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Effect of processing conditions on the constant-volume carbonization of biomass

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ABSTRACT

The effects of processing conditions (closed versus open reactor, pressure, temperature, soaking time, biomass loading, heating rate and fuel particle size) on product yields and char properties from constant-volume carbonization are reported. Increasing the pretest, inert-gas, system pressure from 0 to 2.17 MPa did not significantly affect product yields or char proximate analysis results. Increasing the reaction time from 30 to 190 minutes and the temperature in a 300-550°C range improved fixed-carbon contents and reduced volatile matter while maintaining or slightly increasing the fixed-carbon yields. In contrast to flash-carbonization or traditional carbonization observations where larger particles produce beneficial effects, constant-volume carbonization produced equal or higher fixed-carbon contents and yields from smaller biomass particles. This offers possibilities that smaller size, lower-grade biomass can be used to produce high, fixed-carbon yield charcoal. Under certain processing conditions, the particulate biomass underwent a transient plastic phase transition that produced a single solid piece of final char. The roles of processing conditions in the formation of this transient plastic phase are also discussed.

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1. Introduction

A vast spectrum of carbonization processes has been developed ranging from traditional labor-intensive methods performed in simple kilns (still used in developing regions where manual labor is inexpensive) to modern automated industrial processes in more complex retorts. The novelty of modern carbonizers does not reside in the fundamentals of pyrolysis but in the equipment designs aiming to improve energy efficiency, facilitate material loading and unloading and recover volatile by-products released during the carbonization process.[1] The improvements developed for carbonization processes have increased final charcoal yields from a modest ~25 wt% (dry basis) reported in traditional simple carbonizers to around 30-34 wt% (dry basis) in modern retorts. [1–4] From lab-scale to commercial-scale and from traditional to modern, the majority of carbonization units have a common feature: They are equipped with openings and/or a sweep gas that, to varying degrees, remove vapor products from the reaction zone. These units, referred herein as “open” reactors, consequently incur carbon losses due to the gaseous product displacement. Carbonization in sealed vessels (or constant-volume carbonization (CVC)) has nearly gone unnoticed despite the promising results reported in literature from lab-scale studies.

The original published work on CVC dates back to the mid 19th century, when Violette reported that wood heated in sealed glass tubes to temperatures of 320°C transformed into a charcoal characterized by a remarkably high yield of 78.7 wt% and an elemental carbon content of 65.6 wt%.[5] At Violette’s time, the temperature scale was not precisely defined and the reported temperature values were likely to be inaccurate and to represent underestimates of the actual temperatures.[6] In addition, the fixed carbon content or yield were not determined.

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3 The Hawaii Natural Energy Institute (HNEI) under the lead of Dr. Michael Antal examined
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5 Violette's findings over a century later and continued his pioneering research on CVC. First,
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7 Mok, Antal and co-workers[7] confirmed that the retention of the released volatiles in constant-
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9 volume reactors resulted in high concentrations of volatiles that interacted with the pyrolyzing
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11 char material through exothermic secondary reactions to produce additional final charcoal.
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13 Charcoal yields and exothermicity increased with the biomass loading which also results in
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15 increased partial pressure of volatiles. Charcoal yields remained largely unchanged however
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17 when the inert-gas pressure was increased. It was therefore concluded that it was the partial
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19 pressures of volatiles, rather than the total system pressure, that was the dominant variable
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21 influencing product yields and reaction heats.
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27 In this most recent work on CVC, product yields are determined together with charcoal
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29 proximate analysis and in some instances with higher heating values (HHV) and SEM analysis
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31 [6,8,9]. CVC experiments consistently approached theoretical fixed-carbon yields across a
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33 variety of processing conditions [6,8,9], see Supporting Information Figure S1. Although
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35 charcoals maintained fixed-carbon yields near theoretical values, chars suffered a more intense
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37 devolatilization and therefore presented improved fixed-carbon contents from (1) higher heat
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39 treatment temperatures (HTTs) (in a 300-400°C range)[8,9], (2) prolonged soaking times at
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41 carbonization temperature (from less than 30 minutes to almost 3 hours)[9], (3) smaller particle
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43 sizes (from <2 mm to <0.2 mm in tests at HTT of 300°C)[9] or (4) higher mass loadings (from
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45 129 to 165 g/L in spruce CVC tests at 300°C)[9]. Among these factors, char devolatilization was
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47 especially sensitive to the carbonization temperature, while the mass loading had a lesser effect.
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50 An intriguing phenomenon was also observed on the char morphology when testing charcoals
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52 produced at higher temperatures and pressures. As conditions became more severe in the CVC
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3 reactor, the charcoal solid structure transformed from a particulate solid retaining the original
4 biomass morphology to a coke-looking piece that had undergone a transient plastic phase (TPP)
5 and had adopted the shape of the reaction vessel.[8,9]
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10 The ultimate goal of this research is to enable the manufacture of charcoals with physical and
11 chemical properties tailored to a targeted end use with a focus on the manufacture of
12 metallurgical-grade charcoals. The present study provides a deeper understanding of the CVC
13 process by exploring the effect of various processing variables (pretest pressure, temperature,
14 immersion time, mass loading, heating rate and particle size) on char yields and properties.
15 Results from proximate, elemental, bomb calorimetry and scanning electron microscope (SEM)
16 analyses of the chars are also presented.
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27 The study explores the effect of more severe conditions of peak pressures (up to 18 MPa
28 approximately), heat treatment temperatures (up to 550 °C) and immersion times (up to 350 min)
29 than previously reported for CVC processes. Also studied are the effects of processing
30 conditions, such as heating rate, biomass particle size and biomass loading, which were barely
31 examined in previous CVC studies but are known to influence traditional carbonization
32 processes.
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42 Additionally, this study compares the effect of processing conditions on product yields and
43 proximate analyses with the other reported carbonization processes. The effects of processing
44 conditions such as temperature, pressure, particle size, and immersion time on product yields and
45 charcoal proximate analysis from CVC showed remarkable differences in comparison to other
46 carbonization processes presented in literature. This study analyzes and offers an explanation to
47 the differences observed.
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3 A single charcoal derived from a pyrolysis experiment in a reactor with a valve slightly opened
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5 to the atmosphere was also produced for comparison to the charcoals manufactured in the
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7 constant-volume reactor.
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10 11 **2. Methods, apparatus and materials** 12 13

14 The present study reports data obtained from earlier runs on oak pyrolysis (see reference [9] for
15 reactor details) and from the upgraded, current reactor for experiments on spruce and birch
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17 pyrolysis. The current reactor or wall heated tubing bomb (WHTB) design has an internal
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19 volume of ~0.22 L and permits CVC of ~30 g of spruce wood sized below 2 mm. The amount of
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21 biomass loaded in the reactor can be further increased by the use of feedstocks with higher
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23 packing density, (e.g. ~50 g of birch grains <2 mm) or by the use of finer particles.
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29 The burst diaphragm (LaMot Disc Products) of the current WHTB (pressure rating of 21.3 MPa
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31 at 22 °C) allowed testing at more severe conditions than in earlier experiments.[9] The burst
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33 diaphragm is within the allowable working pressure of the weakest part of the WHTB reactor,
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35 i.e. the reactor body rated at 16.24 MPa at 537°C, plus pressure allowances permitted by the
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37 ASME B31.3 piping code. Operation at 33% over the allowable working pressure is permitted
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39 for events that are not longer than 10 hours at any one time nor more than 100 hours per
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41 year.[10]
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46 Selected experiments tested the influence of the biomass loading per unit of reactor volume. This
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48 involved increasing the dead-volume of the WHTB by adding tubing to the unheated, upper
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50 section of the reactor system while holding the fuel mass roughly constant.
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53 The biomass feedstocks in the present study consisted of oak, spruce and birch obtained from
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55 chipped heartwood. Feedstocks were first milled with a Fritsch Universal Cutting Mill
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3 Pulverisette 19 equipped with 2 mm outlet screen. A representative subsample of the 2 mm
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5 material was subsequently processed using a Retsch Ultra Centrifugal Mill ZM200 equipped
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7 with a 0.2 mm outlet screen. Fuels were subjected to moisture and proximate analysis by ASTM
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9 E872-82(2013)[11] and ASTM E830-87(1996)[12] (three replicates), ultimate analysis by
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11 ASTM E777-17[13], E775-15[14] and E778-15[15] (two replicates) and bomb calorimetry (one
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13 analysis per sample). See reference [9] for a detailed study on the uncertainties of each analytical
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15 technique.
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20 Table 1 displays the data collected from the characterization (moisture content, proximate
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22 analysis, ultimate analysis, and higher heating value) of the biomass feedstocks along with
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24 compositional data (cellulose, hemicellulose and lignin) taken from literature [16].
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Table 1. Moisture content, ultimate and proximate analysis, higher heating value, and structural composition (cellulose, hemicellulose and lignin) of spruce, birch, cellulose and oak feedstocks. Spruce and birch analytical results are replicated from reference[9].

		Spruce	Birch	Cellulose	Oak
Moisture content [wt.%, wet basis]		7.8	7.9	5.9	7.5
Ultimate analysis ^a [wt.%, dry basis]	C	46.93±0.05	47.4 ±0.3	41.9 ±0.1	45.4 ±0.1
	H	6.26±0.02	6.32±0.03	6.3±0.1	6.1±0.1
	O ^d	46.3	45.43	51.7	47.1
	N	0.20±0.02	0.20±0.02	0.08±0.04	0.215±0.002
	S	0.011±0.001	0.0158±0.001.	0.00	0.017±0.001
Proximate analysis ^b [wt.%, dry basis]	Ash ^e	0.36±0.17	0.67±0.02	0.00	1.18±0.05
	fCC ^f	14.8±0.1	13.1±0.2	6.0±0.2	14.0±0.7
	VM ^g	84.9±0.1	86.2±0.2	94.0±0.2	84.8±0.8
	Ash	0.36±0.17	0.67±0.02	0.0±0.0	1.18±0.05
Higher heating value [MJ/kg]		18.00	18.50	16.15	17.67
Contents of structural components[wt.%, dry-ash free basis] ^c	Cellulose	43.6, 47	50.2, 49.1	100	58.4
	Hemicellulose	27.4, 25.3	32.8, 31.6	0.0	31.4
	Lignin	29.0, 27.7	17.0, 19.3	0.0	10.2
	Extractives	1.8, 2.5	3.0	0.0	NA ^h
^a Average of two analysis, uncertainty indicates range of values. Elemental analysis of cellulose closely resembles C 44.4%, H 6.2% and O 49.4% given by its formula (C ₆ H ₁₀ O ₅) _n .					
^b Average of three analyses, uncertainty indicates standard deviation.					
^c Composition of structural components taken from [16].					
^d Oxygen by difference.					
^e Ash content determined by proximate analysis.					
^f Fixed-carbon content (fCC).					
^g Volatile matter content (VM).					
^h Not Available (NA).					

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3 Pyrolytic products were recovered after each experiment. Non-condensable gases were
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5 subjected to gas chromatography and volume evaluation. Solids from experiments using the dual
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7 reactor body WHTB were combined into a single sample and homogenized using a mortar and
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9 pestle. Charcoals were subjected to ultimate, proximate, and SEM analyses, bomb calorimetry
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11 and weight measurement. Details of the noncondensable gas analysis and standards followed for
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13 each measuring technique are given in Legarra et al.[9] Gaseous, liquid and solid yields were
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15 used to perform a mass balance.
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20 The proximate analysis method for the characterization of the solid char was modified after the
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22 CVC tests on oak wood from a method that followed ASTM -D1762-84[17] to a method that
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24 followed ASTM E872-82(2013)[11] and E830-87(1996)[12] for respective determination of
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26 volatile matter and ash content. The accuracies of both proximate analysis methods were
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28 evaluated as follows: proximate analysis of cellulose samples following both methods (three
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30 samples per method) were deliberately interrupted after the volatile matter removal step. Since
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32 cellulose contains negligible ash, the remaining product would be fixed-carbon. The carbon
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34 purity of this fixed-carbon fraction would be used as an indicator of the accuracy of the reported
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36 values. The original proximate analysis technique revealed a “fixed-carbon” of just 94.54 wt%
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38 carbon with the balance comprising of O and H in decreasing amounts, whereas the updated
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40 technique showed an improved “fixed-carbon” composed of 95.5 wt% carbon. The results
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42 indicated that the measured experimental fixed-carbon contents are likely to represent slight
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44 overestimates of the actual values.
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3. Results and Discussion

This section presents experimental CVC conditions and results. The CVC results and trends at distinct processing conditions are evaluated against trends reported in literature from other carbonization processes and against theoretical trends predicted by thermodynamics. Supporting Information Table S1 summarizes the experimental conditions and results from the 23 experiments conducted in this study. A total of seven factors were studied—(i) closed vessel versus open vessel, (ii) pretest pressure, (iii) temperature, (iv) immersion time, (v) mass loading, (vi) heating rate and (vii) particle size—on the product yields, gas composition and properties of the final charcoal (proximate analysis, ultimate analysis, HHV and SEM).

In line with previous observations,[9] the results confirmed the production of negligible free-tars in the CVC process and the approach of its maximum efficiency, especially when higher temperatures (400-500°C) were used.

3.1 Plastic behavior of chars from CVC

Under certain CVC conditions, the char morphology appeared to undergo a transient plastic phase that converted the original grainy biomass structure into a single piece that took on the shape of the reactor vessel interior and had the appearance of coke. Figure 1 shows the contrasting appearances of some CVC charcoals.

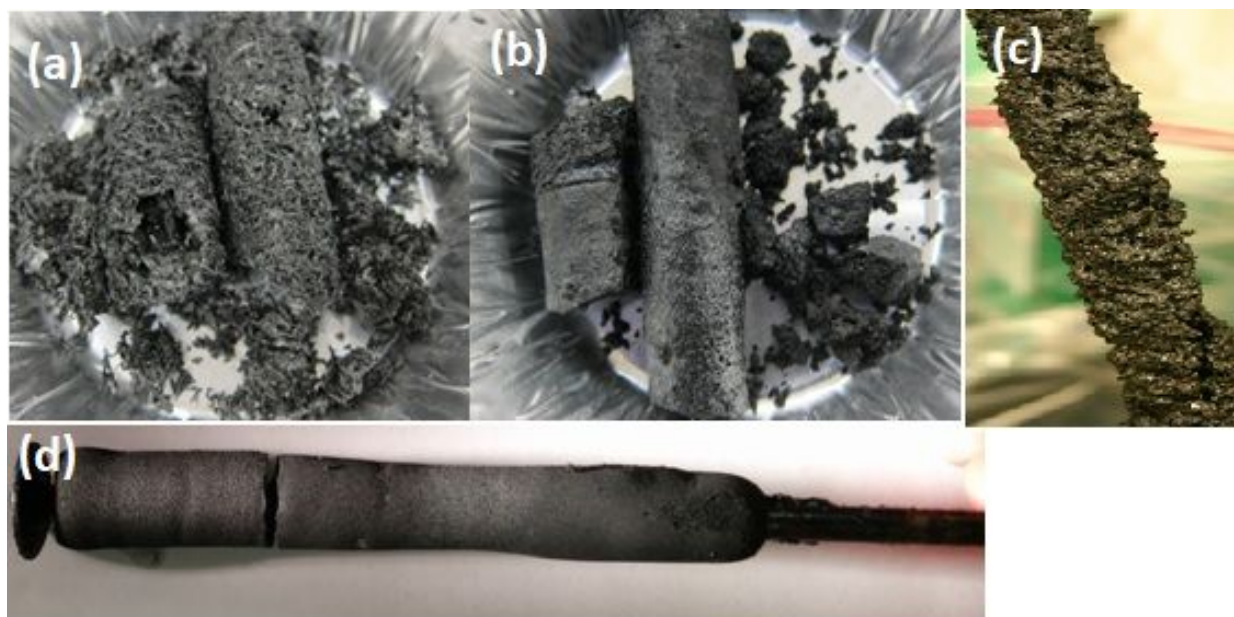


Figure 1. (a) Birch charcoal produced in a CVC test under a HTT of 550°C, an initial nitrogen pressure of 0.1 MPa, biomass particle size <2 mm, biomass loading of 130 g/L and an immersion time of 190 minutes. (b) Birch charcoal produced in a CVC test under a HTT of 300°C, an initial nitrogen pressure of 0.1 MPa, particle size <0.2 mm, biomass loading of 240 g/L and an immersion time of 190 minutes. (c) Oak charcoal produced in a CVC test under a HTT of 300-400°C, an initial nitrogen pressure of 2.69 MPa, a coarse particle size, biomass loading of ~120 g/L and an immersion time of 55 minutes. (d) Cellulose charcoal produced in a CVC test under a HTT of 300-400°C, an initial nitrogen pressure of 2.4 MPa, a particle size of 50-180 μm, biomass loading of ~200 g/L and an immersion time of 85 minutes.

Signs of a molten phase were evident in chars derived from CVC of birch particles of size <2 mm at a pretest pressure of 0.1 MPa N₂, a HTT of 400 °C and a heating rate of ~1°C/s,[9] and in chars from the CVC of cellulose grains in a size range from 0.050-0.18 mm, at a pretest pressure of 2.40 MPa N₂, a HTT of 260 °C and a similar heating rate[8]. To our knowledge, this is the first time molten charcoals have been observed in pyrolysis processes operating at moderate conditions of temperature and slow heating rates.

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3 These temperatures and heating rates contrast with those reported in “open” reactor
4 configurations. In “open” reactors, the morphological transformation of the char into a plastic
5 state have been studied by a limited number of authors using fast pyrolysis processes operating at
6 temperatures $>550^{\circ}\text{C}$ [18–20], heating rates of $\sim 500^{\circ}\text{C/s}$ [18] to $\sim 10^4^{\circ}\text{C/s}$ [18,19,21], small
7 particles and small amounts of sample. If the heating rates typical of slow pyrolysis (or
8 carbonization) processes were employed, the transient plastic phase vanished and the structure of
9 the charcoals resembled skeletons of the virgin biomasses.[19]

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20 In conclusion, it appears that volatiles act as plastifying agents. CVC processes foster the
21 prolonged retention of a high concentration of volatiles within the char matrix. The result is the
22 shift of the char point to lower temperatures and heating rates. Conditions employed in the CVC
23 process such as temperature, pressure, heating rate, particle size or biomass loading played key
24 roles in the evolution of the char morphology. Details of the influence of each variable are given
25 in the following sections.

34 ***3.2 Effect of a Closed Vessel versus an Open Vessel***

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37 Figures 2 illustrates the effect of sealing the WHTB reactor on the product yields and proximate
38 analysis of chars from oak pyrolysis at a HTT of 300°C and an initial pretest pressure of 0.1 MPa
39 N_2 (Experiments # 1 and 2 in Supporting Information Table S1). Notice that proximate analysis
40 values in Figure 2b represents the normalization to 100% of the solid fractions from Figure 2a.
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42 Carbonization in the sealed WHTB (i.e. CVC) and carbonization in a reactor slightly opened to
43 the atmosphere resulted in charcoal yields of 58.6 wt% and 69.8 wt%, respectively but the CVC
44 char product was characterized by a dramatically improved fixed-carbon content (55 vs 34 wt%,
45 respectively) and fixed-carbon yield. Yields of free tars constituted a considerable fraction (not
46 quantified) of the final products of the pyrolysis in the open reactor but became a negligible
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3 fraction in the CVC process. The liquid yield of the CVC test shown in Figure 2a, as well as in
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5 the rest of the figures in the article, represents the char moisture content.
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8 Notice that the prolonged immersion time employed with the closed reactor (134 min) versus the
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10 “open” reactor (34 min) can partially account for the differences in the final products from both
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12 processes (see Section 3.8). Nonetheless, the higher extent of secondary char formation observed
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14 in the CVC process is mainly explained by the retention of volatiles in the reaction zone and
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16 consequent prevention of carbon losses in the outflow of gases and tars. In the CVC process,
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18 released volatiles are in contact with the solid at a higher partial pressure and for longer periods
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20 of time than in the “open” reactor. These effects promote secondary reactions between volatiles
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22 and the solid char that produce secondary char and lead to higher fixed-carbon contents and
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27 fixed-carbon yields.
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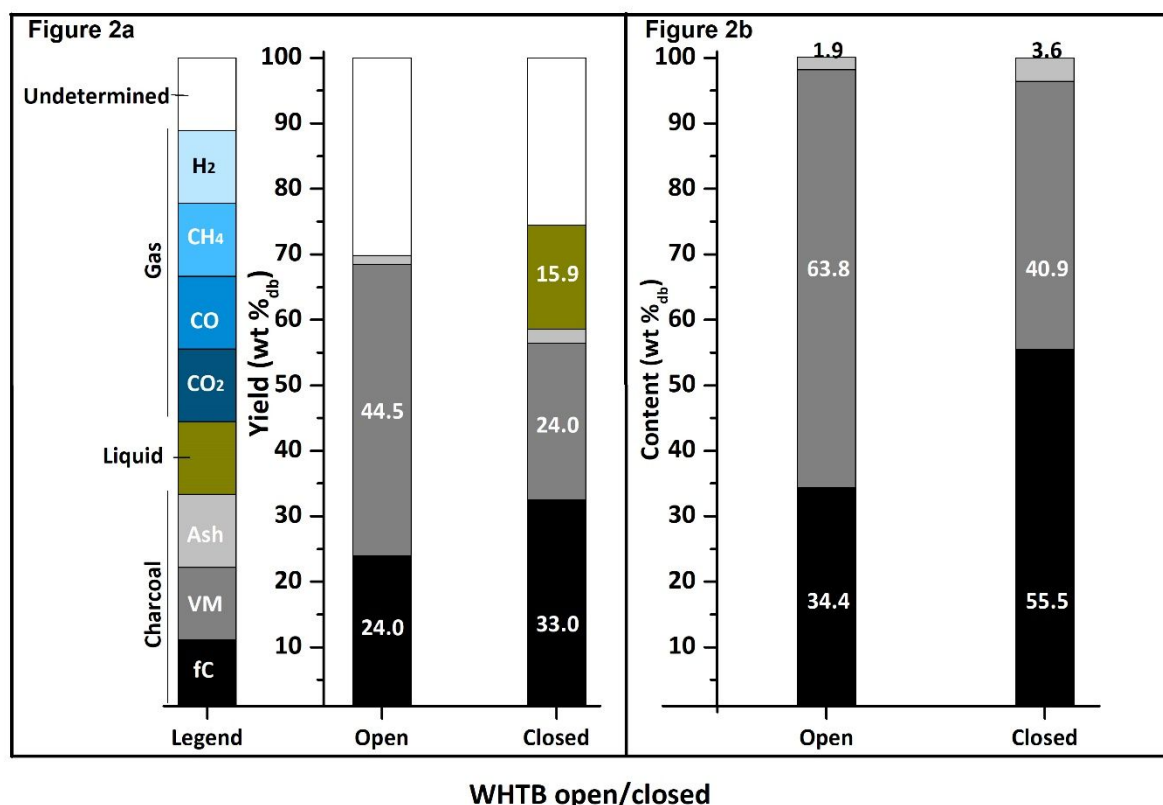


Figure 2. Effect of sealing the reactor on the yields of char, condensate and gas (Figure 2a) and on the proximate analysis of chars (Figure 2b) from oak carbonization at a HTT of 300°C, initial atmospheric pressure, feedstock particle size of 0.149-0.425 mm and mass loading of ~100 g/L. Negligible free tars are recovered from the closed reactor experiments (CVC). Liquid yield represents water content of the final moist charcoal.

3.3 Effect of Pressure

Figures 3a and 3b illustrate the effect of pretest N₂ pressure on the product yields from oak CVC experiments at a HTT of 300°C (Experiments # 2-5 in Supporting Information Table S1) and the char proximate analysis. An initial decrease in the char fixed-carbon content and fixed-carbon yield was observed when the pretest nitrogen pressure was increased from 0.1 to 1.48 MPa and a subsequent plateau followed at higher pressures. The initial decline of the char fixed-carbon content (from 55.5 to 49.7 wt%) and fixed-carbon yield (from 32.5 to 28.4 wt%), however, seem

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3 to be the result of a considerable shorter immersion time (from 134 to 34 minutes) (see Section
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5 3.7) rather than to a pressure effect. At higher pretest pressures (from 1.48 to 4.79 MPa), oak
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7 experiments used similar immersion times (21 to 38 minutes) which offers an explanation to the
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9 subsequent plateau observed in fixed-carbon contents and yields. Careful control of the
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11 immersion time, and refinements made to the WHTB equipment (see Apparatus Evolution
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13 section in Legarra et al.[9]) and the proximate analysis technique (see Section 2) permitted the
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15 acquisition of more accurate results in later experiments that used birch and spruce feedstocks.
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18 Figures 3c and 3d display the results for birch CVC experiments with the current WHTB reactor
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20 at pretest pressures of 0.1 and 2.17 MPa N₂ and HTTs of 300 and 400°C (Experiments # 9 and
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22 10 in Supporting Information Table S1 for the high pressure tests and see Legarra et al.[9] for the
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24 tests at atmospheric pressure). The results from these experiments confirmed the lack of
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26 influence of the inert gas pressure on product yields and proximate analysis.
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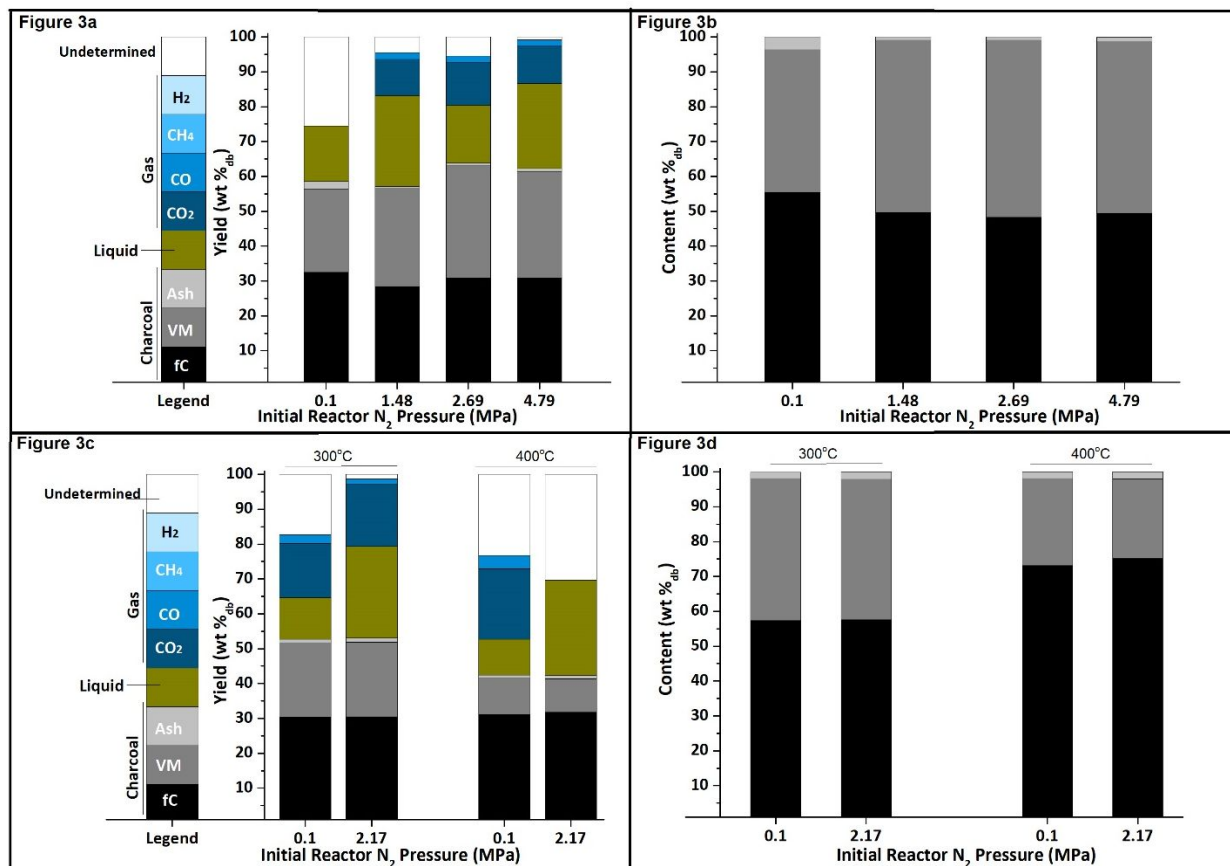


Figure 3. Effect of the initial nitrogen pretest pressure on the yields of char, condensate and gas (Figure 3a) and on the proximate analysis of chars (Figure 3b) from oak CVC at HTT of 300°C, immersion times of 21-134 minutes, feedstock particle size of 0.149-0.425 mm and mass loadings of ~100-160 g/L. Effect of the initial nitrogen pretest pressure on the yields of char, condensate and gas (Figure 3c) and on the proximate analysis of chars (Figure 3d) from birch CVC at HTT of 300°C, immersion time of 190 minutes, feedstock particle size <2 mm and mass loading of 130 g/L. Experimental conditions and results for experiments at 0.1 MPa pretest pressure are given in previous work.[9]

These findings differ from those reported in literature. Generally, pressure has presented a beneficial effect on char yields and properties. For instance, Mok and Antal[22] observed a doubling in the char yields when they combined elevated pressures and low carrier gas flow rates in a fixed bed reactor. Likewise, Zaror and co-workers[23] more than doubled the char recovered during cellulosic pyrolysis when a flowing gas stream was interrupted in a Gray-King retort. In

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3 contrast, studies on carbonization under pressure with high flows of carrier gas in fixed bed and
4 hot-rod reactors conducted by Palmer,[24] Frolich et al.[25] and Pindoria and co-workers[26] did
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6 not observe a clear influence of pressure on char yields.
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10 These discrepancies can be explained by the distinct reactor configurations employed by the
11 researchers. The type of process dictates the role of pressure during pyrolysis due to its effect on
12 volatiles partial pressure and /or their residence times and therefore on the extent of secondary
13 charring reactions. In “open” reactors, higher pressures and/or lower gas flows increase both the
14 partial pressure and residence time of volatiles, which therefore enhance cross-linking
15 reactions[27–31] that promote formation of secondary char at the expense of tar.[28,29] In
16 addition, if the gas flows employed are high enough that tarry vapors quickly escape the reaction
17 zone (even when operating at elevated pressure as in Palmer,[24] Frolich et al.[25] and Pindoria
18 et al.[26]), it limits and minimizes secondary reactions and consequently, pressure appears to
19 have an insignificant effect on the yields. The results obtained by Shafizadeh and co-workers[32]
20 regarding carbonization under vacuum can also be explained by the suppression of these
21 secondary charring reactions. CVC is able to use an external inert gas in order to decouple the
22 effects of the volatiles partial pressure and the total reactor pressure. Adding an inert gas to the
23 reactor prior to sealing the system and conducting biomass carbonization increases the total
24 system pressure while keeping the vapor pressure and residence time of volatiles unchanged.
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26 Therefore, yields and fixed-carbon contents remain roughly constant.
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31 Mok et al.[7] investigated decoupling the volatile pressure from the total system pressure when
32 they added dry ice and cellulose inside closed crucibles prior to heating during pyrolysis
33 experiments. They found that increasing the total system pressure with CO₂ did not influence the
34 yield of charcoal (fixed-carbon content was not measured) or the amount of heat released.
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3 Additionally, increasing the initial cellulose mass loading resulted in greater charcoal yields and
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5 faster, more exothermic reactions that originated at lower temperatures. Thus, Mok et al.
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7 identified the volatile partial pressure—instead of the total system pressure— as the prevailing
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9 parameter which affects the char yield and amount of heat released.
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12 Proximate analysis on the final charcoals produced from later CVC experiments on cellulose
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14 confirmed the lack of influence of an inert gas pressure on the product yields.[8] Nonetheless,
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16 the fixed-carbon contents showed a slight improvement with higher inert pressures.[8] For
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18 example, when the initial nitrogen pressure was increased from 0.1 to 4.79 MPa, the fixed-carbon
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20 content improved from 54 to 58%. Nevertheless, the increased carbon mass balance (from 92%
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22 to 101.5%) may indicate that these differences in fixed-carbon content are not significant. The
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24 most recent studies on CVC experiments with birch under various pressures with upgraded
25
26 analytical techniques and equipment presented herein support the conclusion that it is the
27
28 concentration of volatiles and/or their increased residence time, and not the total system pressure,
29
30 that dictate the product yields and charcoal proximate analysis values.
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36
37 In agreement with CVC experimental observations, FactSage equilibrium calculations of
38
39 products formed under CVC conditions show a negligible pressure effect on theoretical fixed-
40
41 carbon yields (see Supporting Information Figure S2) with solid carbon as the major product
42
43 followed by gaseous byproducts of water, carbon dioxide, methane, and traces of carbon
44
45 monoxide and hydrogen. The lack of an influence of increasing pressure on equilibrium product
46
47 yields and product distributions were reported by Antal et al.[33] for constant-pressure pyrolysis
48
49 (not CVC) of cellulose at 400°C. Skreiberg et al.[34] also observed an insignificant pressure
50
51 effect on the theoretical product yields of biomass pyrolysis at constant pressure within a
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53 temperature range of ~300-600°C.
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CVC experiments with oak and birch also confirmed the morphological findings observed for chars derived from cellulose.[8] Visual observations and SEM images of charcoals produced at different CVC conditions showed that higher inert pressures—as well as higher temperatures, faster heating rates and possibly smaller particles (see later sections)—produced charcoals that experienced greater extents of melting appearance. Figure 10 in Legarra et al.[9] and Figure 4 display large differences in the surface morphology of birch charcoals produced at a temperature of 300°C and pretest pressures of 0.1 MPa and 2.17 MPa, respectively.

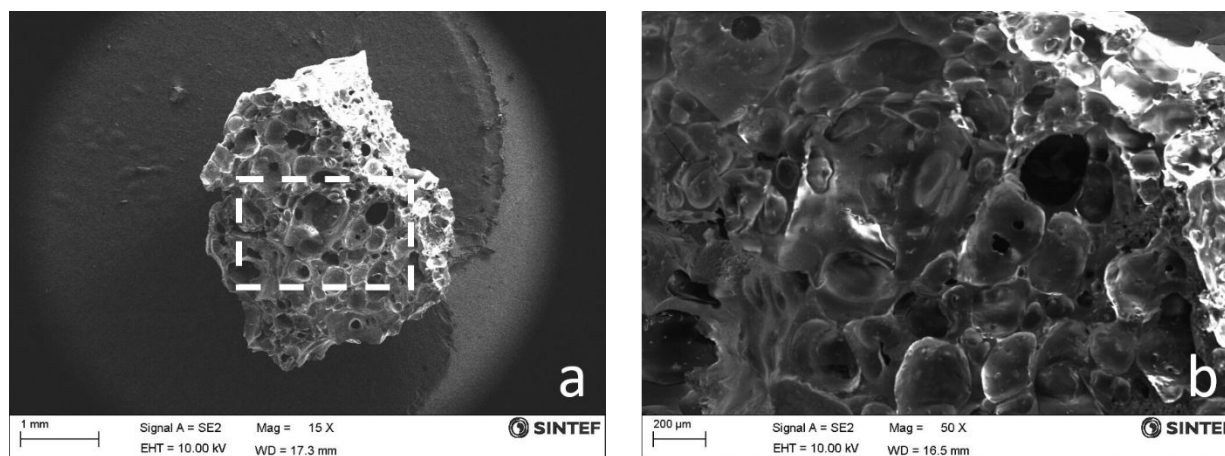


Figure 4. (a) SEM image of birch charcoal from CVC at HTT of 300°C, initial nitrogen pressure of 2.17 MPa, immersion time of 190 minutes, feedstock particle size <2 mm and mass loading of 130 g/L, (b) higher magnification view of selected area in (a).

Based on the CVC results, a distinction was made between time and concentration of volatiles inside the pyrolyzing char and outside, but in close proximity to, the pyrolyzing char particle surface. It is hypothesized that prolonged intraparticle times of high volatile concentrations favor a plastic state of char. Once the volatiles escape from the interior of the char matrix, their plastification activity is reduced or blocked. If the released volatiles remain in close contact with

1
2
3 the solid, as in CVC processes, they can continue reacting with the solid through secondary
4
5 reactions to form additional charcoal without losing carbon to the gaseous outflow. Raising the
6
7 reactor pressure by the pre-addition of an inert gas in CVC processes lead to higher intraparticle
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9 volatile retention enabling the transformation of the charcoal structure towards the formation of a
10
11 TPP without altering char yields and proximate analysis. Further research is required to better
12
13 understand this phenomenon.
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15

16 17 18 ***3.4 Effect of Heat Treatment Temperature*** 19

20 Figures 5a and 5b illustrate the effects of a 300-400°C HTT range on product yields and
21
22 proximate analyses of chars derived from oak CVC experiments at a nitrogen pretest pressure of
23
24 4.79 MPa (Experiments #5-8 in Supporting Information Table S1). Figures 5c and 5d illustrate
25
26 the HTT effect for birch CVC experiments in an expanded range of 300-550°C at a pretest
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28 pressure of 0.1 MPa (Experiments # 11 and 12 in Supporting Information Table S1 for CVC at
29
30 500 and 550°C and see Legarra et al.[9] for CVC at 300 and 400°C). CVC methods for oak and
31
32 birch were different. For oak, the WHTB reactor was immersed in a 300°C sandbath that was
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34 subsequently heated to a final target temperature. For birch, the WHTB was immersed in a
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36 sandbath heated to the final target HTT.
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41 In agreement with observations from the CVC of spruce and cellulose,[8,9] raising the
42
43 carbonization temperature leads to a pyrolytic product richer in gas and lower in char, and a solid
44
45 char with higher fixed-carbon and lower volatile contents. Exotherm temperature peaks and
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47 reactor pressure peaks also increased as HTT increased, and char higher heating values (HHV)
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49 increased asymptotically. Exothermic peaks which are prominent at the lower HTT of 300°C
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51 became less evident or they were masked by the heating rate experienced by the biomass at
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53 higher HTTs.
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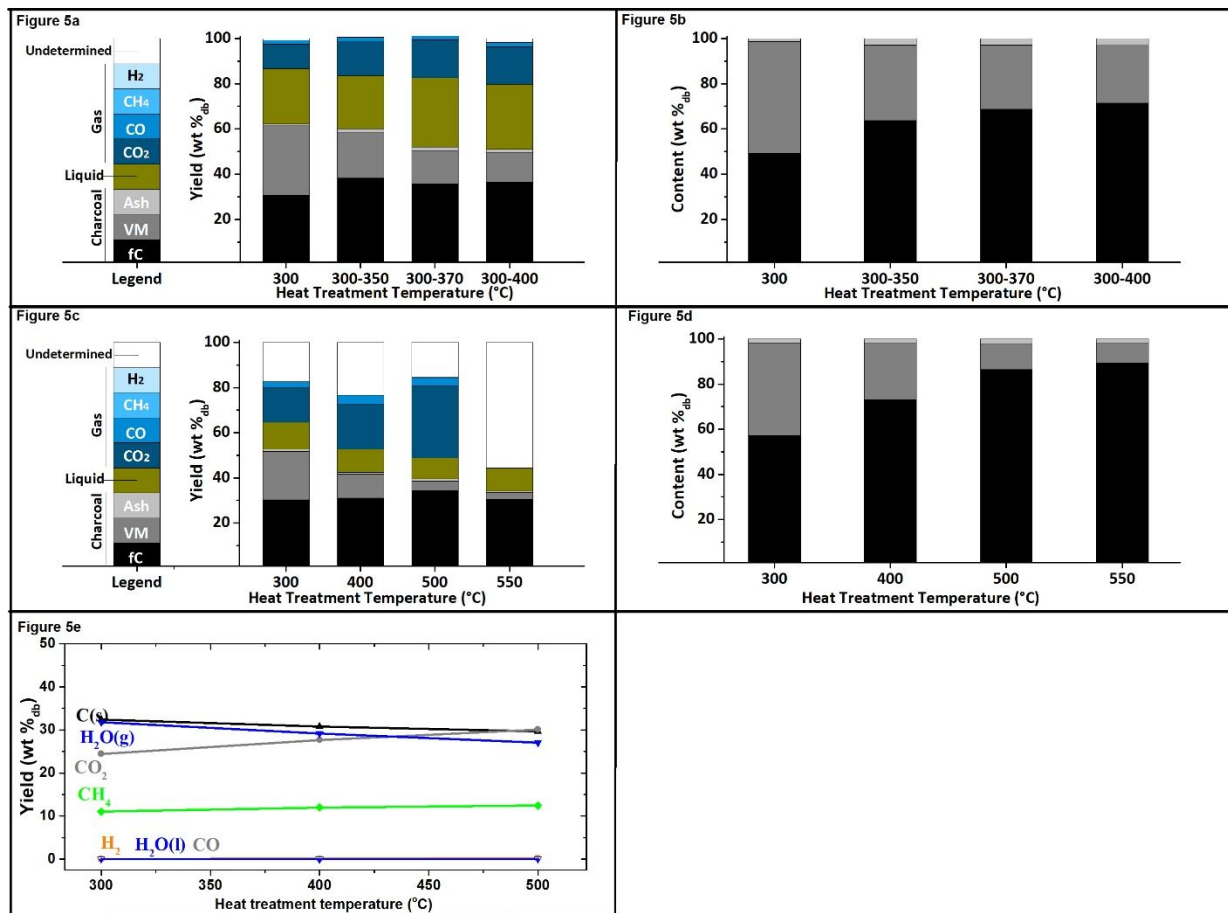


Figure 5. Effect of HTT on the yields of char, condensate and gas (Figure 5a) and on the proximate analysis of chars (Figure 5b) from oak CVC at an initial N₂ pressure of 4.79 MPa, immersion time of 21-181 minutes, feedstock particle size of 0.149-0.425 mm and mass loading of ~120-155 g/L. Effect of HTT on the yields of char, condensate and gas (Figure 5c) and on the proximate analysis of chars (Figure 5d) from birch CVC at an initial N₂ pressure of 0.1 MPa, immersion time of 190 minutes, feedstock particle size <2 mm and mass loading of 130 g/L. Birch experimental conditions and results at HTTs of 300 and 400°C are given in earlier work.[9] Effect of HTT on the theoretical product distribution from birch CVC predicted by FactSage (Figure 5e).

The possibility of maintaining or slightly raising the fixed-carbon yield as char properties improved (higher fixed-carbon content and less volatiles) was emphasized in preliminary CVC work in a 300-400°C range with cellulose[8] and spruce[9] feedstocks. Birch was tested over a wider temperature range (300- 550°C) and fixed-carbon contents increased concomitantly from 57.7 to 89.3 wt%. Fixed-carbon yields, however, experienced a slight downturn. From 300 to

1
2
3 400 to 500°C, the birch experimental fixed-carbon yield went from 30.3 to 31.1 to 34.2 wt%.
4
5 Further increasing the temperature from 500 to 550°C slightly reduced the fixed- carbon yield
6
7 matching yields obtained at 300°C. At 500°C, the manufactured charcoal is characterized by the
8
9 maximum fixed-carbon yield observed (34.2 wt%) and a fixed-carbon content (86.5 wt%) of
10
11 high metallurgical grade.
12
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14
15 Figure 5e shows theoretical fixed-carbon yields of birch with temperature predicted by FactSage.
16
17 Theoretical and experimental results display minor temperature effects albeit with different
18
19 trends. Theoretical fixed-carbon yields slightly but continuously decrease with temperature.
20
21 Ongoing reactions during the CVC experiments as indicated by the continuous rise in pressure
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23 throughout the experiments, especially when operating at lower temperatures, may explain
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25 differences observed in trends. Even though thermodynamics set meaningful limits for the fixed-
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27 carbon yields,[27] complete agreement should not be expected.
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31
32 In agreement with morphological observations from previous work,[8,9] a more intense TPP was
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34 observed as the carbonization temperature was increased. Scanning electron microscopy was
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36 used to examine birch charcoal samples. The 300°C-birch charcoal (Figure 10, Legarra et al.,
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38 reference [9]) presented a granular appearance that largely retained the original biomass
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40 morphology.[9] In comparison, the 400, 500 and 550°C-birch charcoals (see Figure 11, Legarra
41
42 et al.[9] for the 400 °C-birch charcoal and Figures 6 and 7, below, for the 500 and 550°C
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44 charcoals) revealed some charcoal grains with a structure that resembled that of the virgin wood
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46 and larger porous aggregates with molten surfaces that indicated more intense TPP stages.
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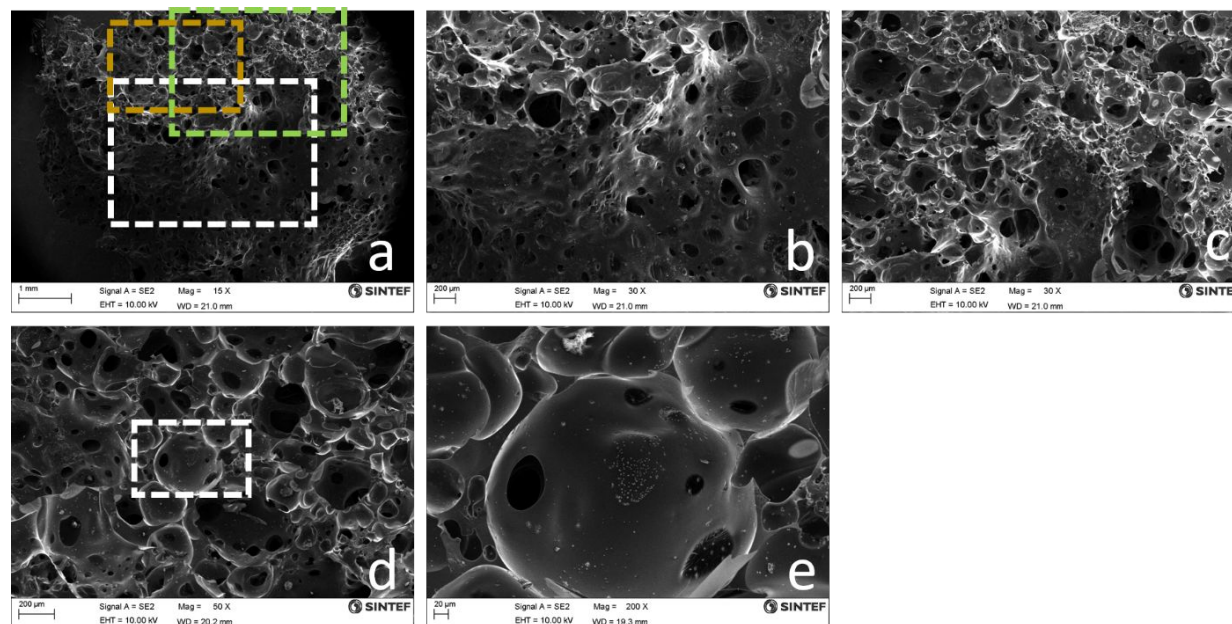


Figure 6. (a) SEM image of birch charcoal from CVC at HTT of 500°C, initial nitrogen pressure of 0.1 MPa, immersion time of 190 minutes, feedstock particle size <2 mm and mass loading of 130 g/L, (b)-(d) higher magnification views of selected areas in (a), (e) higher magnification view of selected area in (d).

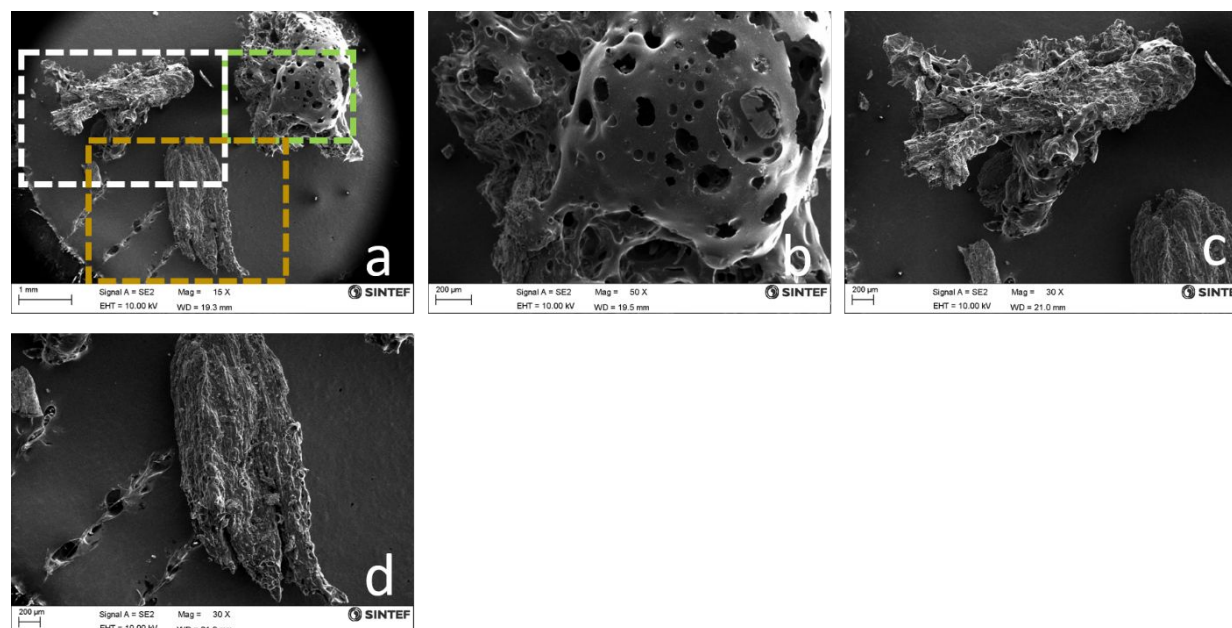


Figure 7. (a) SEM image of birch charcoal from CVC at HTT of 550°C, initial nitrogen pressure of 0.1 MPa, immersion time of 190 minutes, feedstock particle size <2 mm and mass loading of 130 g/L, (b)-(d) higher magnification views of selected areas in (a).

3.5 Effect of Heating Rate

The WHTB system is not the ideal equipment for studies concerning heating rate effects. The sandbath does not provide fine control of the heating rate. Thus, the study of the heating rate effect on CVC was limited to a qualitative study in which two classes of heating rates, “fast” and “slow”, were tested. Precise quantitative studies would require the use of a different reactor configuration.

In the WHTB system, the maximum achievable heating rate was limited by the use of deep-packed beds of biomass particles and the two rates tested, “fast” and “slow”, fall in the range of slow pyrolysis processes ($<1^{\circ}\text{C/s}$). “Fast” heating is the procedure followed in a typical CVC experiment and consists of immersing the reactor into a sandbath preheated to the HTT. The “slow” heating procedure consists of immersing the reactor into a $\sim 110^{\circ}\text{C}$ sandbath that is subsequently ramped to the target HTT.

Figure 8 shows the influence of heating rate on CVC processes (see experiments # 11, 21, 23 in Supporting Information Table 1 and Legarra et al.[9] for birch fast CVC experiment at 300°C). The rate employed to reach the carbonization temperature showed no influence on product yields or char proximate analysis results of CVC as long as the soaking time at the HTT was maintained for a specific time period.

In “open” reactors, the findings regarding the role of heating rate tell a different story. A broad range of heating rates have been covered in “open” configurations, from rates of ~ 0.1 - 1°C/s reported in slow pyrolysis or carbonization processes to rates as high as $\sim 1000^{\circ}\text{C/s}$ (or greater) reported in fast pyrolysis or gasification processes. As the rate is reduced, the product composition shifts in favour of the formation of more char and less tar. If the analysis of the

1
2
3 heating rate effect in “open” reactors is limited to just slow pyrolysis processes, the same trends
4
5 of less tar and more char with lower heating rate are generally observed until an apparent
6
7 asymptote in the char yield is reached.[35]
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9

10 The lack of influence of the heating rate on char yields and fixed-carbon content from the CVC
11
12 tests could be explained by the asymptotic behavior of char yields as the heating rates decrease.
13
14 An alternative explanation of the results from both reactor configurations, “open” and CVC, can
15
16 also be found in the role that heating rate plays on the rate and amount of volatiles extracted.
17
18 Observations in carbonization processes have shown a link between a more profound release of
19
20 volatiles when higher temperatures are used. Bradbury et al.[36] reported a volatile/char ratio of
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22 two at 300°C, versus a ratio of fifty at 600°C. When slow heating rates are used, the pyrolyzing
23
24 solid spends additional time at lower temperatures which enhance repolymerization reactions
25
26 between tar molecules and the solid matrix. Under rapid heating, biomass spends less time at low
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28 temperatures and is intensely broken down into volatiles. In “open” reactors, these volatiles
29
30 escape the reaction zone, resulting in carbon losses in the form of tarry vapors or gases and
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32 leaving behind a charcoal with less carbon. In CVC, the carbon present in tarry vapors remains in
33
34 the reaction zone and is not lost, but instead reacts to form secondary charcoal. As a result,
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36 charcoal yields or proximate analysis results may be less sensitive to the heating rate used to
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38 reach the carbonization temperature in CVC processes. The role of particle size in both reactor
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40 configurations (see Section 3.7), which heavily determines the particle heating rate, also supports
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42 this explanation.
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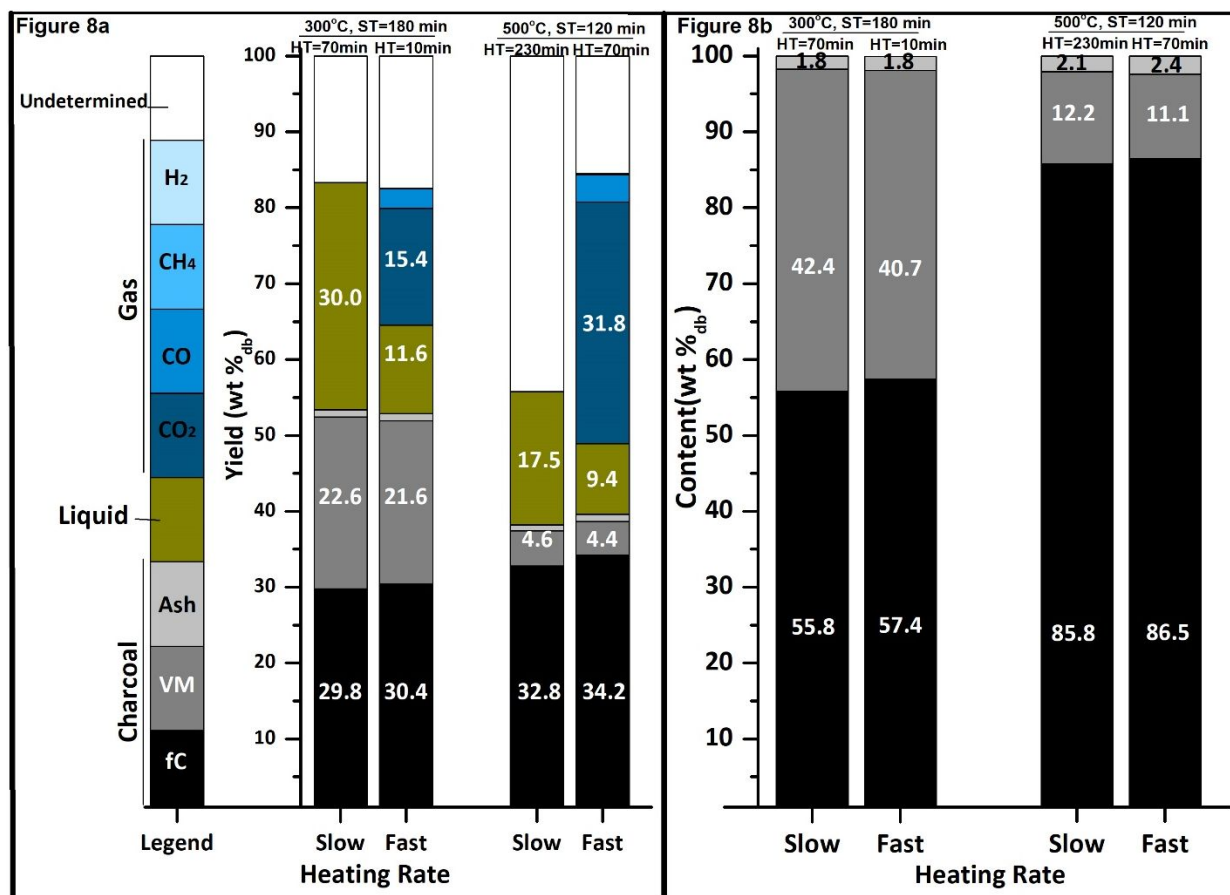


Figure 8. Effect of heating rate on the yields of char, condensate and gas (Figure 8a) and on the proximate analysis of chars (Figure 8b) from birch CVC at an initial N₂ pressure of 0.1 MPa, feedstock particle size <2 mm and mass loading of 130 g/L. HT stands for heating time and ST stands for soaking time. Experimental data of the birch fast heating rate experiment at 300°C is given in reference[9].

The reactor configuration, “open” versus CVC, also dictates the heating rate impact on the morphological evolution of char. In “open” reactors, its effect was clearly depicted by Newalkar et al.[19] In a slow pyrolysis process (~1°C/s), biomass decomposition (~250–300 °C) largely preceded the softening of the char (~600°C). As the biomass particle is heated to 600°C, up to 80% of the solid weight of the original biomass forms volatiles and the char structural matrix becomes a skeleton of the original biomass with very little or no morphological changes. In fast pyrolysis, the morphological evolution is radically different. Biomass decomposition overlaps

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2
3 with char softening as it swells and evacuates volatiles from within its matrix. These effects
4
5 completely disrupt the original biomass structure and transform it to an amorphous form that
6
7 later reorders into one more graphite-like.
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10 In CVC, the enhanced intraparticle residence time and concentration of volatiles differ from
11
12 those produced in “open” reactors (see Section 3.2). Nonetheless, there are some analogies that
13
14 can be made with findings derived from “open” reactors by Newalkar et al. [19] At the low
15
16 temperature of 300°C, the structures of the chars manufactured in CVC at initial atmospheric
17
18 pretest pressure under the two “slow” and “fast” heating rates (~0.09 and 0.5°C/s respectively)
19
20 mainly resembled that of the virgin biomass (Figure 9 and Figure 10 from Legarra et al. [9],
21
22 respectively). At temperatures $\geq 400^\circ\text{C}$ and the “fast” heating rate, biomass decomposition
23
24 products interacted to form a TPP. The same conditions with a slow heating rate did not produce
25
26 a TPP. Notice the contrasting appearances of the 500°C-chars at both “fast” (~0.09°C/s) and
27
28 “slow” (~0.03°C/s) heating rates (Figures 6 and 10, respectively). Keep in mind that the CVC
29
30 heating rates reported herein represent average values over the entire heating period. For
31
32 example, the average rate of ~0.09°C/s reported in the birch CVC under “fast” heating to 500°C
33
34 represents a mean value of instantaneous rates ranging between <0.001°C/s and 5.5°C/s. While
35
36 the average rate of ~0.03°C/s reported in the birch CVC under “slow” heating to 500°C
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38 represents a mean value of instantaneous rates in a range between <0.001°C/s and 0.27°C/s.
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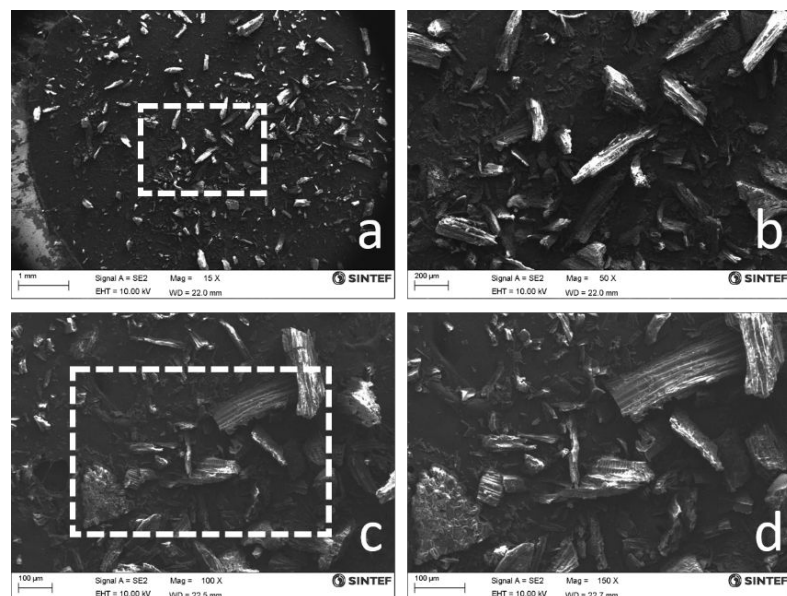


Figure 9. (a) and (c) SEM images of birch charcoals from CVC at a “slow” heating rate, HTT of 300°C, initial nitrogen pressure of 0.1 MPa, feedstock particle size <2 mm and mass loading of 130 g/L. (b) and (d) higher magnification views of selected areas in (a) and (c).

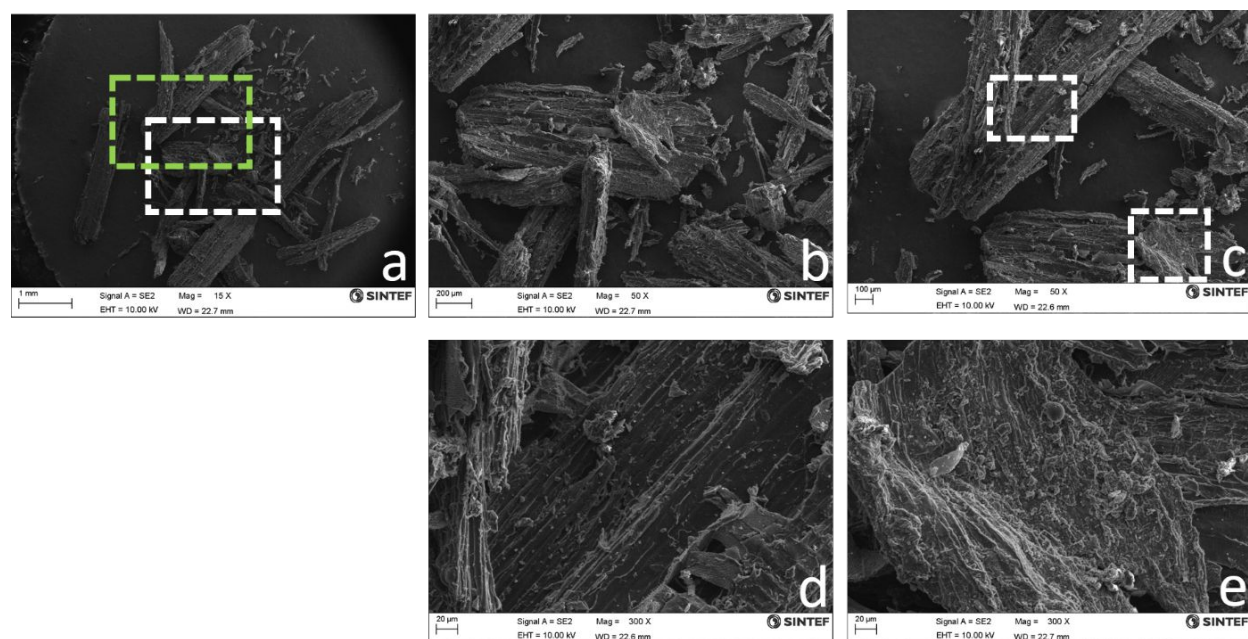


Figure 10. (a) SEM images of birch charcoal from CVC at a “slow” heating rate, HTT of 500°C, initial nitrogen pressure of 0.1 MPa, feedstock particle size <2 mm and mass loading of 130 g/L. (b) and (c) higher magnification views of selected areas in (a). (d) and (e) higher magnification views of selected areas in (c).

3.6 Effect of Particle Size

Figure 11 illustrates the effect of two different biomass particle sizes (<0.2 mm and <2 mm) on product yields and proximate analyses of chars from birch CVC experiments at 300°C HTT and 0.1 MPa pretest pressure (Experiment #13 in Supporting Information Table S1 for CVC of birch particles <0.2 mm and see Legarra et al.[9] for CVC of birch particles <2 mm). At these experimental conditions, the product yields and proximate analyses of charcoal did not show any dependence on the particle size, however the rates of the carbonization reactions changed. When the smaller particles (<0.2 mm) were pyrolyzed, reactions became faster, with reactor pressure and temperature stabilizing within the first hour. Carbonization of the larger particles (<2 mm), however, required at least three hours to reach steady state.

These recent results complement those previously obtained from the CVC of spruce at analogous pyrolysis conditions.[9] The use of smaller spruce particles led to a somewhat faster devolatilization of the biomass and resulted in higher pressures, more pronounced exotherms, chars with slightly higher fixed-carbon contents and chars with slightly higher or similar fixed-carbon yields.[9] HHVs of charcoals produced from smaller and larger spruce particles under the same conditions were similar. It is possible that differences observed in the proximate analyses and yields of chars were the result of reactions not reaching completion for the larger particles (<2 mm) whereas reactions for the smaller particles (<0.2 mm) reached termination or neared completion. Results from CVC of the larger spruce grains at immersion times of 30, 190 and 300 min confirmed the continuous improvement of char properties as the reaction time was prolonged (see Section 3.8).

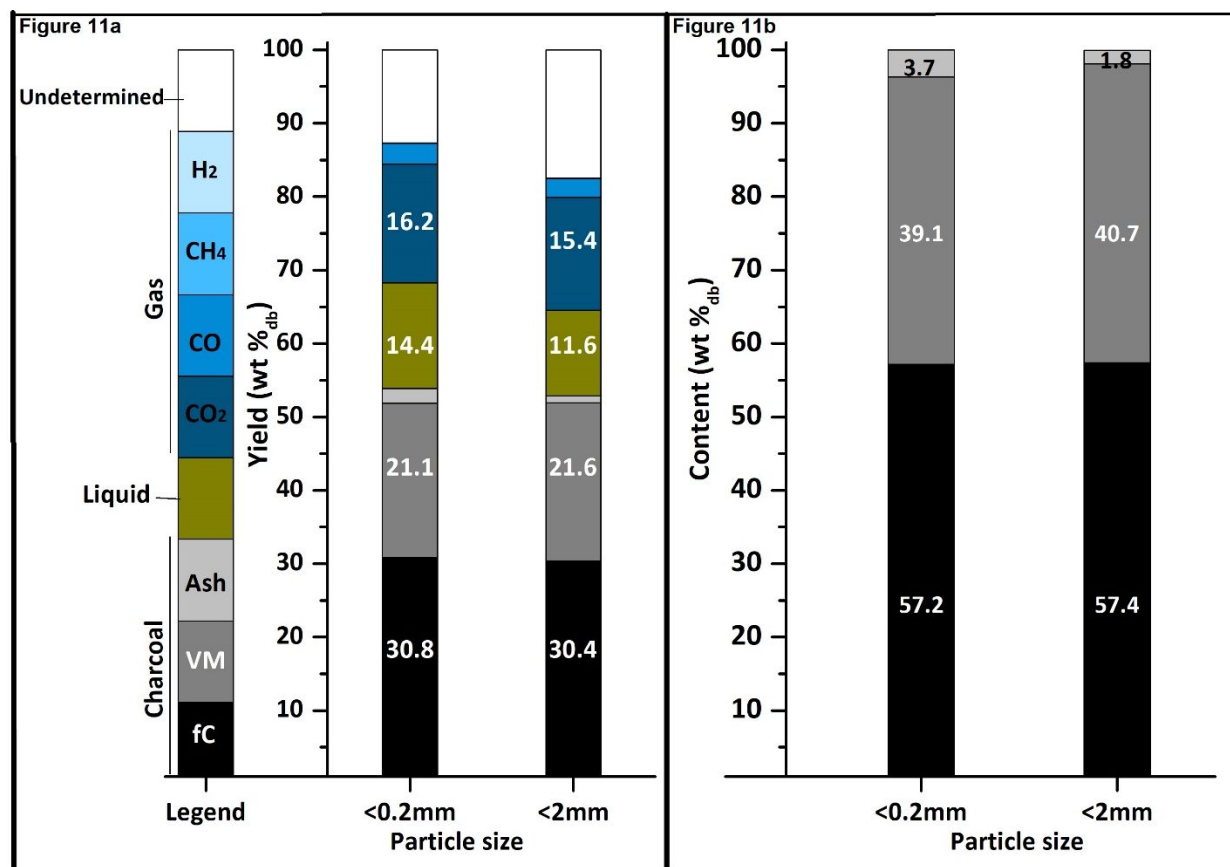


Figure 11. Effect of particle size on the yields of char, condensate and gas (Figure 11a) and on the proximate analysis of chars (Figure 11b) from birch CVC at an initial N₂ pressure of 0.1 MPa, HTT of 300°C, immersion time of 190 minutes and mass loading of ~130g/L. Experimental data of CVC of birch particles <2 mm is given in reference [9].

Birch CVC reactions appeared to be faster than those for spruce. By 190 minutes, CVC of the larger birch particles was near completion resulting in similar product yields and proximate analysis as the ones reported for the smaller particles. In line with these findings, cellulose fine powder (50-180 μm) carbonized in the original WHTB needed ~30-60 minutes to reach steady state.[8] Differences in reaction rates between feedstock materials could be due to different chemical or physical properties. For example, larger packing densities (as in the case of birch or cellulose) appear to lead to improved heat transfer coefficients.[37] The role of particle size in

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3 CVC contrast those from “open” reactors. In the latter configurations, trends show an increase in
4 char yield [26,38,39] and less tar [40] or volatiles[41] as larger particles are carbonized.
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8 Explanations of particle size effects in both “open” reactors and CVC experiments follow the
9 same lines of reasoning used for heating rate and pressure effects. The particle size of biomass is
10 strongly linked to the intraparticle heating rate and the residence time of volatiles within the char
11 particle. Larger particle sizes slow down heat transfer through the char particle and retard the
12 release of volatiles from the pyrolyzing char matrix.[27,42–45] Thus, an increase in particle size
13 would have a similar effect to that of slower heating rates combined with an increase in pressure
14 or a reduced gas flow. All these factors favor the promotion of secondary charring reactions in
15 “open” reactors but are not influential in CVC. In fact, CVC of smaller grains presented an
16 advantage over CVC of larger particles. Carbonization rates became faster and, as the released
17 pyrolytic vapors were kept captive in the reaction zone, carbon partitioning to the gas and oil/tar
18 phase was prevented in favor of secondary charring reactions.
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38 ***3.7 Effect of Immersion Time***

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40 The effect of immersion time on product yields and char proximate analysis from the CVC of
41 birch is depicted in Figures 12a and 12b (Experiments #13-16, 20-23 in Supporting Information
42 Table S1). The figures corroborate the findings observed from spruce CVC experiments.[9]
43
44 Prolonging the soaking time at the carbonization temperature led to higher gas yields and chars
45 with greater fixed-carbon contents and greater (or similar at temperatures of 400°C or above)
46 fixed-carbon yields. HHVs of char products were similar, likely due to their approach toward an
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3 asymptote as the chars approached theoretical fixed-carbon yields. Differences in fixed-carbon
4 and elemental composition are not apparently high enough to reflect on char calorific values.
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8 Notice that in “slow” tests (last four runs depicted in Figures 12a and 12b), differences in char
9 yields and proximate analysis between the short and long tests were drastically reduced as the
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HTT increased from 300 to 500°C. The behaviour is associated with the distinct heating times at
the two temperatures of 300 and 500°C (see Section 3.6 for the heating procedure followed in the
“slow” tests). At 500°C, the sandbath heating rate considerably slows down throughout the
experiment especially as the sandbath approaches the target temperature, elongating the heating
period and giving time for the charcoal to further devolatilize which lessens differences in yields
and fixed-carbon contents between the short and long duration tests.

Results from CVC tests with spruce feedstock at immersion times of 30, 190 and 300 minutes
are given in Figures 12c and 12d (experiment #19 in Supporting Information Table S1 for spruce
CVC at 300 min; see Legarra et al.[9] for spruce CVC at 30 and 190 min). At a HTT of 300°C
and a pretest pressure of 0.1 MPa, lengthening the soaking time at the carbonization temperature
improved the fixed-carbon yield and fixed-carbon content. Soaking time increases from 190 to
300 minutes at higher HTTs are likely to result in smaller or negligible increases of the fixed-
carbon content and yield due to the accelerated reaction rates produced by the higher HTT.

SEM analysis was performed for charcoals manufactured in short (around 20-30 min) and long
duration (190 min) CVC experiments at HTTs of 300°C and 400°C. The runs at 300°C used
birch grains <0.2 mm under a pretest pressure of 0.1 MPa and a mass loading of 240 g/L. SEM
images of the charcoal produced at 300°C are presented in Supporting Information Figures S3
and S4. At the modest temperature of 300°C, signs of TPP are weak and conclusions regarding
the TPP evolution with time cannot be clearly discerned.

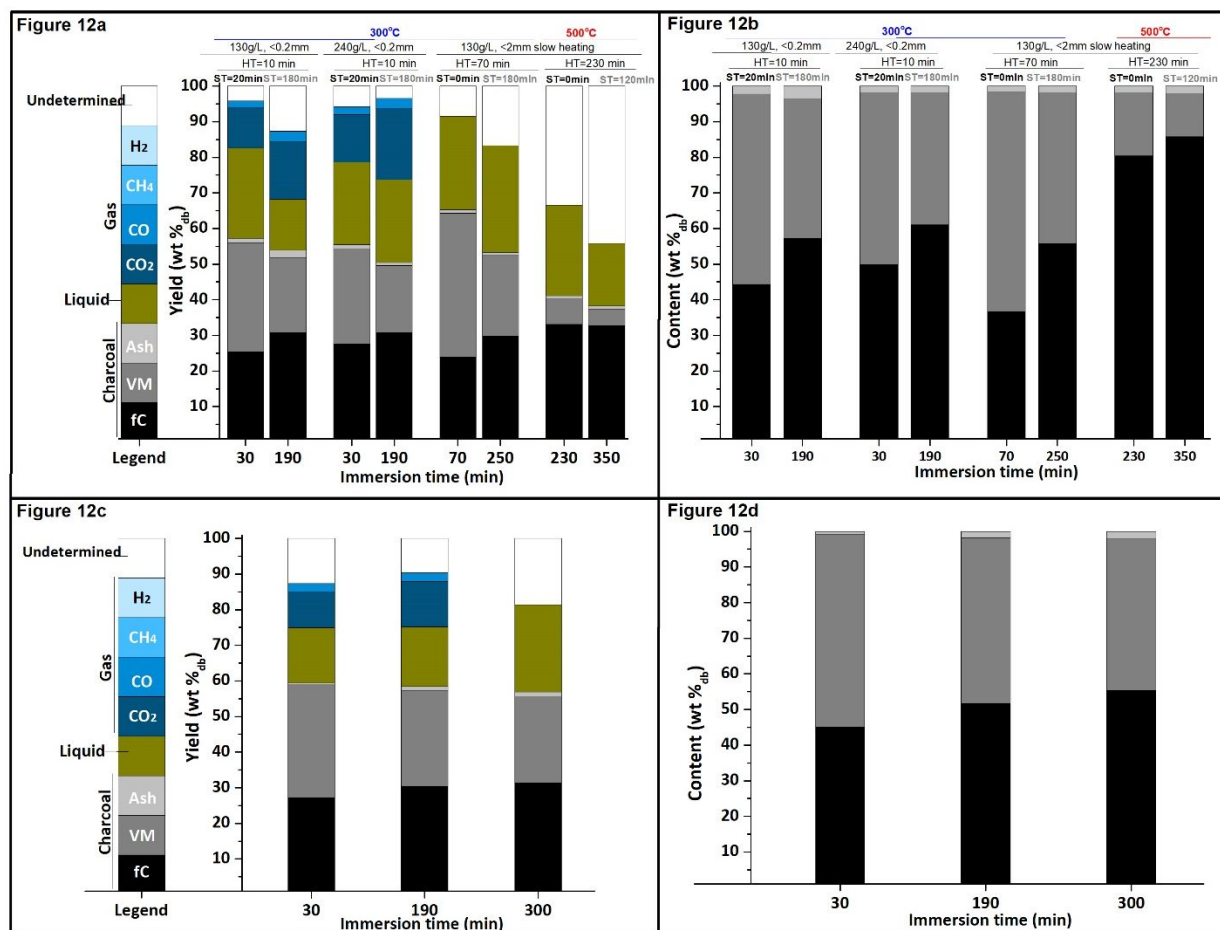


Figure 12. Effect of immersion time on the yields of char, condensate and gas (Figure 12a) and on the proximate analysis of chars (Figure 12b) from birch CVC at an initial N₂ pressure of 0.1 MPa. Effect of immersion time on the yields of char, condensate and gas (Figure 12c) and on the proximate analysis of chars (Figure 12d) from spruce CVC at an initial N₂ pressure of 0.1 MPa, HTT of 300°C, feedstock particle size <2 mm and mass loading of 130 g/L. Experimental conditions and results for experiments at 30 and 190 min immersion times are given in previous work.[9]

The runs at 400°C used spruce grains <2 mm under a pretest pressure of 0.1 MPa and a mass loading of 130 g/L. Experimental conditions, yields and proximate analysis results for the 400°C tests were described in Legarra et al.[9] At 400°C, a TPP behaviour with time becomes clearer and charcoal morphology evolves with reaction time as seen in Figures 13 and 14. Charcoals produced in 18-min did not present TPP characteristics, but showed some tar condensation on the char surface. In contrast, charcoals produced in the 190 min run showed clear TPP formation.

Morphological conclusions derived from SEM observations are not absolute since the analyses were performed for small uncrushed portions of charcoal samples that can be heterogeneous and variable.

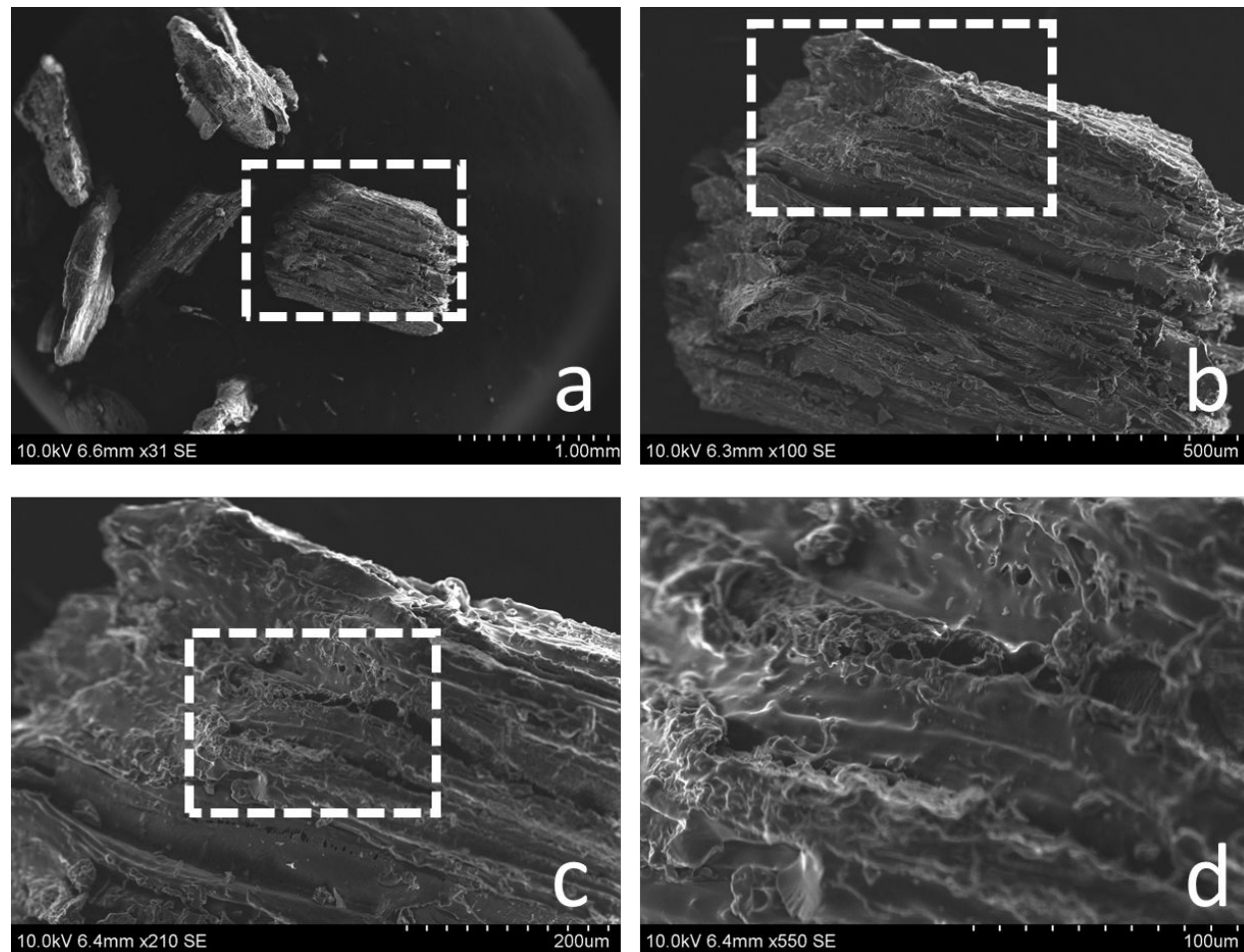


Figure 13. (a) SEM images of charcoal from CVC of spruce grains of particle size <2 mm at a mass loading of 130 g/L, HTT of 400°C , an initial nitrogen pressure of 0.1 MPa and a short immersion time of 18 min, (b), (c) and (d) higher magnification views of selected areas in (a), (b), (c) respectively.

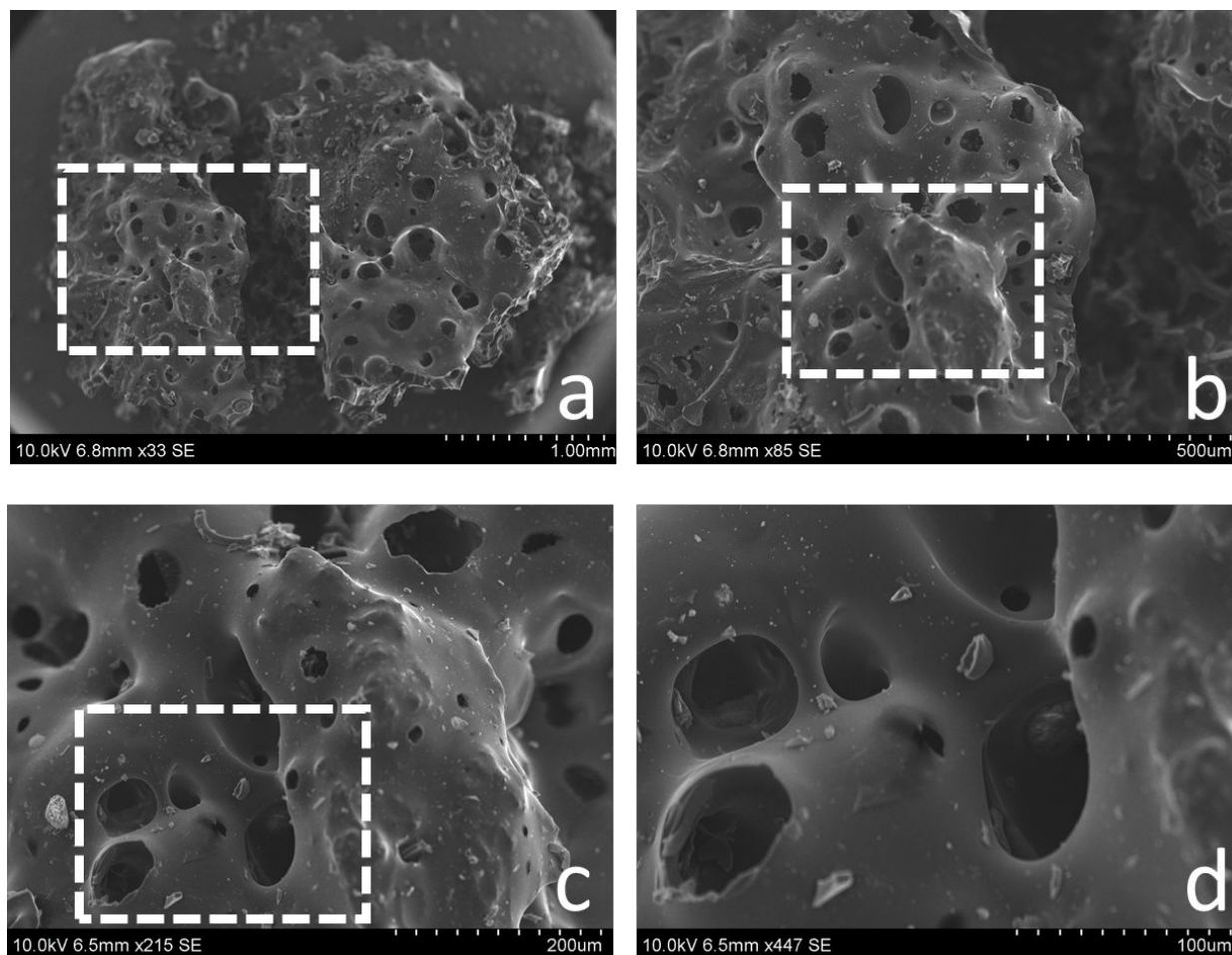


Figure 14. (a) SEM images of charcoal from CVC of spruce grains of particle size <2 mm at a mass loading of 130 g/L, HTT of 400°C , an initial nitrogen pressure of 0.1 MPa and a long immersion time of 190 min, (b), (c) and (d) higher magnification views of selected areas in (a), (b), (c) respectively.

The CVC tests showed TPP evolution at a much later stage than the one described by Newalkar et al.[19] in an “open” reactor operated at a pressure of 0.5 MPa and at a considerably higher temperature (600°C) and heating rate (at least 1000°C/s). As the char residence time increased from 4 to 15 to 28 seconds, the char morphology changed from a solid that resembled the parent pine feedstock to a char piece slightly molten and swollen to a final oblong char piece considerably swollen and with a surface almost completely molten.

3.8 Effect of Mass Loading

The mass loading in the CVC tests is defined as the mass of biomass per unit volume of reactor. Its influence was tested through two distinct approaches; (1) the mass loading was altered by varying the amounts of biomass loaded in the WHTB reactor, and (2) the amount of biomass was kept constant and the reactor volume was changed by adding a tubing extension to the cold section of the reactor system above the sandbath.

Results on yields and proximate analysis from the first approach are depicted in Figure 15a and 15b (Experiment #13-17 in Supporting Information Table S1). The mass loading effect was analyzed for birch CVC tests at an initial N₂ pressure of 0.1 MPa and a HTT of 300°C at two different immersion times of ~30 min and 190 min. Increased mass loading produced minor improvements in the fixed-carbon yields and proximate analysis values in the 30-minute runs that were not observed for the 190-min tests. In the latter case, differences were not statistically significant. In all cases, mass loading had a strong influence on the reactor peak pressures. For example, as the mass loading was raised from 129 to 165 to 238 g/L in the 190-min tests, a higher amount of volatiles was released into the gas phase increasing maximum pressure values from 5.01 to 7.25 to 9.57 MPa, respectively. Char HHVs were similar for all mass loadings in Figures 15a and 15b.

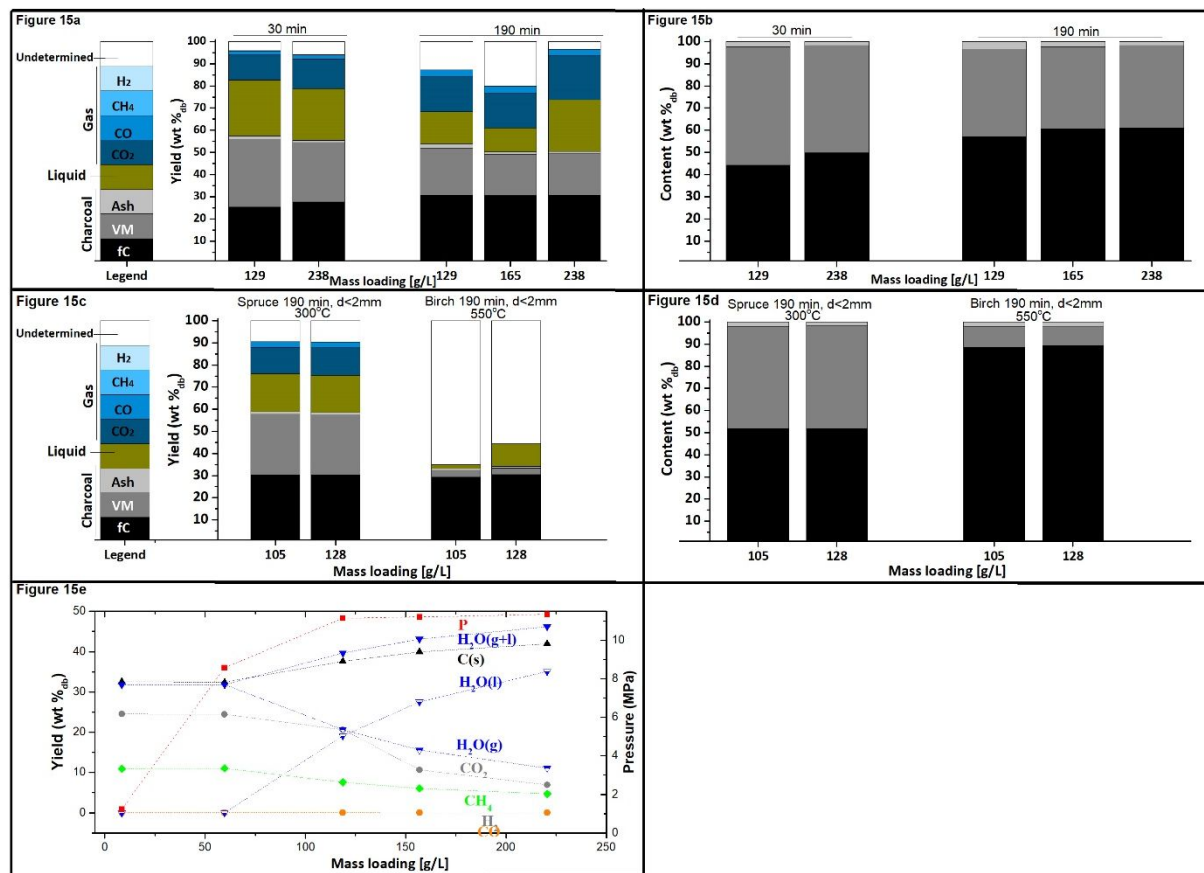


Figure 15. Effect of mass loading by varying the biomass absolute mass on the yields of char, condensate and gas (Figure 15a) and on the proximate analysis of chars (Figure 15b) from birch CVC at an initial N₂ pressure of 0.1 MPa, HTT of 300°C and feedstock particle size <0.2 mm. Effect of mass loading by varying the dead volume on the yields of char, condensate and gas (Figure 15c) and on the proximate analysis of chars (Figure 15d) from CVC at an initial N₂ pressure of 0.1 MPa. The 105g/L mass loading was obtained by keeping the same absolute biomass amount as in the 128g/L test and enlarging the dead volume by 46 mL. Effects of changes in mass loadings of the WHTB reactor on the products of birch pyrolysis at thermochemical equilibrium at 300°C (Figure 15e).

Results for the second approach to changing mass loading are given in Figures 15c and 15d (Experiment #12 and 18 in Supporting Information Table S1 for CVC of birch particles; spruce particle CVC conditions are reported in Legarra et al.[9]). Prior to running the increased volume tests, the reactor dead volume was incremented by almost 80% (from 59 to 105 mL) while maintaining the same feedstock mass. CVC results showed a dramatic decrease in peak

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3 pressures, from 4.7 to 2.7 MPa for tests using spruce at 300°C and from 17.9 to 7.5 MPa in birch
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5 CVC experiments at 550°C. Char HHVs, proximate analysis and product yields were essentially
6
7 the same. These final results gave hope to reactor scale-up possibilities. Adding a dead volume in
8
9 the WHTB enabled the production of chars of similar qualities (i.e. proximate analysis, yields
10
11 and energy density values) while drastically reducing the maximum pressures and the design
12
13 requirements of the reactor vessel, pointing to a reduction of capital costs. It is anticipated that
14
15 non-condensable and lighter gas products will have a tendency to occupy the upper parts of the
16
17 cooler incremental dead volume thereby reducing the reactor pressure. The heavy tarry vapors
18
19 and moisture are more likely to condense in the long vertical tubing at the top of the reactor body
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21 prior to reaching the cooler incremental dead volume. The condensate will reflux back into the
22
23 reaction zone, offering additional opportunities for secondary char formation. This reflux could
24
25 be fostered by cooling and/or elongating the vertical dead-volume tubing,
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31 When these recent results are considered in light of previously reported findings, it suggests the
32
33 existence of a limit to the mass loading effect on product yields and proximate analysis values.
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35 Mok et al.[7] conducted the original studies concerning the mass loading role in CVC. In 1992,
36
37 they reported an increase in reaction rates, exothermic heats and charcoal yields (fixed-carbon
38
39 contents were not measured) as the mass loading of cellulose was raised in a 10-160 g/L range.
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43 A few decades later, Wang et al. also proved that higher loadings of woody biomass in a 80-115
44
45 g/L range pyrolyzed in both open and closed crucibles with pinholes (not strictly CVC) improved
46
47 yields of charcoal[46] with similar fixed-carbon contents [47], hence, higher fixed-carbon yields.
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49 Both the Mok et al. and Wang et al. results were explained by the promotion of secondary
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51 charring reactions as the mass loading, and therefore concentration of volatiles, increased in the
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53 carbonization reactor.
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3 Recent spruce [9] and birch CVC tests were conducted with incremental biomass was loaded to
4 produce mass loadings ranging from ~130-240 g/L or where the reactor dead volume was
5 incremented to give mass loading values in a ~100-130 g/L range. These tests produced minor
6 or insignificant changes in product yields, char proximate analysis and char HHVs. It may be
7 possible that as the loading is increased in a sealed vessel, char and fixed-carbon yields initially
8 improve due to greater volatiles partial pressure and therefore greater volatile-char interactions.
9 Increased biomass loaded in the reactor releases more volatiles which increases the reactor
10 pressure but the extent of secondary interactions appear to barely change, as do solid yields and
11 fixed-carbon contents. Further research is required to test whether or not this is the case, and if
12 so, the point at which increasing the mass loading has no beneficial effect on char properties.
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27 Experimental trends of fixed-carbon yield with mass loading strongly differed from theoretical
28 trends. Experimentally, raising the mass loading in the lower range appeared to manifest a
29 favorable impact on the fixed-carbon yield. In the higher range, a plateau was observed.
30 Theoretically, FactSage predicted an initial plateau on the product yields with increasing mass
31 loading until a limiting value is reached (see Figure 15e). Above it, liquid water begins to form,
32 the fixed-carbon yield escalates while water vapor, CO₂ and CH₄ yields decline. Oak and
33 cellulose theoretical predictions showed similar behaviours.
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43 Carbonization conditions introduced in FactSage and experimental conditions in Mok et al., [7]
44 Wang et al. [46,47] or the WHTB are not equivalent. Consequently, results from experiments
45 under similar mass loadings cannot be directly compared. In the first case, FactSage assumes a
46 constant-volume reactor at a uniform temperature. In the second case, Mok et al. [7] performed
47 CVC experiments in a constant-volume reactor at an almost uniform temperature wherein solid
48 and gaseous volumes are expected to keep changing as carbonization takes place. Next in line,
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3 Wang et al.[46,47] did not perform strict CVC since the carbonization reactors had small
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5 openings that provided release routes for the volatiles. And finally, the CVC reactor presented
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7 herein, the WHTB, consists of two distinct temperature zones, the hot reaction zone and the cool
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9 near-room temperature dead volume. The pyrolyzing solid is kept in the hot reaction zone while
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11 volatiles and non-condensable gaseous products keep circulating between the hot and cold areas.
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13 The different reactor configurations will lead to their own reaction rates, mass and heat transfer
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15 phenomena and consequently, to their own final product distribution. Additionally, equilibrium
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17 calculations do not include the full range of complex reaction products and intermediates formed
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19 during the carbonization experiments, such as the high molecular weight, organic tarry vapors.
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24 Based on the available SEM images of charcoals derived from birch CVC at 0.1 MPa pretest
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26 pressure, 300°C HTT and mass loadings of 130, 165 and 240 g/L (see Supporting Information
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28 Figures S5, S6 and S7), robust conclusions cannot be made regarding the role of mass loading on
29
30 the char morphological evolution. For example, some TPP formation was observed for chars
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32 derived from CVC of small birch particles (<0.2 mm) at a mass loading of 165 g/L whereas
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34 signs of TPP are not clear at the lower mass loading of 130 g/L and the higher mass loading of
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36 240 g/L.
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45 **4. Conclusions**

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48 The results demonstrate that the CVC process and appropriate processing conditions can produce
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50 charcoals with properties tailored for their end use. For example, lower rank charcoals can be
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52 produced at moderate temperature (300°C) and short reaction time (<60 mins) in greater yield
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54 (50-60 wt%) than any other known process; these charcoals are suitable for combustion
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3 applications. At the other end of the spectrum, high rank and high value biocarbons with low
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5 volatiles and high fixed carbon content (>85 wt%) can be produced by using higher temperature
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7 (500-550°C) and longer soaking times at carbonization temperature (~3 hours). This opens up
8
9 the opportunity for the production of metallurgical grade chars in a single step process, which is
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11 of great interest to this industry.
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15 In addition, the morphological characteristics of charcoals can also be tuned. Higher HTT,
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17 pretest pressures, heating rates and possibly smaller particle sizes resulted in a change from a
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19 particulate charcoal that retained the structure of the virgin feedstock to a solidified single piece
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21 of coke-like material that had undergone a TPP transition and formed to the shape of the reactor
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23 vessel interior.
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27 The main findings from the research are listed below:
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31 1. CVC produces negligible free tars and a gaseous product mainly composed of CO₂. CVC
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33 products consequently present minimum disposal issues and environmental impacts (i.e.
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35 due to the lack of tar products).
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37 2. CVC trends regarding the effects of temperature, pressure, heating rate and particle size
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39 contrast with those typically reported in literature for carbonization in “open” reactors,
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41 i.e. reactors with openings or gas flows that remove volatiles from the reaction zone to
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43 some extent.
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- 46 • *Temperature influence:* Raising the temperature in a 300 -550°C range for CVC
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48 improved fixed-carbon contents while preserving the valuable fixed-carbon yield
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50 near-theoretical values.
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 - 52 • *Pressure effect:* CVC did not show an influence of the reactor pretest pressure on
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54 product yields and char proximate analysis. The lack of an effect of the pretest
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3 pressure on tar retention offers the possibility of a simplified reactor system with
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5 reduced costs.
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- 8 • *Heating rate:* Over the range of heating rates tested, no apparent affect was
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10 observed on product yields and proximate analysis of chars from CVC as long as
11
12 the soaking time at the carbonization temperature was maintained for a certain
13
14 period of time.
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 - 17 • *Particle size:* Smaller particles resulted in faster heating rates and quicker char
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19 devolatilization. Since the released volatiles are maintained in close contact with
20
21 the reacting char, secondary char formation is not adversely affected. As a result,
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23 CVC offers opportunities for small biomass particles, previously impractical for
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25 carbonization processes, to produce a good quality charcoal in terms of yield and
26
27 proximate analysis composition.
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- 30
- 31 3. Prolonging immersion times in CVC by lengthening the soaking time at the carbonization
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33 temperature led to higher gas yields and charcoals with improved fixed-carbon contents
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35 and improved (or similar) fixed-carbon yields.
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 - 38 4. The most recent CVC tests indicate that there is a limit to the mass loading effect in
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40 sealed vessels. It is speculated that as the loading is raised, volatiles are released favoring
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42 secondary interactions until a limit is reached. Above it, peak pressure would keep
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44 increasing but char yields and proximate analysis remain unaffected.
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 - 47 5. CVC has produced a variety of char morphologies ranging from particulate to solidified
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49 single pieces of char resembling coke, which suggests the latter chars had undergone a
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51 transient plastic phase (TPP) transition.
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