However, the outer bark contains less triglycerides than the inner bark [44]. In addition, the average concentrations of major stilbenoid glucosides i.e. isorhapontin and astringin are mainly localized in the inner bark and the concentrations are 30–200 times higher in the inner bark compared to the outer bark [45]. The higher up the tree, the greater the amounts of bark extractives, probably since the more inner bark regions are towards the top of the tree [46,47]. In the present study, the upper part of the young pinewood was cut, whereas the lower and intermediate parts of old pinewood were collected for the supercritical CO₂ extraction. Thus, young pinewood with the small stem diameter provides extractives in a greater yield than that from old bark pinewood. The content of resin acids after extraction of cones was greater than in both bark samples and similar to resin acid yields in needles and branches. The major compounds in needles, branches and cones were α -pinene, myrcene and β -pinene [48]. In addition, abietic, neoabietic and isopimaric acids could be the dominant compounds in cones [34].

3.4. Char yields in fast pyrolysis

Pyrolysis experiments in a N₂ flow atmosphere were carried out in the wire mesh reactor. The char yields of non-treated needles,

branches, bark from small and large diameter pinewood, stumps and cones and samples after scCO₂ extraction from pyrolysis at 1000°C were plotted on a dry basis in Fig. 4. The results demonstrated that extractives intrinsically contributed to the pyrolysis product yields. The char yields from pyrolysis of scCO₂ extracted stumps, cones and bark from large diameter pinewood were greater than those of non-treated wood fractions. During the scCO₂ extraction, the extractives were not only removed from the inner layers of wood fractions but were also transported to the particle surface. Thus, the layer of extractives on the surface of wood fractions could act as a mass transfer barrier for the pyrolysis products on the way to the gas phase, as suggested by Ahmed et al. [18,19]. The secondary reactions i.e. recondensation and cross-linking of pyrolysis products could prolongate the contact time between the pyrolysis products leading to greater yields of solid char and gas, and concurrently reducing the formation of liquid products. The non-polar components including fatty and resin acids, non-polar phenols and oxidized resin acids form a layer covering the surface of cones, stumps and bark from large diameter pinewood, as suggested by Shebani et al. [49].

The presence of non-polar extractives and formation of a layer of extractives on the wood particle surface, may cause less severe plasticization [50,51]. In contrast, the char yields from pyrolysis of scCO₂ extracted branches, needles and bark from small diameter pinewood were less than that of non-treated wood fractions. This may be due to a random distribution of extractives on the surface or through different layers in needles, branches and bark from small diameter pine. Such distribution of extractives in a wood particle

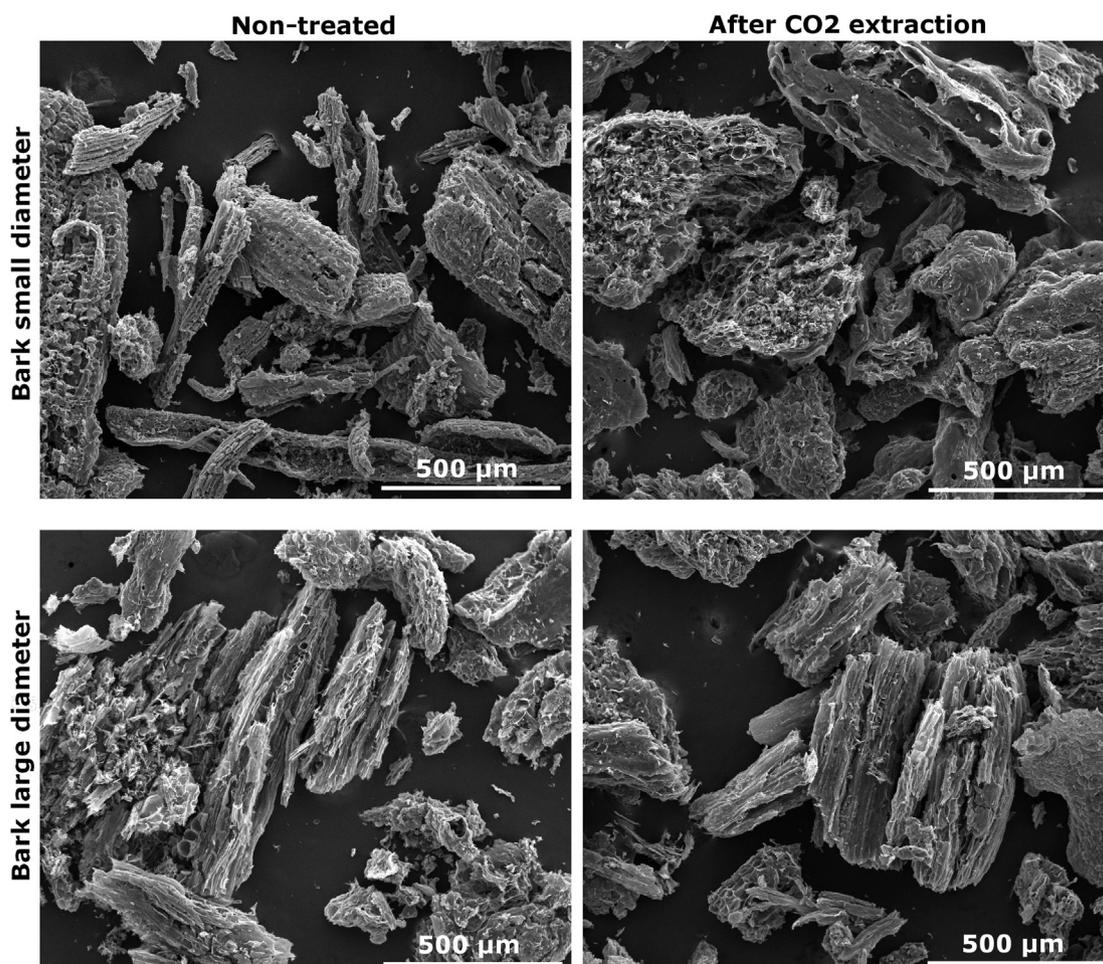


Fig. 6. SEM images of chars from non-treated bark and scCO₂ extracted feedstocks reacted at 1000°C in the wire mesh reactor.

will reduce the contact time between pyrolysis products leading to the low yield of char and high yields of gaseous and liquid products [52,53]. In addition, the presence of polar extractives in the wood particles i.e. phenols, oxidized resin acids, lignans and other compounds could decrease the char yield due to their degradation in the temperature range 200–500 °C in slow pyrolysis [54,55]. During fast heating a low molecular weight metaplast is formed due to the fast bond breaking, leading to an increased pressure inside the particle, fast volatiles evaporation, and a low char yield [56]. Overall, during fast pyrolysis, the contact time between pyrolysis products remained short, leading to significant bridge-breaking before it starts to cross-link and thus, forming less solid char.

3.5. Char morphology and structural transformation

The morphology of selected chars obtained at 1000 °C pyrolysis was investigated using SEM. Selected images are presented in Fig. 5 for chars from pyrolysis of non-treated needles and branches and samples after scCO₂ extraction. The char surface of non-treated needles showed the most molten structures compared to other char samples, as shown in Figs. 6–7.

The structural differences could be related to the inorganic matter or lignocellulosic compositional differences in the raw feedstocks. Bark from large diameter pine contained more lignin (47.1 wt. %) than other wood fractions, but concurrently similar ash content as non-treated cones. Potassium and calcium are known to play a role as active catalysts that may additionally affect the

metaplast formation [57]. However, the ash compositional differences between non-treated bark from large diameter pine were double the potassium content of cones and a five-fold higher calcium amount in bark. This indicates that the differences in ash content and composition did not influence the char morphology during the high heating rate pyrolysis. The differences in lignocellulosic composition played a dominating role in plasticization during fast pyrolysis [25].

Char from large diameter pine bark was highly cross-linked with only minor melting due to the high content of suberin acid, which is found in the bark of old conifer trees. Suberin extractives are known to provide stability to cells of conifer trees [58]. Alternatively, chars from needles, small diameter pine bark, cones and stumps underwent clear fluidisation with the formation of large vesicles and bubbles on the surface. These char samples behaved similarly to the bituminous coals and underwent a significant bridge-breaking reaction prior to cross-linking and repolymerization processes which could lead to the increased fluidity [50,59]. This work confirmed the previous results where the influence of lignin and extractives was considered to be more dominating than the effect of cellulose and hemicellulose on the morphology [51]. High heating pyrolysis led to the formation of more open and closed vesicles with the fraction of brittle and conchoidal fractures, as reported by Sharma et al. [60]. However, the lignin content varied significantly among wood fractions. It would be expected that the strongest melting to be observed on the surface of large pinewood bark char was due to the highest lignin content.

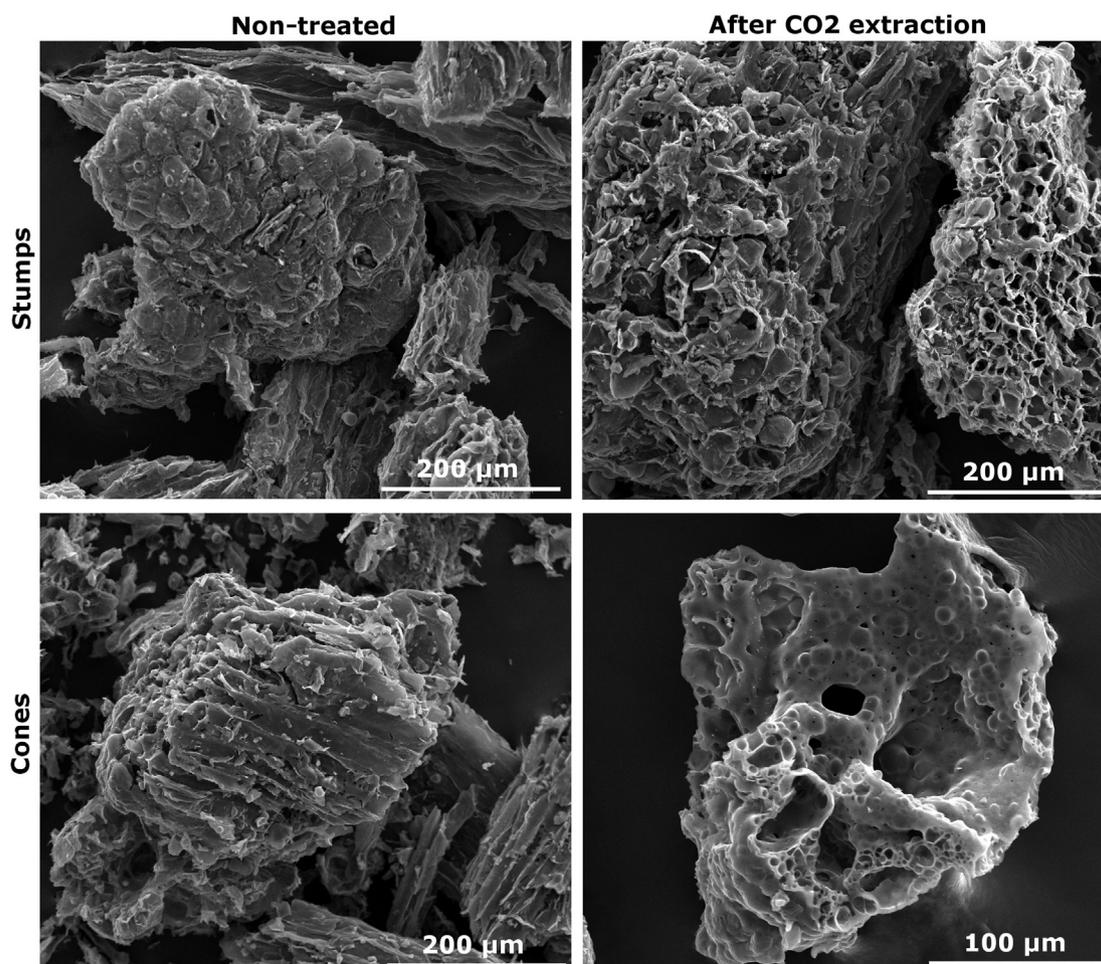
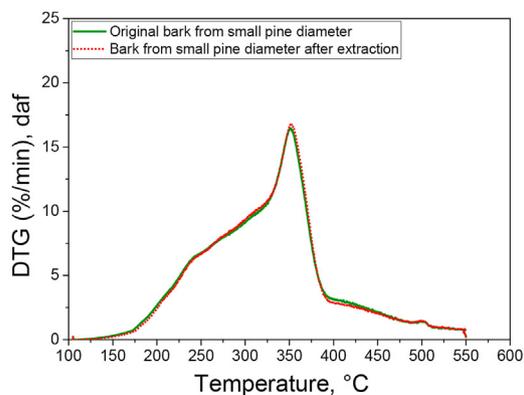
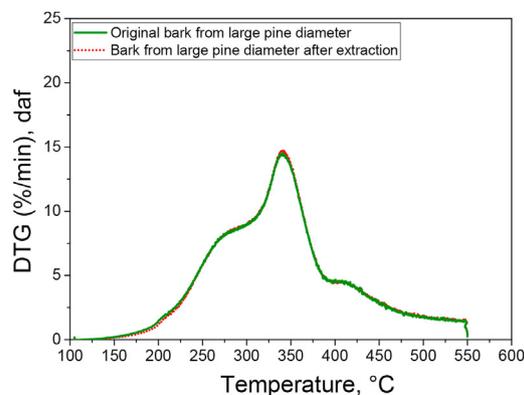


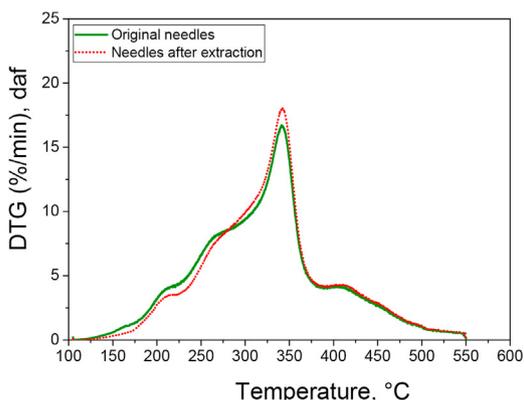
Fig. 7. SEM images of chars from non-treated stumps and cones and scCO₂ extracted feedstocks reacted at 1000 °C in the wire mesh reactor.



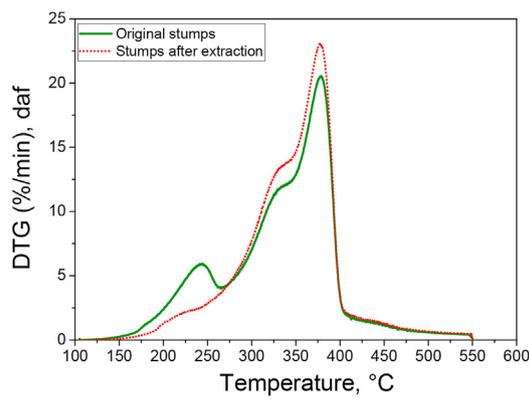
8(a): Bark from small pine diameter



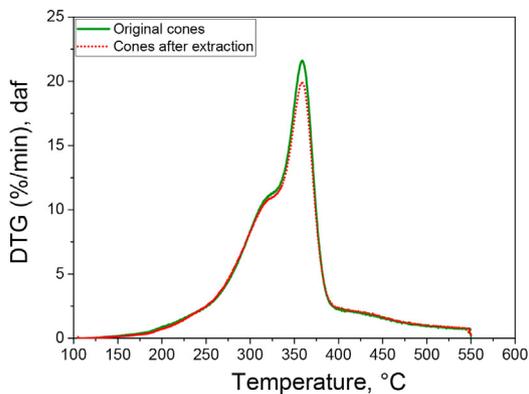
8(b): Bark from large pine diameter



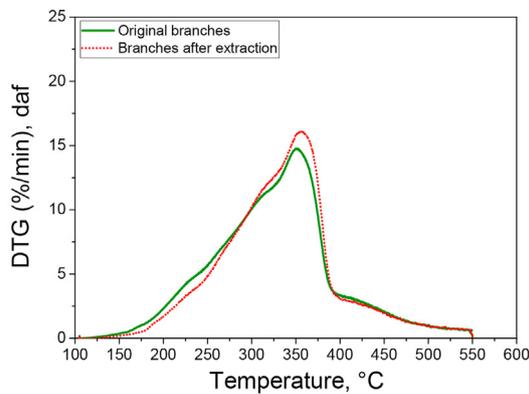
8(c): Needles



8(d): Stumps



8(e): Cones



8(f): Branches

Fig. 8. DTG curves of bark from small pine diameter, bark from large pine diameter, needles, stumps, cones and branches in (100% volume fraction N₂). The DTG curves of wood fractions are green (non-treated samples) and red (after extraction).

However, the strongest morphological changes with the smooth molten surface and micropores were determined in the pyrolysis of needles which have a similar lignin content to stumps (26.7 wt. %). This indicates that probably extractives have also a strong effect on the char morphology at high heating rate pyrolysis. The results correspond to the additional melting on the char surface from the pyrolysis of scCO₂ extracted feedstocks. Especially, the removal of extractives from cones led to the strong plasticization with the formation of mostly micropores with occasional large pores indicating an intensive swelling and foaming of lignin. Char particles of scCO₂ extracted stumps and branches formed large pores that preserved a structure of original wood architecture. However, the

formation of honeycomb monolayered structures during stumps and branches pyrolysis could indicate the extensive release of volatiles leading to the formation of rectangular brittle films inside of char particles. Interestingly, the char from pyrolysis of scCO₂ extracted needles showed an elongated structure that contained a single layer film with the molten vesicles and occasionally large pores on the surface. More fluidized and plasticized surface of the needle char compared to other samples was probably caused by the presence of extractives closer to the pine needle surface. This could indicate that the location of extractives and bonding of extractives inclusions with the lignin will lead to different char morphology at high heating rate pyrolysis.

3.6. Thermogravimetric analysis

Fig. 8 shows differential weight loss curves (DTG) for the devolatilization of non-treated wood fractions and samples after scCO₂ extraction. During devolatilization, several decomposition processes corresponding to the degradation of holocelluloses, lignin and extractives are observed. The region (150–250°C) is attributed to the extractives decomposition [21]. The hemicellulose degradation (below 300°C) can overlap with the thermal decomposition of biomass polymeric constituents (250–500°C) [21,61]. The maximum reaction rate of different wood fractions was in the temperature range from 325 to 375°C. This mass loss was associated with the decomposition of cellulose [62]. The holocelluloses devolatilization overlapped with the lignin decomposition, that started below 300°C and completed at temperatures greater than 700°C [63].

Fig. 8 shows a continuous slight devolatilization that is attributed to the lignin degradation. The maximum reaction rate of the stumps was shifted to higher temperatures, indicating a lower reactivity compared to other wood fractions. However, the present results showed that the differences in lignocellulosic composition of wood fractions mainly affected the devolatilization. The rates of high potassium containing bark from small diameter pinewood and needles were nearly similar to that of low potassium containing bark from large diameter pinewood. Thus, the impact of alkali metals on the wood devolatilization appears to be less compared to that of lignocellulosic composition as reported by Raveendran et al. [64]. The devolatilization of non-treated and extracted wood fractions took place at nearly the same temperatures. Overall, these results strongly suggest that scCO₂ extraction had a negligible influence on the biomass devolatilization at low heating rates.

4. Conclusion

For the first time, this work showed that the catalytic effect of extractives depends on the heating rate. The char yields from pyrolysis of non-treated and scCO₂ extracted wood fractions varied from approximately 17.5 to 38.5 wt. % on dry basis indicating the impact of supercritical extraction in fast pyrolysis. Supercritical carbon dioxide extraction had also a strong impact on the morphology of char during fast pyrolysis at high temperatures, whereas extractives did not have a strong impact on devolatilization of forest residues at slow heating rates. The catalytic effect of extractives was enhanced by the random distribution of extractives inclusions at fast heating rates leading to the low char yield. Plasticization of the char surface has been shown to depend on the type and distribution of extractives in the interior of a wood particle at high heating rates. Strong plasticization of the char surface was caused by the fast bond breaking that increased the particle pressure, whereas less plasticization on the char surface could be expected with the formation of solid layers of non-polar extractives. Overall, this study underlined the importance of wood lignocellulosic composition on the yield and morphology of solid chars in high temperature fast pyrolysis.

CRedit authorship contribution statement

Anna Trubetskaya: Conceptualization, Formal analysis, Investigation, Data curation, Writing - original draft, Writing - review & editing, Visualization, Funding acquisition. **Vitaliy Budarin:** Conceptualization, Formal analysis. **Mehrdad Arshadi:** Funding acquisition, Software, Writing - original draft. **Duarte Magalhães:** Writing - original draft, Formal analysis, Conceptualization. **Feyza Kazanç:** Software, Validation, Formal analysis, Data curation, Funding acquisition. **Andrew John Hunt:** Conceptualization,

Investigation, Resources, Writing - review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge financial support from FORMAS (CETEX project), Kempe Foundation, Björn Wahlströms, and Jernkontoret Stiftelsen. Dr. Daniel Eriksson from Swedish University of Agricultural Sciences in Umeå is acknowledged for the preparation of pinewood fractions. Andrew Hunt would like to acknowledge the financial support of the Thailand Research Fund, (Grant number RSA6280031) and Khon Kaen University. Financial support from the Materials Chemistry Research Center, Khon Kaen University and the Center of Excellence for Innovation in Chemistry (PERCH-CIC), Ministry of Higher Education, Science, Research and Innovation are gratefully acknowledged.

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