



Determination of size and porosity of chars during combustion of biomass particles

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ABSTRACT

This research focused on the size and overall porosity (pore volume) of carbonaceous chars, originating from high-heating rates and high-temperature pyrolysis and/or combustion of biomass. Emphasis was given to torrefied biomass chars. First, the porosity of char residues of single biomass particles of known mass was determined, based on an assumed value of skeletal density and by comparing experimentally observed temperature-time histories with numerical predictions of their burnout times. The average char porosities (effective porosities) of several raw and torrefied biomass particles were calculated to be in the range of 92–95%. Thereafter, these deduced porosity values were input again to the model to calculate the size of chars of other biomass particle precursors, whose initial size and mass were not known. Such biomass particles were sieve-classified to different nominal size ranges. This time, besides the porosity, representative time-temperature profiles of biomass particles in the aforementioned size ranges were also input to the model. Biomass particles are highly irregular with large aspect ratios and, in many cases, they melt and spheroidize under high heating rates and elevated temperatures. Knowledge of the initial size of the chars, upon extinction of the volatile flames, is needed for modeling their heterogeneous combustion phase. For this purpose, numerical predictions were in general agreement with measurements of char size obtained from both scanning electron microscopy of captured chars and real-time high-speed, high-magnification cinematographic observations of their combustion. Results showed that the generated chars of the examined biomass types were highly porous with large cavities. The average initial dimension of the chars, upon rapid pyrolysis, was in the range of 50–60% the mid-value of the mesh size of the sieves used to size-classify their highly irregular parent biomass particles.

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Introduction

Pulverized biomass particles are irregularly shaped and are often elongated with high aspect ratios. A great deal of past investigations on the pyrolysis behavior of biomass has been focused on low heating rates and long holding times [1–3]. Under such conditions the biomass particles retain their original shapes. However, the effects of fast pyrolysis of biomass particles under high temperatures on the shape and size of biomass particles are quite different. Upon undergoing devolatilization at high heating rates and high temperatures biomass particles have been observed, in this laboratory and elsewhere, to undergo plastic deformation, and in

many cases spheroidize and form highly porous and ceno-spheric, ceno-elliptic, or ceno-cylindrical particles [1,4–8]. These phenomena are particularly pronounced and more uniformly observed in the case of torrefied biomass particles [5]. The resulting size and physicochemical structure of the chars are important parameters in combustion and gasification processes [9–19], since they affect the capacity of combustors and gasifiers [20,21]. This is because the reaction rates of the chars is influenced both by their physical structure, which includes their size, pore volume (porosity), pore surface area and pore size distribution, and by their chemical structure, which includes the amount and composition of inorganic elements and functional groups [22–25]. Specifically, Phounglamcheik et al. and Guerrero et al. [26,27] reported that the heating

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Nomenclature

T_p	Particle surface temperature [K]
F^*	Shape coefficients for the particle
l^*	Characteristic length of the particle[m]
a_0	Ash content of the raw particle
A_{char}	Surface area of the char [m ²]
a_{char}	Char's ash content
c_2	2nd Planck constant, [m•K]
c_p	Heat capacity [J/(kg•K)]
$C_{\lambda_1 \lambda_2}$	Calibration constant of three-color pyrometer
d_{char}	Diameter of the char particle [m]
dT_{char}/dt	Heating rate [K/s]
H_{conv}	Heat loss by convection [J/s]
m_{ash}	Mass of the ash in the particle, [kg]
$m_{biomass}$	Mass of the parent biomass particle, [kg]
m_{char}	Mass of the char residue, [kg]
n_c^p	Reaction rate for carbon per unit surface area of the char particle, [mol.C/(m ² s)],
Nu	Nusselt number
p	Total pressure for the surrounding gas.[Pa]
$p_{O_2,s}$	Partial pressure of oxygen on the particle surface [Pa]
T_{char}	Char particle surface temperature [K]
T_{gas}	Gas temperature around the particle, 1350 K
T_{wall}	Furnace wall surface temperature, 1400 K
V_{char}	Volume of the char [m ³]
VM	Mass of the volatiles matter in the fuel
Δh	Molar heat of reaction at the carbon surface per mol, [J/mol]
Δt	Time step [ms]
γ	Volume change in the boundary layer
ε	Emissivity of the char surface
κ	Modified Péclet number
λ	Thermal conductivity
λ_1, λ_2	Color wavelength for pyrometer [nm]
$\rho_{skeletal}$	Skeletal (solid or true) density for the particle [kg/m ³]
ρ_{app}	Apparent (envelope) char density [kg/m ³]
σ	Stefan-Boltzmann constant [W/(m ² •K ⁴)]
ϕ	Average porosity, %
Ψ	CO ₂ production for global reaction

rate has a drastic effect on the morphological and chemical structure of chars. High heating rate generates chars with large cavities and a plethora of micro-meso- and macro-pore structures. This is a result of the abrupt release of volatiles that pressurize and rupture the softening and melting structure of the chars. At high temperatures, char plasticization occurs due to the formation of liquid metaplast [8]. Charcoal obtained from high heating rates was reported to be more reactive in gasification [28–33]. Chars of high reactivity are typically preferred in practical reactors [26].

High pyrolysis temperatures also affect both the physical and chemical structures of chars. High temperatures promote the pore volume and area. However, at very high temperatures (well above 800 °C) the surface area may become compromised because of thermal annealing and pore coalescence [34–40].

Prediction of the combustion behavior and rate of the char particles, at the very least, requires knowledge of their physical structure, such size, shape and porosity. However, knowledge of these parameters for biomass chars has been hard to pin down. Accurate characterizations of biomass structures has been challenging and the characterization of porosities has been elusive [41]. For instance, measurement of the apparent (envelope) densities of the

chars by conventional mercury porosimetry has been problematic. This is because, under the involved high compression, the working fluid (typically mercury) may either crush the friable walls of the chars or penetrate them through blowholes at the outer walls. Hence, other methods for calculating porosities have received attention [41]. Herein an alternative method is introduced and applied.

Schiemann and Vorobiev [42,43] developed a numerical model to calculate the combustion rate and the extent of burnout of highly porous char particles. The present investigation used this model to determine the important parameters of porosity (pore volume) and of particle size of the biomass char residues, upon completion of the devolatilization process of biomass particles. The first part of this investigation (Part 1) was to determine representative total porosity values of biomass chars. To validate this method, before applying it to the biomass chars, the porosity of the spherical and monodisperse glassy carbon particles of Levendis and Flagan [44], of known initial size, was calculated and results were compared with their experimentally determined porosities. Inputs to the model were the diameter of the glassy carbon spheres, their pyrometrically-measured temperature-time profiles and their measured skeletal (solid) densities. Upon validation, the method was applied to raw and torrefied biomass chars. To accomplish this task, a number of individual biomass particles of known initial mass, density and elemental composition (based on Ultimate and Proximate analyses) were considered. Those particles were burned in this laboratory by Panahi et al. [45] and their temperature-time profiles were recorded pyrometrically. Based on the pyrometric data and the recorded properties of those particles their total porosity was calculated using the aforesaid kinetic model of Schiemann and Vorobiev [42,43]. This was accomplished by iteratively matching the predicted char burnout times with the burnout times measured pyrometrically and cinematographically. After obtaining values of representative average porosities for the aforesaid biomass chars, the model was applied to calculate the initial char diameters of other biomass particles of unknown initial mass, upon their devolatilization. These biomass particles were size-classified by sieving. Sieving classifies solid particles in rather wide size ranges, for instance (180–212) μm , (212–300) μm , (300–350) μm ; however, the actual size and the mass of individual particles in any given range are unknown. This is because for different types of biomass the particle aspect ratios are very high (particularly for needle-shaped particles), taking values in the range of 1–12 [46]. These shape and aspect ratio variations can introduce large uncertainties to the mass of particles, which can penetrate through the same size of mesh during sieving. As a result, the actual size of the particles, as classified by sieving, is not known and, consequently, the size of their resulting chars is not known either. This can certainly hamper kinetic modeling efforts. Hence, the second part of this investigation (Part 2) deals with determining the initial size of the char particles, upon devolatilization, under high heating rates and high temperatures, to support the modeling of suspension-fired boilers.

Materials and methods

Physico-chemical properties of the biomass chars

A number of different types of biomass char particles were chosen for this study, both raw and torrefied. Torrefaction of biomass samples was performed in nitrogen in a horizontal muffle furnace. The furnace was preheated to 275 °C before inserting gram-quantities of biomass, placed in ceramic boats. The torrefaction treatment lasted for 30 min. Milling of biomass took place after the torrefaction treatment. The range of the mass of the individually-burned particles is given in Table 1, along with their volatile mass

Table 1

Physical properties of biomass particles, both raw (R) and torrefied (T), whose initial weight was measured [47].

Parameter	MI (R)	MI (T)	EU (R)	EU (T)	PI (R)	PI (T)	WI (R)	WI (T)	CS (R)	CS (T)
Mass range of particles (kg) $\times 10^{-8}$	2.6–19.2	5.1–19.1	1.7–16.5	2.0–26.8	2.4–10.3	2.7–22.0	5.0–16.0	1.7–11.1	4.7–13.8	5.7–18
VM wt%	93.8	88.6	94.6	84.9	95.4	75.6	94.2	84.9	77.2	78.5
Ash, wt%	3	3.4	0.8	3.1	1.9	3.7	1.8	3.1	9.4	8.9

MI: Miscanthus; EU: Eucalyptus; PI: Pine; CS: Corn straw; WI: Willow; R: raw T: torrefied.

fractions and the ash mass fractions. Additional data on these particles is provided in Ref. [45].

Biomass particle pyrolysis experiments at high heating rates and temperatures

Pyrolysis experiments of biomass samples (both raw and torrefied) of different nominal dimensions classified by sieving in the ranges of 180–212, 212–300, 300–350, 350–500 μm , were conducted in a drop tube furnace (DTF), manufactured by ATS. The furnace was operated at the temperature of $T_{\text{wall}} = 1400$ K and the particles experienced high heating rates (10^4 K/s). The particle heating rate (prior to the onset of volatile ignition) was determined from the profile of the measured gas temperature along the axis of the drop tube furnace (DTF), T_{gas} , starting at the exit of the water-cooled particle injector, see Ref. [48]. The gas temperature profile was measured with fine, type K thermocouples and it was subjected to appropriate radiation corrections, see Ref [48,49]. This particle heating rate was also confirmed by cinematographic recordings of elapsed times between the particle exit from the injector to the particle ignition point. Experiments were conducted by injecting a constant stream of raw or torrefied biomass particles in the DTF, in nitrogen, and collecting the pyrolyzed particles (chars) on a paper filter at the exit. Optical microscopy photographs of both initial biomass particles and char particles are shown in Fig. 1. In these photographs, biomass particles in their initial state (raw or torrefied) were placed adjacent to pyrolyzed particles and were photographed together. The transformation of the raw biomass particles to torrefied biomass particles, in the muffle furnace in N_2 , is evident by changes of color and appearance. The additional structural transformation of either raw or torrefied particles to chars, upon pyrolysis in the DTF in N_2 , at high temperature and high heating rate pyrolysis, is more remarkable. Upon completion of the pyrolysis process, where the volatile matter mass loss amounted to as high as 95%, extensive shrinking of the biomass particles and in most cases reduction of their high aspect ratios took place, as they transformed to chars. The dimensions of the resulting char residues are much smaller than those of their parent biomass particles. In an ensuing section of this paper the dimensions of such chars will be determined.

Close observation of the photographed particles reveals evidence of plastic deformation and fusion. The fact that under high heating rates biomass char particles undergo plastic deformation (i.e. melting) has already been reported for different types of biomass by Panahi et al. [5], Cetin et al. [30] and Gill et al. [50], among others. In all examined cases of torrefied biomass and in most cases of raw biomass, spherodization of char particles was also evident. The spherodization term is used herein to signify that a biomass particles' aspect ratio decreases drastically at high temperatures, and that the shape becomes well-rounded. Particles of some raw biomass types (notably raw Corn, raw Willow and to a lesser extent raw Pine) resisted spherodization to various degrees. Subsequent examination of the biomass particles was performed by scanning electron microscopy (SEM) and results are shown in Fig. 2. Inspection of these micrographs reveals the particle structure and surface details. The physical transformation of biomass particles during melting results in the formation of bubbly and frail



Fig. 1. Optical microscope photographs of particles of pulverized biomass samples (both raw and torrefied) at both their initial and their pyrolyzed states (left and right sides of each photograph). Furnace wall temperature was 1400 K. A size bar at the right bottom of this figure denotes magnification. The nominal initial size of these particles was in the range of 212–300 μm .

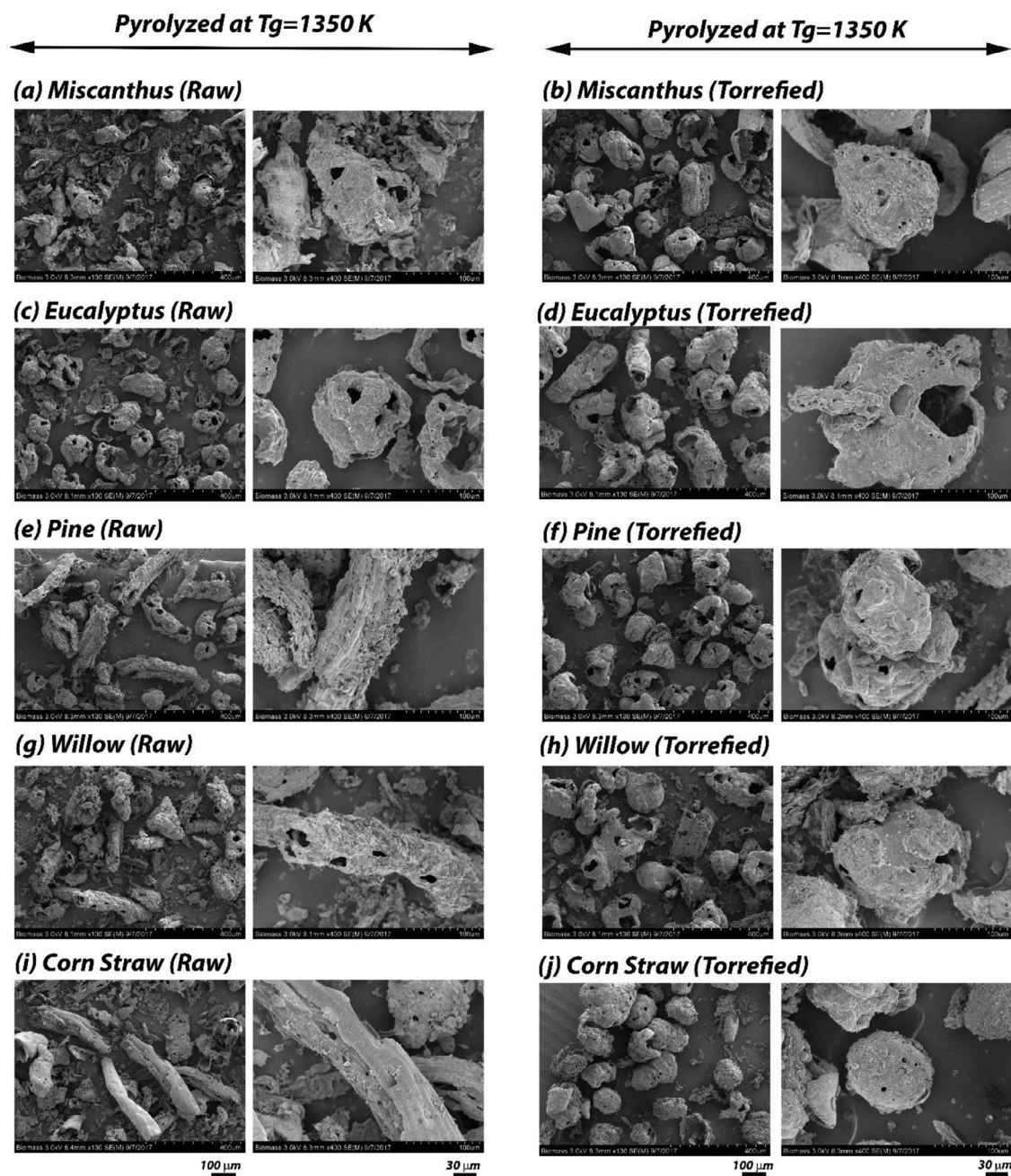


Fig. 2. Scanning Electron Microscope (SEM) photographs of biomass char particles (both raw and torrefied) at low and high magnifications. Pyrolysis of the samples occurred at a high heating rate and at a furnace wall temperature of 1400 K. Microscopy magnifications are noted on each photograph. The nominal initial size of these particles was in the range of 212–300 μm .

residual chars with large internal cavities and blowholes on their surfaces. Rapid devolatilization of bituminous coals also forms bubbly chars, but they are not as frail as the biomass chars [51]. Similar physical transformations and formation of cenospheric chars was observed during high heating rate – high temperature pyrolysis of torrefied Willow and Eucalyptus biomass by McNamee et al. [52].

Combustion experiments of biomass particles in air

Single fuel particles were burned in a drop-tube furnace at high heating rates and high temperatures $T_{\text{wall}}=1400$ K. The temperature profiles of the fuel particles were measured by the optical py-

rometer of Levendis, Estrada and Hottel [53] viewing downwards along the path of the falling particles, as shown in Fig. 3. Shadow cinematography was conducted from slotted windows at the sides of the DTF, using an Edgerton high speed camera, as also shown in Fig. 3.

All biomass particles burned in two phases. In most cases, ignition occurred homogeneously and the evolving volatile matter burned in particle envelope flames. Upon consumption of the volatiles, the flames extinguished and the remaining char residues ignited and burned heterogeneously, as shown in Fig. 4. The formation of chars started before the ignition of the volatiles and was mostly completed inside the envelope flames. Corn straw, Miscanthus, Eucalyptus, Willow and Pine, both raw and torrefied, were

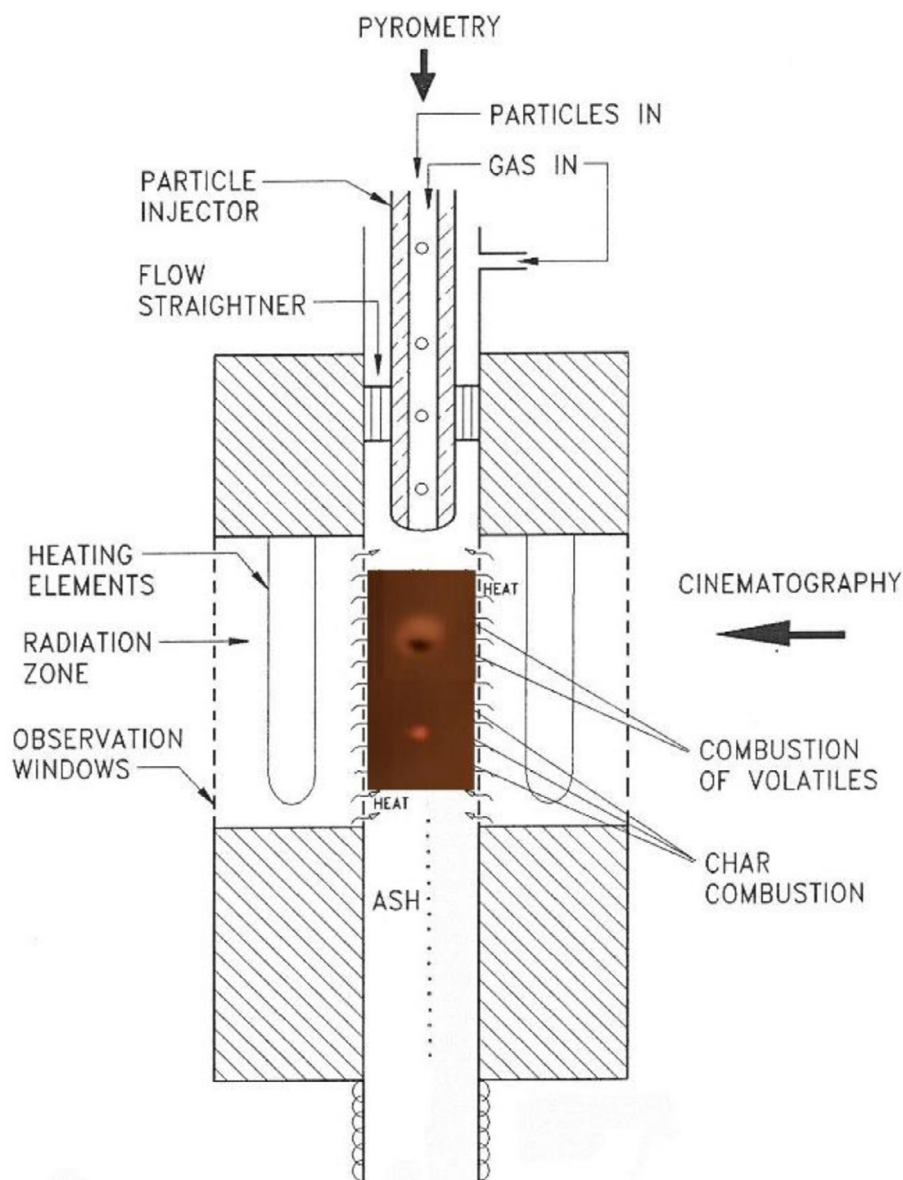


Fig. 3. Schematic of transparent the drop tube furnace used for observations of single biochar particle combustion. The positions of the three-color pyrometer and the high speed camera are marked.

burned. In this set of experiments the nominal size of the parent biomass particles, as determined by sieving, was in the range of 212–300 μm . Time-resolved snapshot photographs of cinematographic sequences for ten biomass particles burning in the DTF, at $T_{\text{wall}}=1400$ K, are shown in Fig. 4. Respective particle burn-times are labeled therein.

The particles ignited close to the injector tip at the top of the DTF, upon entering the radiation zone. It appeared that the particles with the highest aspect ratios ignited more readily than the rest. Levendis et al. [54] investigated preferential ignition of irregularly-shaped coal char particles at localized “hot-spot” sites, where heat generation to heat loss ratios can be favorable. Such phenomena were observed herein sporadically in the case of needle-shaped particles with large aspect ratios, such as raw corn straw, raw willow and raw pine. Particles of those biomass types are more likely to exhibit this behavior than the rest. Upon ignition of the biomass particles in air, the flames surrounding individual particles grew bigger and increasingly luminous. In all

cases, these envelope flames had spherical or ellipsoidal shapes. During combustion of the volatile matter in the envelope flames, energy in the form of convective and radiative fluxes was fed back to the devolatilizing particles. It has been reported that approximately half of the flame’s radiative flux may be received by the particle, with the rest radiated outwards [55]. The resulting heating rates of the forming chars inside the envelope flames increased, perhaps reaching as high as an estimated 10^5 K/s, based on the rise of the measured particle temperature profiles during combustion of the volatile flames. Direct real-time evidence of the phenomenon of plastic deformation of raw and torrefied biomass is obvious at these high heating rates. Again, there is visual evidence that all examined torrefied biomass particles exhibited melting and spherodization. Raw Miscanthus and sugarcane bagasse also exhibited these phenomena, whereas as mentioned before, raw willow, raw pine and, most notably raw corn straw resisted spherodization to various degrees, see Fig. 4.

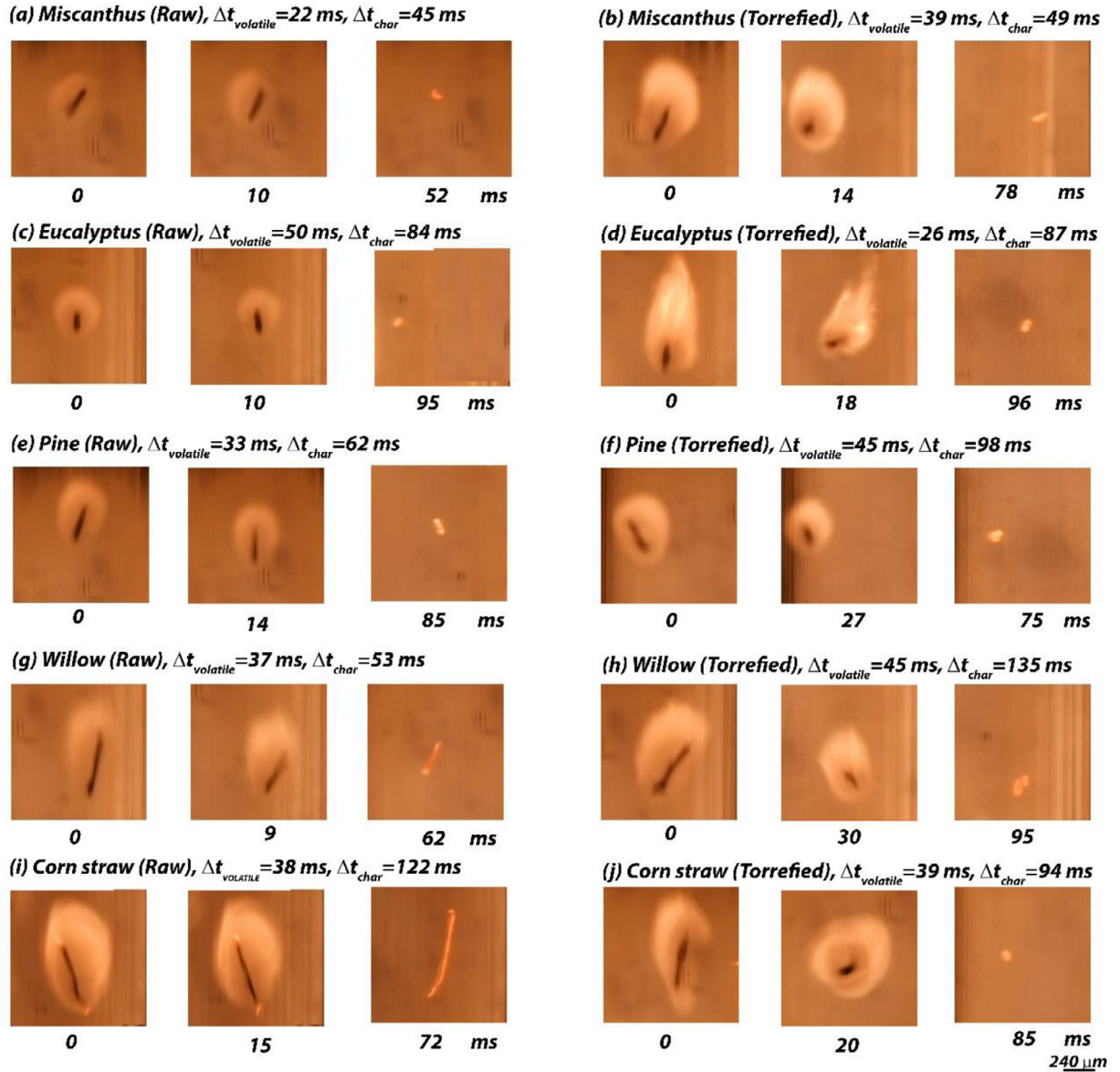


Fig. 4. Images from high-speed high-resolution cinematography of single raw and torrefied biomass particles burning in air in a DTF operated at $T_{\text{wall}} = 1400 \text{ K}$. The displayed numbers in each frame are in milliseconds, where zero does not mark the beginning of ignition, instead, it merely represents the beginning of the depicted sequences. The nominal initial size of these particles was in the range of 212–300 μm .

Two-color pyrometric temperatures of burning particles were deduced based on Wien's approximation to Planck's law [51,53,56]:

$$T_p = \frac{c_2(1/\lambda_2 - 1/\lambda_1)}{\ln \left[\frac{1}{c_{\lambda_1\lambda_2}} \frac{\varepsilon_{\lambda_2} S_{\lambda_1}}{\varepsilon_{\lambda_1} S_{\lambda_2}} \right]} \quad (1)$$

where c_2 is the second Planck constant; $c_{\lambda_1\lambda_2}$ is the calibration constant, which was obtained by using a pre-calibrated US National Institute of Science and Technology (NIST) lamp; and $\frac{\varepsilon_{\lambda_2}}{\varepsilon_{\lambda_1}}$ is the ratio of the char particle emissivities at two different wavelengths. Whereas the entire combustion profile (volatile matter flame stage plus char oxidation stage) of particles was recorded by the pyrometer, this work focused on the latter combustion stage. Herein the chars were assumed to behave as gray bodies, thus their emissivity ratios in the two wavelengths (ranges) λ_1 and λ_2 were assigned the value of unity [56].

Kinetic model

Description of the model

To calculate the overall porosity of biomass char particles the kinetic model of Schiemann and Vorobiev is used [43]. For this purpose, input to this model was the initial mass of the particles, the experimentally measured temperature-time profile and the skeletal density of the particles, along with data from the Proximate and Ultimate analysis. In these calculations the skeletal density was input to the model and it was assumed to stay constant throughout combustion. The assumed value was that of torrefied Beechwood biomass, which was experimentally-determined to be 1750 kg/m^3 , as measured by helium adsorption (by the Particle Testing Authority, Norcross, GA). While not all biomass chars are expected to have the same skeletal density, this value was deemed reasonable for biochars that are produced with fast pyrolysis at high temperatures. Brewer et al. [41] measured the skeletal density

of biochars from a variety of sources, pyrolyzed at a wide temperature range, and found it to be in the range 1340–1960 kg/m³, increasing with pyrolysis temperature, in agreement with values reported by Illingworth et al. [57]. Nonetheless, a perturbation analysis will be presented in an ensuing section to investigate the error that is associated with this skeletal density assumption.

In this model, the energy equation for the time model at each time step is expressed as [45]:

$$\underbrace{\varepsilon \sigma (T_{\text{char}}^4 - T_{\text{wall}}^4)}_{\text{Radiation}} + \underbrace{\frac{2\lambda}{l^*} \left[\frac{\kappa \frac{A_{\text{char}}}{\gamma l^* F^*}}{\exp(\kappa \frac{A_{\text{char}}}{\gamma l^* F^*}) - 1} \right] (T_{\text{char}} - T_{\text{gas}})}_{\text{Convection}} = \underbrace{\dot{n}_c^p \Delta h}_{\text{Reaction}} + \underbrace{\frac{V_{\text{char}}}{A_{\text{char}}} \rho_{\text{app}} c_p \frac{dT_{\text{char}}}{dt}}_{\text{Thermal inertia}} \quad (2)$$

The terms in the left-hand side equation represent energy losses by radiation and conduction, where ε is the emissivity for the char particles and σ is the Stefan-Boltzmann constant; T_{char} , T_{wall} and T_{gas} are char particle surface temperature and gas temperature around the particle, respectively. The terms in the right side of the equation represent the energy generation and the thermal inertia of the char particle; $\dot{n}_c^p$ is the reaction rate for carbon per unit surface area of the char particle, in mol_{carbon}/(m²s), and Δh is the molar heat of reaction at the carbon surface per mol, ρ_{app} is the apparent (envelope) char density; c_p is heat capacity; dT_{char}/dt is the temperature change of the combusting char particle; V_{char} and A_{char} are the volume and surface area of the char, respectively.

To calculate the volume and surface area of the char, the diameter of the char is required, which is not known. The mass of the char (for example biomass) can be written as:

$$m_{\text{char}} = m_{\text{biomass}}(1 - VM) - m_{\text{ash}} \quad (3)$$

m_{biomass} is the mass of the parent biomass particle; m_{char} is the mass of the combustible fraction of the char residue; m_{ash} is the mass of the ash in the particle. VM the mass of the volatile matter in the fuel.

After calculating the mass of the char, m_{char} , the char diameter, d_{char} , can be calculated as:

$$d_{\text{char}} = \sqrt[3]{\frac{6}{\pi} \frac{m_{\text{char}}}{\rho} \frac{1}{1 - \phi}} \quad (4)$$

where ρ is the skeletal density (also called solid density, true density or helium density) for the char particle and ϕ is its average porosity. The relation between skeletal density ρ and apparent density ρ_{app} is:

$$\rho_{\text{app}} = \rho_{\text{skeletal}}(1 - \phi\%). \quad (5)$$

Thereafter, the char's volume and surface area can be calculated using the volume and surface area formulas for a sphere, assuming that the char particles are spherodized.

The heat loss by convection in Eq. (1) is:

$$H_{\text{conv}} = \frac{2\lambda}{l^*} \left[\frac{\kappa \frac{A_{\text{char}}}{\gamma l^* F^*}}{\exp(\kappa \frac{A_{\text{char}}}{\gamma l^* F^*}) - 1} \right] (T_{\text{char}} - T_{\text{gas}}) \quad (6)$$

In Eq. (5), λ is the thermal conductivity of the gas around the particle. κ is a modified Péclet number:

$$\kappa = \dot{n}_c^p \gamma d_p l^* \sum_i v_i c_{pi} / \lambda \quad (7)$$

c_{pi} is the heat capacity of each species, γ describes the volume change in the boundary layer, which is related to the combustion of the char:

$$C_{(s)} + \left(\frac{1 + \psi}{2} \right) O_2 \rightarrow \psi CO_2 + (1 - \psi) CO, \quad (8)$$

$$\gamma = \frac{1 - \psi}{1 + \psi}, \quad (9)$$

where Ψ represents the unit CO₂ production for global reaction (7), which can be expressed as:

$$\psi = 0.02 \exp(-3070/T_{\text{char}}) P_{O_{2,s}}^{0.21} \quad (10)$$

where $p_{O_{2,s}}$ is the partial pressure of oxygen on the particle surface, which can be calculated by:

$$p_{O_{2,s}} = \frac{p}{\gamma} + \left(p_{O_{2,\infty}} - \frac{p}{\gamma} \right) \exp \left(\frac{\psi - 1}{2} \frac{\dot{n}_c^p A_{\text{char}} RT_{\text{char}}}{D F^* p} \right) \quad (11)$$

p is the total pressure for the surrounding gas. F^* and l^* are the shape coefficients for the particle and the characteristic length of the particle. For spherical particles $F^* = 2\pi d_{\text{char}}$ [42], whereas for cylindrical particles $F^* = [8 + 6.95(L/d_{\text{char}})^{0.76}](d/2_{\text{char}})$ [42]. The characteristic length of the particle is determined from the convective heat transport for spherical particle [43]:

$$\frac{Nu \cdot \lambda}{l^*} \Delta T = \frac{F^* \cdot \lambda}{A_p} \Delta T \quad (12)$$

Nu represents the Nusselt number, and it can set as 2 for neglecting relative velocity between particle and gas-phase conditions is neglected [42]. With this assumption, $l^* = d_{\text{char}}$ is used in this model.

For any time-step t_i , the consumed char mass in the time interval Δt can be calculated as:

$$m_{\text{char}}(t_{i+1}) = m_{\text{char}}(t_i) - \dot{n}_c^p A_{\text{char}} M_c \Delta t, \quad (13)$$

With M_c being the molar mass of carbon. The reaction rate of the carbon $\dot{n}_c^p$ at the particle surface can also be expressed as:

$$\dot{n}_c^p = A \cdot \exp \left(-\frac{E}{RT_{\text{char}}} \right) P_{O_{2,s}}^n \quad (14)$$

The apparent reaction rate order n is set as 1 for this model [58].

The temperature profiles from the experiments (typically) show a clear decrease in particle temperature at their end. This endpoint assumedly determines char burnout. As the average porosity and char diameter are not known, a fitting scheme delivers best-fit values for both parameters. The calculation proceeds until char burnout reaches the value of 0.99.

Input data to the model

This sub section lists the assumptions made to the input file of the kinetic model:

- In all cases (Part 1 and Part 2) the value of skeletal density of the biomass chars was set at 1750 kg/m³ and it was assumed to stay constant throughout char combustion. This value was based on the measured skeletal density of torrefied Beechwood biochar.

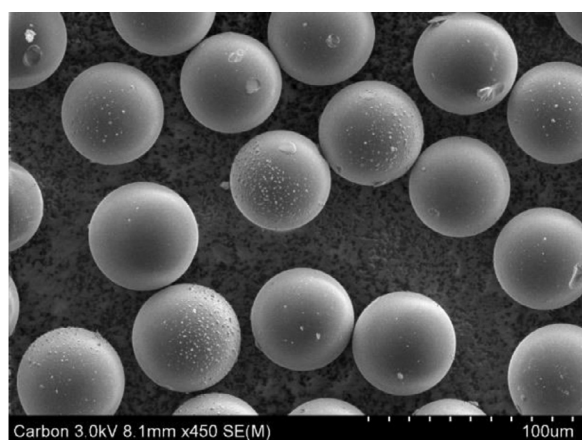


Fig. 5. SEM photograph of spherical and monodisperse glassy carbon particles 43 μm in diameter [44].

- In Part 1 of the investigation the masses of the pre-weighted individual biomass particles, used as feedstock, were input to the model. In Part 2 of the investigation, since the mass of random sieved-classified random biomass particles was not known, a typical char porosity (based on the porosity values determined in Part 1) was input to the model.
- The volatile matter mass fractions of the biomass feedstocks were input to the model.
- The portions of experimental pyrometric temperature-time profiles corresponding to burning char particles were input to the model.
- The thermal inertia term of the burning char (the last term in Eq. (2)) was taken from the pyrometric temperature-time profiles corresponding to the burning char particles.
- The emissivity of the burning chars was set at $\varepsilon=0.8$ and was assumed constant throughout combustion.
- The apparent reaction rate order was set at unity ($n = 1$).
- The Nusselt number was assumed to be: $Nu = 2$.
- The oxygen partial pressure was set at 0.21 atm.
- The furnace gas temperature was set at: $T_{\text{gas}}=1350$ K.
- The furnace wall temperature was set at: $T_w=1400$ K.
- The outputs of the model (char porosity in Part 1 and initial char diameter in Part 2) were determined by the simulation when the final char burnout reached to 99% of the experimental burn-time detected by the pyrometer.
- If the char conversion (burnout) did not reach 99%, the trial-and-error method was used to find the best effective average porosity in Part 1 (or the best initial char diameter in Part 2) for each char particle which could make the burnout closest to 99%.
- Flowcharts of the trial-and-error method for both Part 1 and 2 are shown in the Fig A1 and Fig A2 of the Appendix. The step for the porosity calculation was taken as 0.002 and for the diameter was taken as 2 μm . The accuracy to reach 99% burnout was set to 0.001.

Results and discussion

Part 1: calculation of typical porosities of biomass chars

As mentioned above, before calculating the porosity of the biomass chars, the accuracy of the method was assessed by calculating the porosity of the aforesaid well-characterized monodisperse glassy carbon spheres of known size and mass [44], shown in Fig. 5. The porosity of those carbon spheres was calculated from measurements of their apparent (envelope) and skeletal (solid) densities. A number of these spherical and monodisperse carbon

particles were burned in neat oxygen and their mean pyrometric temperature-time profile and spread of data are shown in Fig. 6.

The initial porosity of these particles was measured to be 11%. However, during their combustion in the DTF in oxygen (which took place in Regime II [59]) their porosity increased during burnout, and at 25% conversion the porosity of collected partially-burned chars was measured to be 28% [56,59]. Based on their size and their measured skeletal density of 1800 kg/m^3 their mass was calculated. Then, in conjunction to their temperature-time profiles [60], the numerically predicted effective porosity of these solid glassy carbon spheres was 23%, which is within the aforesaid range of experimental values; hence, the agreement was deemed satisfactory.

An additional test of the method was performed by addressing the porosity of bituminous coal chars. Bituminous coal particles are known to soften, partially melt and mildly swell, upon experiencing high heating rate – high temperature devolatilization. For bituminous Pittsburgh#8 HVA (PSOC-1451) particles in the size cut of 75–90 μm , burning in air in the DTF furnace, a representative experimental pyrometric temperature-time profile and the predicted burnout is shown in Fig. 7. The measured skeletal density of the chars was 1800 kg/m^3 [61], with 33.6% VM and 13.3% ash [62]. Since the nominal diameter for the coal particles took values in the rather wide range of 75–90 μm , the average predicted porosity varied according to the coal particle size that was input to the model. The resulting porosity values, for given input values of coal char diameters, are shown in Table 2.

The results show that the porosity is sensitive to the assumed initial particle size in a given size cut. Regardless, the entire range of calculated values (57–61%) are in line with published experimental values for bituminous coal chars. For instance, Loewenberg and Levendis [60] reported a porosity of 60% for HVB Bituminous coal char particles (PSOC-176), generated in nitrogen at DTF temperatures and heating rates comparable to those implemented in this study. Gale et al. [63] reported a porosity of 55% for HVA Pittsburgh No. 8 bituminous coal chars (PSOC 1451) for partially burned coal in air, using in a flat flame methane burner (FFB) and nitrogen-quenching to prevent further reactions of chars collected at several different residence times. Both of the above experimentally-determined bituminous coal char porosities are in line with the model's calculations (57–61%); hence, the agreement was again deemed satisfactory.

Next, the effective porosities of a number of individually-weighted biomass chars, burned by Panahi et al. [45], were calculated based on an assumed value for the initial skeletal (solid) density of 1750 kg/m^3 for biomass chars. Example temperature-time profiles for char particles, obtained by optical pyrometry, and corresponding numerically-predicted burnouts, obtained by the model, are shown in Fig. 8. It should be noted that the experimental temperatures in Fig. 8 correspond to the biomass char combustion phase of each particle. The preceding volatile matter combustion phase portions of the profiles have been omitted. Entire profiles for these individual particles can be found in Ref. [45]. Average effective char porosities were calculated based on these profiles by matching the predicted and the measured values of the char burnout times (within 1%). In the case of raw Eucalyptus, raw corn straw and raw pine biomass particles, a significant number of their chars did not appear to spherodize. Most of those particles that did not spherodize, were cylindrical, hence in the calculation of their porosity the shape coefficient of a cylinder was used in Eq. (11). The deduced average porosities (of at least 10 particles in each case) for different types of biomass are listed in Table 3 and shown in Fig. 9. They range from 92% to 95%. Then, corresponding apparent (envelope) densities for these particles are calculated to be in the range of 87.5–122 kg/m^3 , which is within the range of 80–320 kg/m^3 given in Ref. [64]. Such average apparent (particle

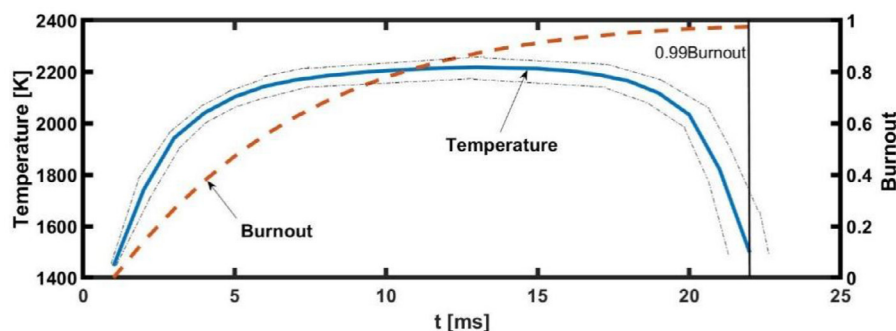


Fig. 6. Typical pyrometric temperature-time profile of a solid glassy carbon spheres 43 μm in diameter and known initial mass, burning in 100% oxygen. The dotted lines represent the temperature spread of a number of particles. The superimposed dashed line represents the numerical prediction of the carbon particle's predicted burnout history. The vertical line denotes 99% burnout.

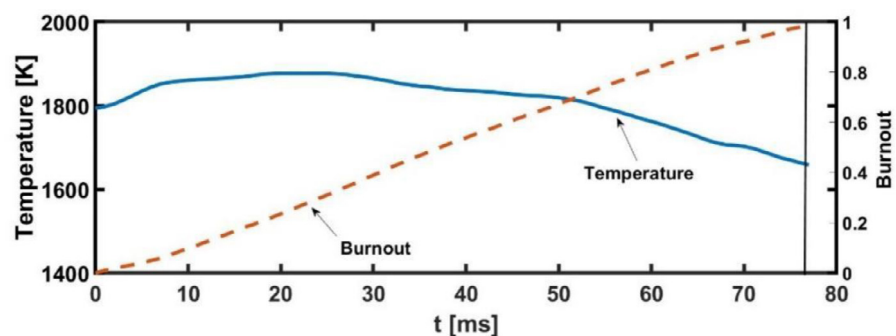


Fig. 7. A pyrometric temperature-time profile of the char combustion portion of single bituminous coal particle (HVA Pittsburgh PSOC-1451) with nominal diameter in the range of 75–90 μm , burning in air. Superimposed is the numerical prediction of its burnout history. The vertical line denotes 99% burnout.

Table 2

Average porosities of bituminous coal char particles.

Assumed initial coal particle diameter in the 75–90 (μm) range	75	80	85	90
Average char porosity	57%	59%	60%	61%

Table 3

Density and Porosity values for biochars, based on an assumed constant skeletal value of $\rho_{\text{skeletal}} = 1750 \text{ kg/m}^3$.

	Mi (R)	Mi (T)	Eu (R)	Eu (T)	Pi (R)	Pi (T)	Wi (R)	Wi (T)	CS (R)	CS (T)
Measured initial apparent (envelope) density (kg/m^3)	120	170	110	280	160	250	110	280	120	170
Calculated initial porosity	93%	90%	94%	84%	91%	86%	94%	84%	93%	90%
Deduced average apparent (envelope) density (kg/m^3)	105	122	122	122	122	105	105	122	140	87.5
Deduced average porosity	94%	93%	93%	93%	93%	94%	94%	93%	92%	95%

envelope) densities are lower than initial bulk densities of the same chars (110–280 kg/m^3), measured earlier in the laboratory with a different method, also listed in Table 3. In that method, small glass vials were packed with char particles and were tapped by 100 taps and rotated [65]. The volume and weight of the packed bed in any given vial were then measured, and the bulk density of the bed of biochar was calculated. These measurements were repeated five times and average density values are listed in Table 3. These bulk densities were assumed to be equal to the apparent densities, also called envelope densities, of these particles. The aforesaid recorded values of 110–280 kg/m^3 are in line with values reported in the literature [66]. Initial apparent densities can be expected to be higher than the average apparent densities throughout char combustion, as porosity increases during combustion. Two mild exceptions are noted, those of CS (R) and Eu (R). These discrepancies, may be explained by (a) the actual skeletal density of these two biochars is a bit different than the assumed skeletal density for all chars (1750 kg/m^3), and/or (b) the diameters of the char particles decrease faster than the carbon consumption (size shrinkage).

From the results listed in Table 3 and Fig. 9, it can be seen that biomass char particles possess elevated levels of average porosity (over both their burn-time histories and over a number of differ-

ent particles) during the combustion process. Porosity values vary from 92% to 95%. For some of the biomass types listed in Fig. 9, chars from torrefied biomass and raw biomass have similar porosities. It is noted that in the aforementioned cases of char particles which appeared to be somewhat cylindrical (raw Eucalyptus, raw corn straw and raw pine) their aspect ratios (length/width) turned out to be important in the prediction of porosity. For char particles with aspect ratios of up to 5, the cylindrical particle porosity was predicted to be $\sim 1\%$ lower than their porosity calculated with the spherical char particle assumption. Correspondingly, for char particles with greater aspect ratios (up to 10) the cylindrical particle porosity was predicted to be $\sim 2\%$ lower than their porosity calculated with spherical assumption. Consequently, in all cases the porosity corrections due to the shape coefficient departure from the spherical shape were small.

Lastly, the initial choice for the initial skeletal (solid) density of 1750 kg/m^3 for all biomass particles was examined. This value was perturbed in the range of 1550 kg/m^3 to 1950 kg/m^3 , given values for intermediate to high temperature pyrolysis values presented in Fig. 2 of Ref. [41]. Calculations showed that the effect of variation of skeletal density in the range causes an error of only 0.3%, which is smaller than the error bar depicted in Fig. 9.

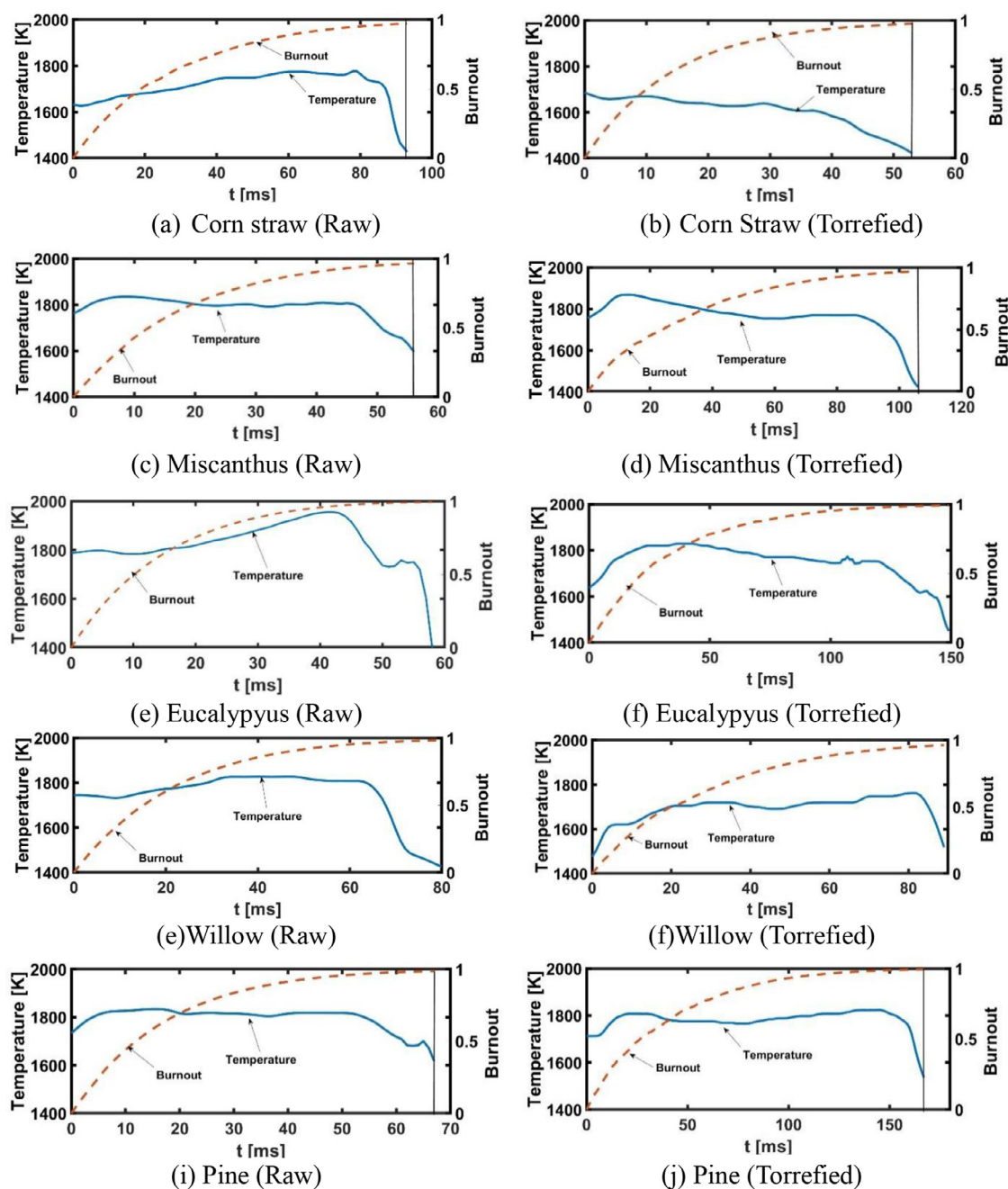


Fig. 8. Pyrometric temperature-time profiles of the char combustion portion of single biomass particles burning in air, of known initial mass, are superimposed with numerical predictions of their burnout. The vertical lines denote 99% burnout.

Part 2: calculation of the biomass char particle size, upon devolatilization, with their skeletal density being an input to the model

In char combustion models, which are typically constructed to predict the reaction rates of chars, knowledge of the initial size of the chars is required. However, in the case of sieve-classified biomass particles in size cuts, their initial dimensions are not known with any kind of precision, let alone the dimensions of their chars upon devolatilization, as illustrated in Fig. 6 in Ref. [67]. Hence, in this second part of this investigation (Part 2) the goal is to predict the initial size of such chars based on the size-classification of their biomass precursor particles. The porosities of these particles are assumed to be those determined in the preceding section and shown in Fig. 9. Results of this calculation

were compared with observations from optical microscopy, scanning electron microscopy and high-resolution cinematography to complete this part of the investigation.

Again, to test the capability of the model to predict the initial char size, solid carbon particles of known diameter, porosity and temperature-time behavior were first simulated. This time, besides the aforementioned 43 μm glassy carbon spheres, two additional monodisperse particle sizes [44] were considered: those of 10 and 15 μm . The average effective porosity of all these glassy carbon particles was calculated in Part 1 of the investigation to be 23%. Typical temperature and burnout profiles of glassy carbon particles of these three different sizes are shown superimposed in Fig. 10. Combining these profiles with the aforementioned porosity value, the model successfully predicted the actual diameters for all these three different size particles, i.e., 10, 15 and 43 μm . Based on this

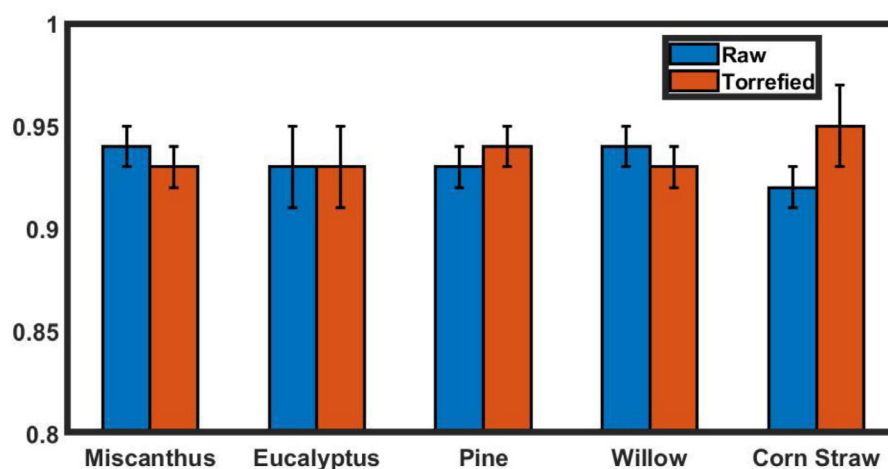


Fig. 9. Calculated average porosity of raw and torrefied biomass char particles of known mass from the study of Panahi et al. [45]. In this plot all particles were assumed to spheroidize.

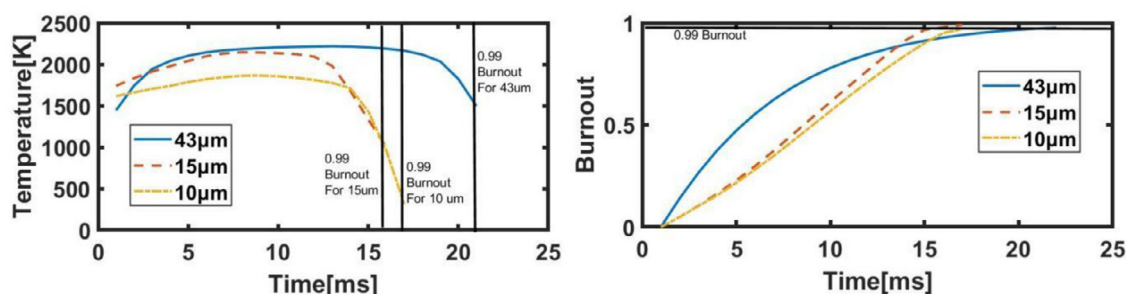


Fig. 10. On the left pyrometric temperature-time profiles are shown for solid carbon spheres of 10, 15 and 43 μm in diameter and known initial masses, burning in 100% oxygen. On the right, numerical predictions are shown of the burnout of these particles with time. The vertical lines denote 99% burnout of the chars. The vertical line denotes 99% burnout.

satisfactory result, the model was used with confidence to address the case of biomass chars.

In the following, pulverized torrefied biomass particles classified by sieves in various size cuts, available in this laboratory (Miscanthus, corn straw, Beechwood and sugarcane bagasse), were burned. The model was used to predict the initial size of chars, upon devolatilization of their parent biomass particles. Since all of the torrefied biomass chars of this study spheroidized, but not all of the raw biomass did, this approach was solely applied to the torrefied biomass chars. For torrefied Miscanthus and torrefied corn straw, the porosities of 93% and 95%, shown in Fig. 9, were input to the model. For torrefied Beechwood and torrefied sugarcane bagasse the effective porosity was not calculated in the previous part (Part 1), because individual particles from these feedstocks of known mass were not burned in the laboratory. Hence, an effective average porosity of 94% porosity was used for these types of biomass, and their skeletal density was set to 1750 kg/m^3 [47]. The apparent (envelope) density was actually measured for torrefied Beechwood chars [47] to be 159.7 kg/m^3 and their initial porosity was calculated to be 91%. This is a little lower than the assumed value of 94% for effective average porosity. The masses of the volatile matter of these two biomass types were taken from their Proximate analysis to be 70% for Beechwood and 74% for bagasse. The ash content of the Beechwood was taken as 0.5% by weight and that of bagasse was taken as 2.71% [68].

A trial-and-error method, which identifies the char mass that allows the burnout to reach 99%, was used to first calculate the initial mass of the biomass char particles, based on their porosities, and then to calculate their initial size assuming spherical shapes. For example, the average porosity for torrefied Miscanthus char particle was calculated, and shown in Fig. 9, to be it 93%. For

torrefied Miscanthus particles of unknown mass, the diameter of the chars was calculated based on their temperature profiles, an example of which is shown in Fig. 11. The calculated char diameters are listed in Table 4. For these four types of feedstock particles, the 180–212 μm , 212–300 μm and 300–355 μm size cuts, based on sieve classification, were chosen. Temperature-time profiles of at least ten particles were used for each case. As an example, the pyrometric temperature-time history for a Beechwood char particle is shown in Fig. 12.

Calculated char particle sizes are shown in Table 4 and are graphically displayed in Fig. 13. The results show that the average diameters of the chars for four types of torrefied biomass are smaller than the mean size of the sieve size cut used to classify their parent biomass particles. For the same type of biomass, increasing the sieve size cut certainly increases the average char diameter. All cases shown in Table 4 exhibit considerable uncertainty in char size, which is expected as their biomass particle precursors have large variations in size, shape and mass, as revealed in the photographs displayed in Fig. 1. This is supported by the uncertainty in the aspect ratio of such torrefied biomass particles, as shown in Fig. 5 of Ref. [46]. However, it is remarkable that the calculated average char sizes, even with the estimated uncertainties, are all smaller than the lower limit of the nominal mesh size of their parent biomass particles. For instance, torrefied biomass particles of Miscanthus, Beechwood, bagasse and corn straw classified in the size cut of 212–300 μm generated chars with predicted average diameters, of approximately 128, 129, 126 and 144 μm , respectively. Again, perturbation of the assumed initial skeletal (solid) density of 1750 kg/m^3 for all biomass particles in the range of 1550 kg/m^3 to 1950 kg/m^3 resulted in an error of 1.5% in size. Even including this error in the determination, the average initial char

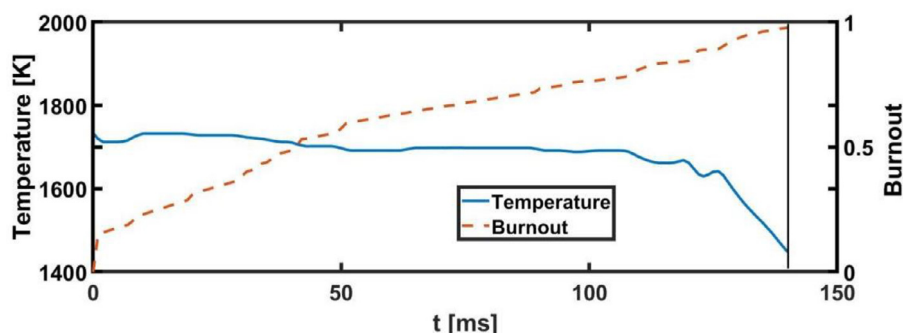


Fig. 11. A pyrometric temperature-time profile of a biomass char particle (torrefied Miscanthus) burning in air. The parent biomass particle of this char was obtained in the sieve size of 300–355 μm . Superimposed is a numerical prediction of the burnout of this particle. The vertical line denotes 99% burnout.

Table 4
Average char diameters for sieve-classified torrefied biomass particles.

Sieve size cut (μm)	Miscanthus (T) (μm)	Beechwood (T) (μm)	Bagasse (T) (μm)	Corn Straw (T) (μm)
180–212	91 $\pm$ 24	81 $\pm$ 12	75 $\pm$ 23	123 $\pm$ 32
212–300	128 $\pm$ 39	129 $\pm$ 33	126 $\pm$ 31	144 $\pm$ 46
300–355	167 $\pm$ 53	151 $\pm$ 34	176 $\pm$ 42	191 $\pm$ 66

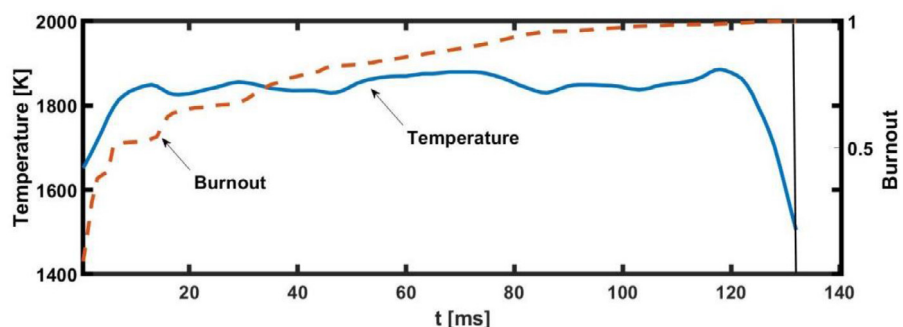


Fig. 12. A pyrometric temperature-time profile is shown of a biomass char (torrefied Beechwood) burning in air. The parent biomass particle of this char was obtained in the sieve size=180–212 μm , burning in air. Superimposed is the numerical prediction of the burnout of this particle. The vertical line denotes 99% burnout.

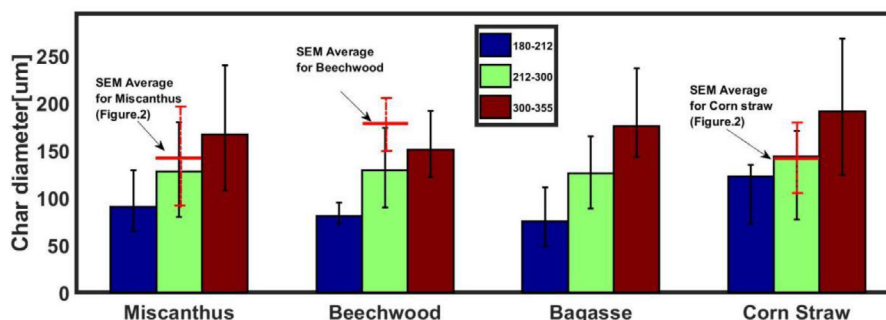


Fig. 13. Average diameters of chars from torrefied biomass particles of three different size classifications by sieving. Superimposed are lines denoting average size of torrefied chars, which spheroidize, based on SEM observations for 212–300 μm parent particles.

sizes are approximately 50–60% of the mean size of the size cut. This observation is in line with the results reported in Refs. [43,69]. Superimposed in Fig. 13 are approximate diameters of chars measured from the SEM micrographs of Fig. 2; these chars were generated from torrefied biomass particles classified in the size cut of 212–300 μm . Results from SEM measurements are in line with the model calculations. Of course, the reader should keep in mind that the torrefied char particles are spheroidal, i.e., not completely spherical. As an example, the average aspect ratios of the torrefied Miscanthus and corn straw chars from SEM observations are calculated to be approx. 1.33 and 1.22. Finally, char particle diameters were also measured from high resolution photographs taken from cinematographic stills during combustion, such as those shown in Fig. 4. From such observations of a limited number of particles rep-

resentative char sizes from torrefied biomass, from the size cut of 212–300, have as follows: corn straw: 110 μm , Miscanthus: 100 μm , Eucalyptus: 100 μm , Willow: 150 μm , Pine: 120 μm , Bagasse: 100 μm , Beechwood: 100 μm . These values confirm that char particle sizes of torrefied biomass are indeed significantly smaller than the lower end of the nominal size cut value of the parent particles, i.e., in this case 212 μm .

Conclusions

This work addressed the porosity and particle size of chars generated from burning various types of pulverized biomass particles. Chars were formed under high heating rates and high tempera-

ture conditions in a drop-tube furnace. Experimental observations made on collected biomass chars generated both in pyrolysis experiments under similar conditions, and on burning particles (in real time) were used to assess the predictions of a numerical combustion model.

The following conclusions were drawn:

- During particle devolatilization and volatile matter combustion biomass experienced softening, melting and formation of cenospheres/ellipses/cylinders. Spherodization was prevalent in all types of torrefied biomass tested, as well as in some types of raw biomass. The presented approach allowed for a certain quantification of this effect.
- Biomass chars were found to be very porous and frail with large cavities and blowholes. Average calculated porosities of raw biomass chars were in the vicinity of ~93%, and those of torrefied biomass chars were in the vicinity of ~94%.
- The generated spherodized char sizes were typically 50–60% of the mid-value of the sieve-based size-cut of their parent biomass particles.

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.

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Appendix

Fig A1
Fig A2

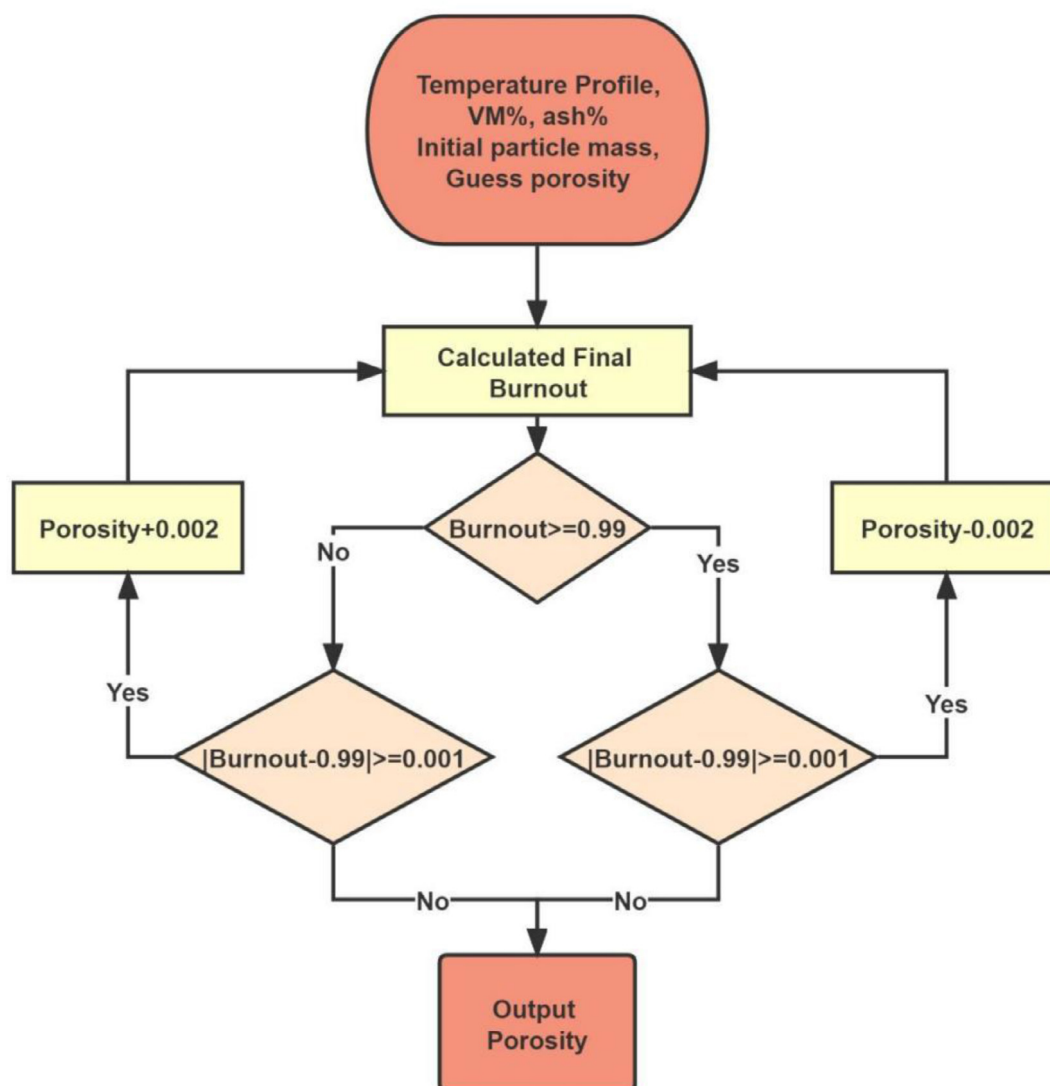


Fig A1. Part 1 with using a trial-and-error method to calculate the effective porosity.

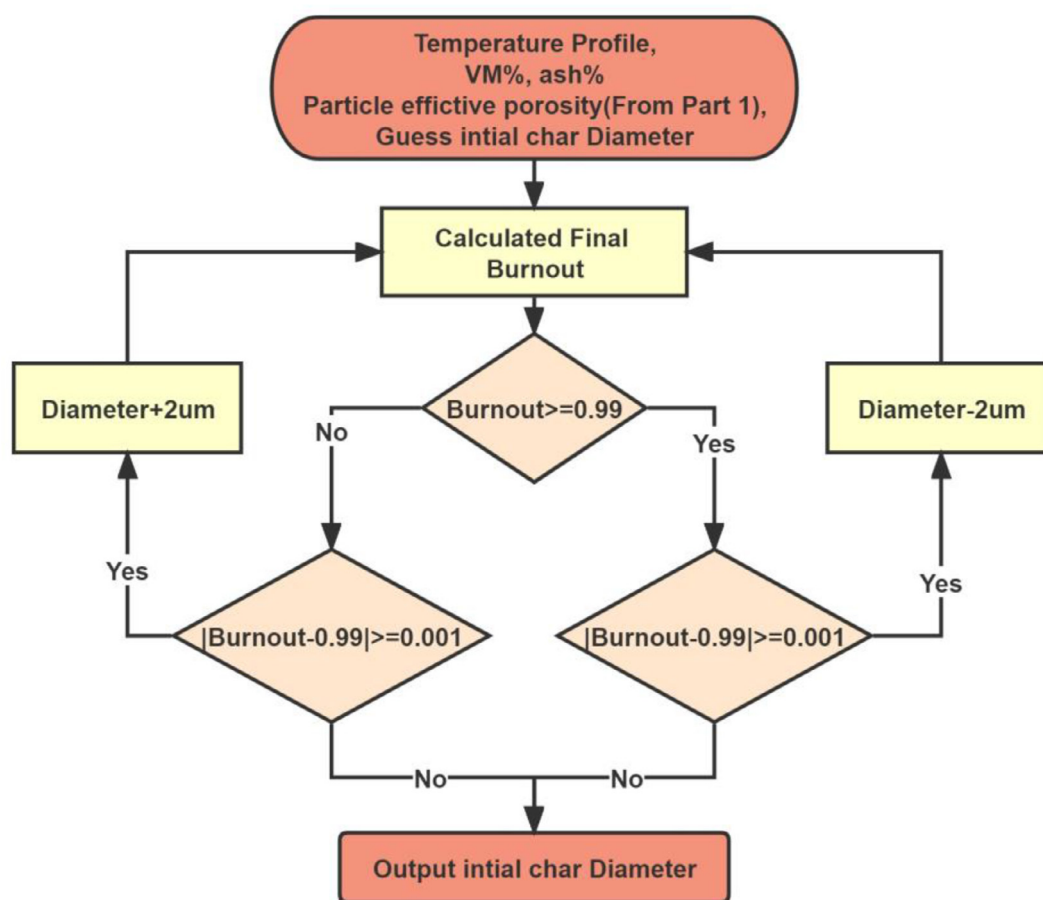


Fig A2. Part 2 with using a trial-and-error method to calculate the Char initial diameter.

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