

Part 2 - Tailoring of pyrolytic char properties with a single particle CFD model with focus on the impact of shrinking, vapor cracking and char permeability

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ABSTRACT

The prediction of structural properties of bio-based carbonaceous materials of pyrolytic origin (chars) with only base feedstock properties and process conditions still poses a challenge that hinders char tailoring for novel applications. CFD modeling of single biomass particle conversion can help solve this issue since it allows for the quantification of relations between parameters that are difficult to measure. A model for char tailoring must include a validated representation of the structural changes coupled to all other relevant phenomena occurring during conversion. Part 2 of this study focuses on finding the description of the mentioned aspects to achieve the highest precision of prediction of the structural changes in char by a CFD model. The investigation in Part 2 is composed of three cases focused on accurate description and prediction of (1) bulk density and porosity, (2) secondary vapor reactions on yields and soot formation, and (3) the permeability, as well as the outflux and conversion of evolved vapors. The experimental results from Part 1 and the literature data were used to find appropriate descriptions of phenomena and assess the accuracy of the model. The model results indicate that for both particle lengths (10 mm and 16 mm), a high accuracy of prediction of base structural parameters was achieved. The average prediction error for temperatures between 400 °C and 840 °C of bulk density was $31 \pm 15 \text{ kg/m}^3$, and porosity was $1.8 \pm 1.1 \text{ vol. \%}$. The results also show low error in the prediction of bulk product yields (dry basis) over the mentioned temperature range, which were: for char $2.8 \pm 1.1 \text{ wt. \%}$, for the condensable fraction $6.5 \pm 3.3 \text{ wt. \%}$ and for the pyrolysis gas $4.1 \pm 1.9 \text{ wt. \%}$. The distribution of secondary char formation was found to be non-uniform below 500 °C. The changes in permeability had a minor influence on the vapor outflux but a non-negligible effect on the soot formation, especially at 840 °C. The results indicate a need for further improvement of the primary degradation model to increase the accuracy of the effect of soot formation on the char structure.

1. Introduction

With the increase of the global society's expectations on reducing greenhouse gas emissions, the global market searches for solutions that may reduce the overall negative impacts in comparison to the currently used solutions. Bio-based substitutes are one of the options for the aforementioned issue. Thermochemical conversion technologies, like biomass pyrolysis and gasification, have the ability to provide such bio-based products. Also, they are scalable to match the market demand. With those technologies, low-engineered, bio-based products for well-known use (e.g., charcoal for energetic applications) are already being provided on the market. However, the market trends also indicate a demand for more developed products with designed-for-purpose characteristics, i.e., those related to the porous structure of materials like bio-based carbons for soil amendment or supercapacitor production.¹⁻³ The supply of such bio-based products still has not reached its final potential, and their introduction on the market on an industrial scale is highly anticipated to replace fossil-based products. Aside from economy-of-scale aspects, the main issue hindering novel bio-based materials from reaching their potential is the low repeatability of material characteristics related to the requirements of their final application. The problem can be distilled into a statement that it is still impossible to make precise quantitative predictions of the final properties of the product (e.g., char water retention or capacitance) based only on known process parameters and basic feedstock properties.

Investigations of changes in structural properties of the resultant material, based on experiments of reactor scale processes, have the most representative outcome in terms of real-scale production systems.⁴⁻⁸ However, in studies on such a scale, the effect of the reactor needs to be considered, which is complex and challenging to assess.^{9, 10} Additionally, extended trials on a reactor scale represent noticeable costs, and their results may be specific to a studied case, instead of leading to

generalizable conclusions. The single particle scale is a smaller scale of investigation that considers the structural changes of a material in an individual particle throughout its conversion. In such studies, only one particle of feedstock is investigated, so the conversion conditions and particle boundary conditions can be set more precisely (i.e. thereby reducing or omitting the effect of the reactor). Additionally, interactions between particles can be neglected. With the reduced impact of the reactor on the conversion process, results from single particle studies may lead to more generalizable conclusions.^{11, 12} Scales smaller than a single particle require pulverization of the material, which leads to loss of the initial structure of the material. Therefore, investigations on such a scale may be irrelevant for many applications since these studies are inapplicable for studying structural changes in the material. Nonetheless, the importance of studies conducted on the powder scale is significant since they bring development in, e.g., chemical conversion mechanisms and kinetic modelling.¹³⁻²¹

Solving the repeatability problem of bio-based material production requires expanding the state of the current knowledge. A comprehensive experimental study of single particle pyrolysis provides a lot of valuable data, and examples of such studies can be found in literature.²²⁻²⁵ Despite being the most reliable, the experimental studies represent a significant cost and are limited to parameters that can be measured in practice in a selected setup. Investigation via numerical simulation, e.g., with CFD models, represents a less cost-intensive option. It additionally unlocks the ability to account for the effects of parameters that are practically difficult (or even impossible) to assess experimentally with the current technological abilities.¹⁰⁻¹² Therefore, with the use of the experimental data, the models can be established and extend the investigation. Numerous attempts can be found in the literature for the construction of reliable single-particle models, each representative of the corresponding state of knowledge and providing a novel development. Also,

comprehensive reviews of subject fundamentals can be found, which ease the identification of the route for further development.^{9, 11, 12, 26-38}

The changes in the particle geometry with conversion (e.g., shrinking) are relevant for the accurate description of changes in structure and thermo-physical parameters, hence indirectly, the conversion route.^{39, 40} Despite their occurrence in real systems, the available studies do not explain unambiguously the impact of these phenomena. Some modeling studies included geometric deformation, with a presumption of its beneficial impact.^{22, 29, 41, 42} However, other studies showed that omitting its implementation still leads to reliable outcomes in terms of the predicted temperature and mass loss profile.^{11, 29, 43} Despite the presumed beneficial effect of implementing geometric deformation in the model, none of the studies so far conducted a direct validation of the model results against experimentally obtained data of bulk density and porosity change.

For conversions at temperatures exceeding 500 °C, secondary reactions of vapors should be considered in the model to predict yields accurately.^{17, 36} However, the majority of the experimental studies on this subject investigated the secondary reactions of vapors in the reactor zone.^{6, 44, 45} A direct comparison of modeling results with and without the secondary reactions can be found in the work of Corbetta et al. This study also indicates that the secondary reactions occur both intrinsically (within particles) and externally (after vapor release into the reactor zone).²⁹ Therefore, both phenomena should be assessed independently for precise quantification of their impact. The modeling studies of single particle conversion include the secondary vapor reactions, but rarely distinguish between intrinsic and external effects or include them both.^{22, 37, 42, 46-48} The secondary vapor reactions, under favorable conditions, lead to the formation of secondary carbon (soot), where the polyaromatic hydrocarbon (PAH) triggered mechanism is considered to be the most reliable.^{17, 45} If it occurs intrinsically, the phenomenon can have a non-negligible effect on

the composition and structure of the material, thereby impacting the final application of the resultant char. However, literature modeling studies that assess the intrinsic effects of the secondary reactions are missing, especially regarding their effect on the char particle structure.

The occurrence of secondary vapor reactions is a result of a combination of a few interconnected factors. Under simplified considerations, the temperature must be sufficiently high and vapors susceptible to secondary reactions must be present in this high-temperature zone with sufficient residence time (RT). Therefore, investigation of RT has to be included when the intrinsic secondary reaction effects are assessed in the modeling study. The RT depends directly on the velocity of vapors, so the pressure build-up due to the vapor formation rate within the particle, which indirectly depends on the primary kinetic scheme and the heating rate. Along with the chemistry, the RT is directly influenced by structural-derived properties related to the used feedstock, especially permeability. Additional complexity in the assessment of the RT of the vapors within the wood and its char structures is the anisotropy of their structural-derived properties (parameter dependence on direction within the structure). It is important to stress that thermal conversion is a transient process, and changes in material properties are dynamic. Additionally, for single particles, the conversion and derivative phenomena may not occur homogeneously volume-wise, so parameter changes may vary depending on the location within the particle. Literature provides a good database for wood properties and mechanistic models that correlate wood structural parameters with thermo-physical properties.^{12, 49-54} However, data about the structure of wood-derived char and its thermo-physical properties is scarce, resulting in low reliability of mechanistic models for this material.^{12, 34, 55} An additional difficulty is a missing description of the structure change and/or thermo-physical properties during conversion. Only recently, promising attempts have been made to model the conversion of real wood structures into

char.⁵⁶⁻⁵⁹ A study of the quantitative impact of permeability on wood drying can be found in the literature, but not on conversion itself.^{33, 35} It is suspected that the high uncertainty of structure-derived parameters of char seems to be the main reason why the impact of permeability is usually neglected in modeling studies. Presumably, this is also the reason why a comparative study of the effect of permeability implementation on RT of vapors and, in general, conversion is missing.

Part 2 of this research makes an attempt to find a reliable description of geometric deformation along with other phenomena that influence the final structural properties of wood-derived chars. The derived descriptions were further implemented into the CFD model of single-particle pyrolysis, and the model was used to investigate the possibility of char tailoring with minimum initial information. The investigation is based on the calibration and assessment of the model performance with results provided in Part 1 and external datasets. It contains stepwise modeling to indicate the relevance of implementing selected phenomena and deriving descriptions in a comparative manner toward the achievement of the most precise ones. The study is composed of the following modeling cases:

- (1) Case 1 – Identification of the relevance of implementing particle geometry deformation during conversion in relation to the bulk structural parameters of the material: volume, density and porosity (comparison between 2 model results: with and without implemented geometry deformation phenomena).
- (2) Case 2 – Identification of the relevance of implementing intrinsic and external secondary vapor reactions. Investigation in terms of the accuracy of model predictions of vapors yields, their composition, and secondary carbon (soot) formation (comparison between 3 model results: without implemented secondary vapor reactions, with intrinsic reactions, and with intrinsic and external reactions).

(3) Case 3 – Identification of the relevance of difference in describing permeability in relation to impact on yields, conversion, and vapor release profile with comparison between 3 models results: permeability correlated directly to conversion (no relation with the pore size), permeability dependent as a function of pore size correlated with conversion (conversion-dependent), and permeability as a function of pore size correlated with temperature (temperature-dependent).

In each case, simulations were run for 10 scenarios: 5 temperatures (between 300 °C and 840 °C) by 2 lengths of wood cylinders ($\text{Ø}8 \times 10 \text{ mm}$ and $\text{Ø}8 \times 16 \text{ mm}$), corresponding to the experimental validation dataset in Part 1. In the final section, this study reports observed imperfections in the formulations of specific phenomena implemented into the CFD model and provides suggestions for their future improvement.

2. Model setup

2.1. Model foundations

The following was applied for all investigated scenarios within the modeled cases:

(1) The computation was made using the commercial CFD software COMSOLTM (version 5.5).

The model geometry only covered the particle, and the surrounding environment was not included in the CFD-modeled domain. Nonetheless, in the cases where the effect of the environment that surrounds a particle was relevant (external secondary reactions), the reactor zone was accounted for indirectly (not included directly in the CFD model domain). The dimensions of the reactor corresponded to the one used in the experimental Part 1, and its details can be found elsewhere.^{60,}

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(2) In the CFD model, each cylinder was represented as a 2D-axisymmetric, porous matter domain (solid + pores). The model included only two phases (solid + gaseous volatiles) since the initial

feedstock material was assumed to be dry (no moisture present, so no corresponding water phases). Similarity between the tangential and radial directions in a cylindrical wood particle was assumed. In the model, thermal conductivity and permeability of solids were considered two-dimensional anisotropic properties (longitudinal along the z-axis and radial along the r-axis).

(3) The gas phase was represented as an ideal gas. Reynolds number (Re) of flowing vapors and Forchheimer number (Fo) were calculated as in Maziarka et al.¹¹ For all scenarios both criteria, $Re \ll 10$ and $Fo \ll 0.11$, were satisfied.^{62, 63} Therefore, the description of fluid dynamics was simplified from Darcy and Forchheimer to pure Darcy's law.

(4) Mass transfer within the porous structure was driven by convection and diffusion. The latter was implemented in accordance to Fick's binary diffusion law and was temperature-dependent. The boundary condition for mass transfer at the particle's surface was applied as a convective mass transfer with an open boundary.

(5) For all modeled cases, local thermal equilibrium (LTE) was assumed between the gas and solid phases at any location within the domain due to a sufficiently low Péclet number (for heat transfer).⁶⁴ Internal heat transfer was driven by conduction, convection, and radiation. The thermal boundary condition was described by radiative and convective heat transfer. The convective heat transfer coefficient was calculated separately for a given scenario (flow and temperature of inert gas in proximity of the particle) using the Churchill–Bernstein equation.^{65, 66}

(6) The biochemical composition of wood was represented as three base wood constituents: cellulose, hemicellulose, and lignin. Other components (ash, extractives) were neglected due to their low concentration (below 5 wt.%) for the wood species considered in this work.^{18, 67} The values of the biochemical composition and thermo-physical parameters of wood and corresponding char were applied in accordance with measured values in Part 1. The parameters

implemented into the model, which were not measured in Part 1, were sourced from literature and matched as closely as possible to the investigated scenario.¹²

(7) The volatiles were lumped into groups: pyrolysis gas, i.e., compounds that do not condense at standard conditions (PG), light condensable compounds (CD), heavy condensable compounds or tars (T), and water (W). The Solid was represented via two groups of components: biomass, which refers to the bio-components and their derivatives (BS), and char, including its metaphase (CM).

(8) The enthalpy of components of each phase was simplified as a linear function of the local temperature. The effective specific heat was not based on the concentration of an individual, specific compound. Instead, the specific heat was calculated separately for each solid group (BS and CM) and volatile group (PG, CD, T and W), and the effective value was assessed as a mass average from groups. The viscosity and thermal conductivity of the volatile phase were set as a constant.

In this study, 10 scenarios were simulated for each case, which included 5 temperatures and 2 particle lengths. In each case, the description of only one parameter/phenomenon (sub-model) varied between cases, while all other parameters and phenomena descriptions (sub-models) remained constant. Table 1 provides values applied for all investigated scenarios within a case, which corresponds to the experimental scenarios investigated experimentally in Part 1 of this research. However, temperatures were adjusted in relation to the measured temperatures within their presumed uncertainty (details in Part 1). The T_{ini} represented the initial temperature of the particle (°C), T_W – temperature of reactor wall (°C), T_G – inert gas temperature (°C) in the vicinity of a particle (represented by the final surface temperature assessed experimentally), $\dot{V}_G(T_G)$ – volumetric flow rate of the inert gas (dm³/s) at a given temperature in the vicinity of the particle (re-calculated from bottom flow to the reactor = 0.167 Ndm³/s), $u_{G,max}(T_G)$ (in m/s) – maximum

velocity of inert gas (velocity within a fully developed laminar flow through a pipe, $u_{G,max} = 2 \cdot u_{G,avg}$), and h_T (in $W/(m^2 \cdot K)$) – convective heat transfer coefficient calculated for the cylinder side wall surface and applied for all boundaries with the assumption of a negligible difference between the value for top/bottom surface and side wall surface.

The models were based on a formulation previously provided by Maziarka et al., so the following section will provide only modifications to the mentioned model.¹¹ It needs to be highlighted that Maziarka et al.'s model was already extensively validated with experimental data from Lu et al. (for description of anisotropy and moisture evaporation)⁶⁸ and Bennadji et al. (for primary reaction scheme, release profiles, and heat of reaction).²⁴ Moreover, the model showed a reliable performance with satisfactory precision during validation with a broad dataset obtained from Atreya et al. (temperatures: 500 °C – 840 °C, particle sizes: 10 mm – 20 mm, and particle shapes: cylindrical, spherical).⁴⁷

All newly formulated auxiliary functions are represented by a 4-variable sigmoid function, suitable for application in an artificial neural network, possibly in future works.^{69, 70} Sections S1.1, and S1.3. provide detailed information regarding fundamental and governing equations, and boundary conditions. Details about the calculation of the convective heat transfer coefficient are provided in Section S1.4. Section S3 provides additional information on the hardware, applied numerical parameters (mesh, time step), and solver configuration.

Table 1. Values of initial and boundary parameters for all scenarios applied for all investigated cases.

Scenario	Particle (D x H)	T_{ini}	T_W	T_G	$\dot{V}_G(T_G)$	$u_{G,max}(T_G)$	h_T
[-]	[mm]	[°C]	[°C]	[°C]	[dm ³ /s]	[m/s]	[W/(m ² ·K)]
T1_10	Ø8 x 10	24	310	305	0.330	0.336	20.7

T2_10	Ø8 x 10	24	395	390	0.390	0.397	22.8
T3_10	Ø8 x 10	24	470	465	0.431	0.439	24.2
T4_10	Ø8 x 10	30	665	650	0.548	0.558	27.9
T5_10	Ø8 x 10	40	830	820	0.649	0.661	30.9
T1_16	Ø8 x 16	24	310	305	0.338	0.345	21.0
T2_16	Ø8 x 16	24	395	390	0.391	0.398	22.8
T3_16	Ø8 x 16	24	470	465	0.433	0.441	24.2
T4_16	Ø8 x 16	30	665	650	0.554	0.565	28.1
T5_16	Ø8 x 16	40	830	820	0.651	0.663	31.0

2.2. Auxiliary equations

The true density of the solid was implemented in the model as a function of local temperature, instead of being a constant value. The formulation was based on experimental data from Part 1 and literature data.^{12, 32, 71-78} The true density, with variable formatting according to Grønli, was implemented as:³²

$$\langle \rho_s \rangle^s(t) = \Gamma_\rho + \frac{\alpha_\rho}{1 + e^{-\left(\frac{T(t) - \delta_\rho}{\beta_\rho}\right)}} \quad (1)$$

Where $\langle \rho_s \rangle^s(t)$ is the density of the solid phase (true density) at a specific time (kg/m^3), $T(t)$ is the local temperature ($^\circ\text{C}$), t is the time of conversion (s), Γ_ρ is the initial true density (1450 kg/m^3), and α_ρ , β_ρ and δ_ρ are parameters with values 575 kg/m^3 , $85 \text{ }^\circ\text{C}$ and $735 \text{ }^\circ\text{C}$, respectively. The function was derived from a dataset covering conversion temperatures from $20 \text{ }^\circ\text{C}$ to $1000 \text{ }^\circ\text{C}$ of dry solid, so it is valid only within the mentioned range of conditions. Additionally, it needs to be pointed out that the derived function can slightly overpredict the true density of chars produced up to $500 \text{ }^\circ\text{C}$ due to its simple construction. An additional elaboration on the derivation and reliability of the function is provided in Section S1.6. along with the assessment of its performance in relation to experimental data, which is shown in Figure S1.

Various descriptions of thermal conductivity and values for the thermal conductivity coefficients of wood and char can be found in the literature.^{32, 49, 52, 53, 79} In this study, the anisotropic thermal conductivity of the solid was implemented in accordance with the conductivity model proposed by Maku and formulated by Siau.^{49, 53} The effective thermal conductivity in the longitudinal direction (parallel to the wood fibers) was implemented as:

$$\lambda_{eff,\parallel} = (1 - \varepsilon) \lambda_{eff,F,\parallel} + \varepsilon (\lambda_g + \lambda_{rad}) \quad (2)$$

And in radial/transverse (perpendicular to fibers) direction as:

$$\lambda_{eff,\perp} = \frac{1}{\frac{1-a}{\lambda_{eff,F,\parallel}} + \frac{a}{(1-a) \lambda_{eff,F,\perp} + a(\lambda_g + \lambda_{rad})}} \quad (3)$$

Where all parameters are related to a specific time of the conversion, λ is thermal conductivity (W/(m·K)), ε is vapor phase fraction (voids/porosity), and a is lumen width to cell width in a dry state calculated as $a = \sqrt{\varepsilon}$, and subscripts denote: *eff* – effective properties, *F* – fiber properties, $\parallel$ – parallel direction (longitudinal), $\perp$ – perpendicular direction (radial/transverse), *g* – gas/volatiles phase (pores), and *rad* – radiative component of heat transfer. The fiber properties were set as dependent on the composition of the solid, hence conversion of bio-components, defined as:

$$\eta(t) = \frac{\sum_j^K \langle \rho_{BS,j} \rangle (t)}{\sum_j^K \langle \rho_{BS,0,j} \rangle} \quad (4)$$

Where $\langle \rho \rangle (t)$ is the density in a mesh cell volume at a specific time (kg/m³), and $\langle \rho_0 \rangle$ is the initial density in the mesh cell volume, and subscripts denote: *BS* – biomass component, and (j...K) corresponds to all compounds assigned as biomass. Therefore, the fiber properties were implemented as:

$$\lambda_{eff,F,Y}(t) = \lambda_{wood,F,Y} \cdot \eta(t) + \lambda_{char,F,Y} \cdot (1 - \eta(t)) \quad (5)$$

Where Y denotes the direction of fiber ($\parallel$ or $\perp$). The values of thermal conductivity of wood fibers and char “fibers” were calibrated to the model (set as constant for all cases) from available values for corresponding wood species from literature (as a starting point).^{49, 80-82} In this study, for wood, $\lambda_{wood,F,\parallel}$ and $\lambda_{wood,F,\perp}$ were set as 0.7 W/(m·K) and 0.55 W/(m·K), respectively. For char, $\lambda_{char,F,\parallel}$ and $\lambda_{char,F,\perp}$ were set as 0.535 W/(m·K) and 0.35 W/(m·K) respectively. Details about the applied auxiliary equations are provided in Sections S1.2, S1.5, and S1.6, including additional information about the derivation of true density and thermal conductivity.

2.3. Geometric deformation

Case 1 of the investigation involved the effect of particle geometry change on the conversion and bulk properties of a particle. It involved two cases: first, without geometry deformation (NO_SHR) and second, with particle deformation (SHR). Geometric deformation was implemented as a volumetric phenomenon. The description was based on the work of Gentile et al. and it was based on the solid mass balance when the volume and porosity of the domain change in time.⁴¹ It was formulated as a general equation:

$$\frac{dm}{dt} = \langle \rho_s \rangle^s \cdot (1 - \varepsilon) \frac{dV}{dt} - \langle \rho_s \rangle^s \cdot V \frac{d\varepsilon}{dt} \quad (6)$$

Where $\frac{dm}{dt}$ is the mass change of the particle due to thermal conversion reactions, V is the total volume of the particle. In this study, geometrical changes were correlated with the mass change during the conversion, as suggested by Davidsson and Petersson.⁸³ As the changing variable was selected, mass loss ($ML(t)$) was defined as:

$$ML(t) = 1 - \frac{m(t)}{m_0} \quad (7)$$

Where $m(t)$ is the mass of the particle at a specific time and m_0 is the initial mass of particle. Since the model represented two dimensions, the experimentally obtained changes in radial and tangential dimensions were merged into an “artificial” or composite radial dimension, named R-simul. (obtained by matching the volume change). The increase in particle dimensions (so-called “swelling”) was not included, since this phenomenon was assessed as related to the occurrence of cracks and layering and not to volumetric changes (details in Part 1). The equation for change in a specific dimension was implemented as:

$$SHR_{\Lambda}(t) = \Gamma_{\Lambda} + \frac{\alpha_{\Lambda}}{1 + e^{-\left(\frac{(ML(t) - \delta_{\Lambda})}{\beta_{\Lambda}}\right)}} \quad (8)$$

Where $SHR(t)$ is the dimensional change factor (-), Γ (-), α (-), β (-) and δ (-) and subscript Λ denotes the direction (L – longitudinal = z-axis and R –, radial = r-axis). Parameters derived from experimental data are shown in Table 2, and the functions with their performance against data from Davidsson and Pettersson are presented in Figures S2 and S3.⁸³

Table 2. Parameters of dimensional changes for geometric deformation of a particle.

Direction (Λ) [-]	Γ [-]	α [-]	β [-]	δ [-]
z-axis (L)	0.851	0.149	-0.060	0.658
r-axis (R)	0.668	0.337	-0.112	0.475

The velocity of the domain boundary was expressed as:

$$u_{SHR,\Lambda}(t) = \frac{1}{2} \Lambda_0 \cdot \frac{d(SHR_{\Lambda}(t))}{dt} \quad (9)$$

Where $u_{SHR}(t)$ is the boundary velocity (m/s), Λ_0 is initial dimension of the particle (height or diameter) (m). The factor $\frac{1}{2}$ was used since the movement was applied separately to each boundary. Change in the boundary position corresponded to changes in the surface area of the particle, hence the flux of vapors. The vapor movement within the particle was coupled with the boundary movement by the following general equation:

$$u_{g,\Lambda} = u_{g,\Lambda,D} + u_{SHR,\Lambda} \quad (10)$$

Where $u_{g,\Lambda}$ is the effective velocity of gas in a specific direction and $u_{g,\Lambda,D}$ is the velocity of gas in a specific direction calculated with the Darcy equation. The changes in the mesh due to the geometric deformation are presented in Figure S6. Details about the derivation of the geometry deformation equations, parameter fitting, and implementation of the phenomenon into COMSOLTM software can be found in Section S1.7.

2.4. Primary and secondary reactions

In case 2 of this study, the effect of secondary reactions on the composition of vapors was investigated. It involved a comparison of three cases: without secondary reactions (NO_SCR), with secondary reactions in the interior of the particle (SCR), and with secondary reactions in the interior and exterior of the particle, hence also the reactor zone (SCR_R) was considered. As the primary bio-components degradation scheme, the Chemical Reaction Engineering and Chemical Kinetics group degradation scheme (CRECK scheme) with adjustments by Anca-Couce et al. (RAC scheme) was used. It is composed of 24 reactions, 33 compounds, and 4 adjustable parameters “ x ” defining an alternative degradation route (secondary charring).^{22, 84} The extent of secondary charring is assigned separately for each bio-component group: hemicelluloses (x_{HCE}), cellulose (x_{CELL}), lignin (x_{LIG}) and metaphase compounds ($x_{G[X]}$). In this study, the “ x ” parameter

was simultaneously calibrated for all 10 scenarios (5 temperatures and 2 particle lengths), which resulted in the best fit for the following values: $x_{HCE} = 0.08$, $x_{CELL} = 0.12$, $x_{LIG} = 0.08$ and $x_{G[X]} = 0.05$.

The reaction scheme of secondary reactions of evolved vapors was based on the scheme of Mellin et al. and modified by Anca-Couce et al.^{22, 85} Reactions were assumed to be first order, with pre-exponential factors and activation energies set as the same for all compounds but with different heats of reaction.^{22, 86, 87} The intrinsic secondary reactions were directly incorporated into the domain. The reactions of vapors after release from the particle were added through a conversion factor, calculated as the time integral of the secondary reaction effect, the same for all compounds for a specific scenario. For the calculation, the final, experimentally obtained surface temperature was used. The vapor residence time (i.e. in the reactor and exterior to the particle) was derived from the velocity of the sweep gas in the reactor and the distance between the place of conversion (i.e. particle surface) and the reactor outlet (i.e., the porous diluter), as presented in Figure S5.

It needs to be mentioned that in literature, more detailed secondary reaction schemes, such as the BIO_1311 and POLIMI_1311 schemes can be found.^{17, 29} These detailed models include the formation of the soot via a polyaromatic route, as opposed to the applied secondary model, which includes soot formation only from lignin-derived vapors. However, the POLIMI scheme includes a vast number of reactions and intermediate compounds (450 species and about 15000 reactions), whose implementation will induce an enormous computational burden to the already complex CFD model of single particle pyrolysis. Additionally, in the literature, an example of its direct implementation into a CFD model cannot be found, e.g., in COMSOLTM software. However, indirect use can be found in the study of Corbetta et al.²⁹ The available studies do not indicate that the scheme of Mellin et al.⁸⁵ introduces a critical error in the representation of the secondary

reaction behavior (available sources suggest only that a more detailed model can be more precise). Moreover, the latter mentioned secondary reaction scheme was successfully implemented in computational studies.^{22, 26} Therefore, the decision was made to apply in this study, the more simpler secondary reaction scheme of Mellin et al., for two reasons. First, to conduct a detailed analysis of its performance before making a statement about its (in)ability to make a prediction with the required precision. Second, to not overcomplicate the computational model without a clear need as such.

Primary degradation and secondary reaction kinetic schemes implemented in this study are shown in Sections S2.1 and S2.2, respectively. Derivation and implementation of the effect of secondary reactions outside of the particle are shown in Section S2.3.

2.5. Permeability

In Case 3 of this study, three descriptions related to permeability and their effect on vapor flow and composition were investigated. In the first model (CP), the permeability was assumed to be dependent only on the particle conversion, and the permeability was implemented as:

$$K_{eff,\Lambda}(t) = K_{BS,\Lambda} \cdot \eta(t) + K_{CM,\Lambda} \cdot (1 - \eta(t)) \quad (11)$$

Where K is permeability (m^2) and subscripts denotes: *eff* – effective parameter used in Darcy equation, *BS* – biomass, *CM* – char with its metaphase and Λ – specific direction (L - longitudinal or R - radial). The values of $K_{BS,L}$, $K_{BS,R}$, $K_{CM,L}$ and $K_{CM,R}$ were based on literature data, and were set as $10^{-12} m^2$, $10^{-15} m^2$, $10^{-11} m^2$ and $10^{-14} m^2$, respectively.³²

In the second model (VP), the permeability was assumed to be dependent on porosity and the effective pore diameter. Therefore, the permeability was implemented based on the Kozeny-Carman equation, expressed as:

$$K_{eff,\Lambda}(t) = \frac{\varepsilon^3(t) \cdot d_{p,eff,\Lambda}^2(t)}{16 \cdot f \cdot \theta \cdot (1 - \varepsilon(t))^2} \quad (12)$$

Where $d_{p,eff}$ is the effective pore diameter (m), f is volume shape factor, and θ is tortuosity. The two latter factors were assumed to be isotropic, and their values were related to transport in the longitudinal direction. For transport in cylindrical pores having a circular cross section, the volume shape factor f was set as 2.⁸⁸ The tortuosity through hardwood wood vessels and its char were set as 1, since numerically estimated values were sufficiently close.⁵⁹ The effective pore diameter, in this case, was defined as:

$$d_{p,eff}(t) = d_{p,wood,\Lambda} \cdot \eta(t) + d_{p,char,\Lambda} \cdot (1 - \eta(t)) \quad (13)$$

The values of $d_{p,wood,\Lambda}$ and $d_{p,char,\Lambda}$ were calculated with the Kozeny-Carman equation using the above-mentioned permeability and corresponding to porosity. Applied porosity was taken from Part 1, where wood had $\varepsilon = 0.545$ and char from thermal conversion at ca. 840 °C had $\varepsilon = 0.892$. Implemented, porosity-derived parameters $d_{p,wood,L}$, $d_{p,wood,R}$, $d_{p,char,L}$ and $d_{p,char,R}$ had values of 6.40 μm , 0.20 μm , 2.29 μm , and 0.73 μm , respectively.

In the third model (VPT), the permeability was also assumed to be dependent on porosity and effective pore diameter. However, in this model, the effective pore diameter was correlated with temperature, and not with conversion. The relation between pore diameter and temperature was derived from external data provided in Part 1. In accordance with the literature, pits are structures that determine transport in a direction along the vessels (longitudinal) and across the vessels (radial and transverse). The effective opening of hardwood pits can vary in size between 0.1 μm and 170 μm , where the upper size limit is related to the size of vessels. For beech wood, the pit size can be assessed for a range from 4 μm to 11 μm .^{50, 53, 89} In this study, it was assumed that the effective

diameter for vapor transport and in radial/transverse direction corresponds to the diameter of ultra small macropores (Ma-U: 0.1-5 μm) and in the longitudinal direction, to the diameter of small macropores (Ma-S: 5 – 30 μm). The temperature-dependent function of the effective diameter of pores was implemented as:

$$d_{p,eff,\Lambda}(t) = \Gamma_{d,\Lambda} + \frac{\alpha_{d,\Lambda}}{1 + e^{-\left(\frac{T(t)-\delta_{d,\Lambda}}{\beta_{d,\Lambda}}\right)}} \quad (14)$$

Where $T(t)$ is the local temperature ($^{\circ}\text{C}$), Γ_d (μm), α_d (μm), β_d ($^{\circ}\text{C}$) and δ_d ($^{\circ}\text{C}$) are parameters of the function, and subscript Λ denotes the direction (L – longitudinal = z-axis and R – radial = r-axis). Parameters derived from experimental data are shown in Table 3. Details of the derivation of the temperature-dependent change of pore diameter from experimental data are provided in Section S1.8, and the performance of the established functions are presented in Figure S4.

Table 3. Parameters of temperature-dependent change of specific pore diameter.

Direction (Λ)	Γ	α	β	δ
[-]	[μm]	[μm]	[$^{\circ}\text{C}$]	[$^{\circ}\text{C}$]
R (Ma-U)	0.33	0.57	55	550
L (Ma-S)	14.00	3.00	-55	490

2.6. Overview of investigated models

Table 4 provides a brief overview of the main differences in the description between investigated Cases is provided. As it is presented, the study was conducted using a stepwise approach.

Table 4. Overview of the main differences in the description of the models between investigated cases (“0” – phenomenon not implemented, “+” - phenomenon implemented)

Case	Model	Geometry deformation	Secondary reactions		Permeability dependence
			Intrinsic	External	
1	NO_SHR	0	0	0	$K \sim f(\eta)$
	SHR	+	0	0	$K \sim f(\eta)$
2	NO_SCR	+	0	0	$K \sim f(\eta)$
	SCR	+	+	0	$K \sim f(\eta)$
	SCR_R	+	+	+	$K \sim f(\eta)$
3	CP	+	+	+	$K \sim f(\eta)$
	VP	+	+	+	$K \sim f(d_p(\eta))$
	VPT	+	+	+	$K \sim f(d_p(T))$

3. Results and discussion

The total mass yield was calculated as the mass of char plus the total mass of produced vapors and divided by the initial mass of the particle to check if the model is reliable in terms of the predicted mass yield. The model (for 10 scenarios) accurately predicted the total mass yield regardless of the pyrolysis temperature, particle length, and implementation of the geometric deformation. For all scenarios, the total mass yield did not show excess (overprediction) or loss (underprediction) for more than 0.5 wt.% of the initial feedstock mass. The numerical error was considered negligible and the model as reliable regarding mass balance.

3.1. Effects of geometric deformation

Figure 1 presents model-predicted profiles of temperatures (left) and mass (right) as a function of time, compared to experimentally obtained data for the 10 mm particle (TC – temperature at center, TSS – temperature of the side surface, TST – temperate at the top surface). The same plots for the 16 mm particles are shown in Figure S7. The shapes of the temperature and mass profiles were related to the reaction of specific constituents in the wood and to the thermal effects in its conversion. Detailed study on the shape of these temperature/mass curves can be found in the literature, and since this is outside of the scope of the current study, elaboration on this subject will

be omitted.^{11, 30} As it can be observed, modeled profiles resembled experimentally obtained profiles very well. However, with a decreasing conversion temperature, the accuracy of the modeled profiles of temperature as well as mass also decreased. At temperature T1 ($T_G = 300\text{ }^{\circ}\text{C}$), for both particle lengths and regardless of the implementation of geometry deformation, the model overestimated temperature and mass loss.

Regardless of the case, for all scenarios, a premature start of conversion is visible in the model-predicted profiles. The experimentally obtained TST profiles for both particles suggest that during the experiment, the introduction of the sample could cause a disturbance in the temperature equilibrium within the reactor. Therefore, the conversion did not start at the equilibrium temperature in the reactor but at a lower temperature, which regained equilibrium over a certain time. Such an effect was not included in the model, where the conversion started immediately from the equilibrium conditions as initial condition(s) set in the model. The latter is suspected to be a factor that led to the apparent premature start of the modeled conversion or delayed conversion represented in the experimental data. Additionally, regardless of taking special care in minimizing the moisture absorption during experimental trials (especially during biomass sample handling and introduction into the reactor as indicated in Part 1), the absorption of the moisture close to the surface of the particle cannot be completely ruled out. The absorbed moisture could also induce the observed effect of surface temperature, but it is not confirmed to what extent the mentioned moisture had an impact. Figure 1 and Figure S7 show a delay in the rise of the particle center temperature when the modeled results are compared against the experimental results. In the model, the value for the thermal conductivity of wood was selected from the upper allowed range, which should lead to the highest predictable heating rate in the center of the particle. Therefore, it was suspected that in the experiments, the thermocouple measurements were biased to too high

temperature readings in the initial part of the conversion, due to the thermocouple's own higher thermal conductivity. Objective confirmation of such an effect should be made in a specific study.

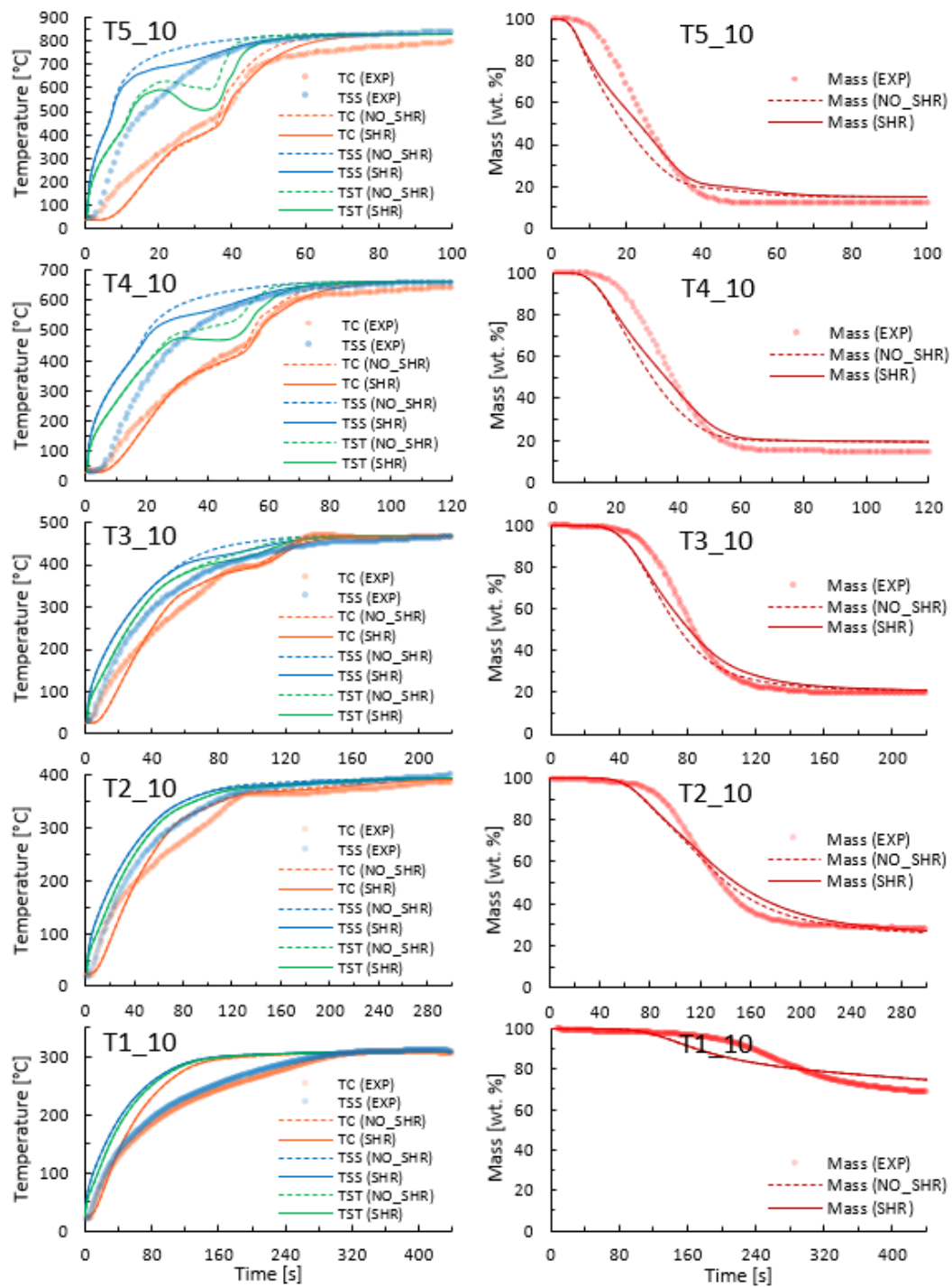


Figure 1. Comparison of modeled profiles (NO_SHR and SHR model) of temperature (TC – center, TSS – cylinder side surface, TST – cylinder top surface) and mass for the 10 mm particle for all investigated scenarios with corresponding experimental data (from Part 1).

Differences in the temperature profiles between NO_SHR and SHR scenarios can be distinguished, especially for the model-predicted surface temperature. The differences became noticeable in scenario T3 ($T_G = 480\text{ }^{\circ}\text{C}$) and were more profound in scenario T4 ($T_G = 680\text{ }^{\circ}\text{C}$) and T5 ($T_G = 840\text{ }^{\circ}\text{C}$). The temperature deviation between the NO_SHR and SHR model was more visible for 16 mm than for 10 mm particles. As it can be observed in Figure 1, the cooling effect in the periphery of the particle, which is induced by the outflowing pyrolysis vapors, influenced not only the top surface but also the side surface of the cylindrical particle. The cooling effect on the top surface was more profound for the SHR model and the 16 mm particle. This corroborates the presumption that the elevated cooling effect is related to the increased volumetric vapor concentration, hence stronger conversion caused by mass densification due to the geometric deformation (i.e., particle shrinking). Also, the particle size reduction due to geometry deformation led to a shorter distance of the vapor release pathway towards the particle's surface, which led to the presence of a more profound cooling effect on the particle surfaces. Nonetheless, the cooling effect and, in general, the geometrical deformation (and consequent changes in the heat transfer and distribution) did not significantly influence the char yield. Results of the char yield for the NO_SHR and SHR models showed negligible differences (on average, $0.12 \pm 0.07\text{ wt.}\%$ for all scenarios). Therefore, it can be stated that the implementation of geometry deformation in models for particles with a length of 10 mm and 16 mm influenced the conversion of the implemented primary degradation scheme only marginally. However, the effect may become more significant when larger and longer particles than the ones used in this study are modeled.^{39, 43}

Figure 2 presents a comparison between modeled and experimental results for char yield and its composition for both particle lengths for the SHR model. The model for both particles predicted char yields with high accuracy with an average difference of 2.8 ± 1.1 wt.% between experimental and modelled data for scenarios T2-T5. For scenario T1 ($T_G = 300$ °C), the modeled char yield was significantly higher than the one experimentally obtained (by 14.6 ± 7.3 wt.% for both particles). A comparison of the elemental composition of the initial feedstock material shows that the wood implemented in the model had higher carbon content (2.4 wt.%), lower hydrogen (0.4 wt.%), and lower oxygen content (1.8 wt.%) than beech wood assessed experimentally. The cause of these differences is suspected to be related to the possible imperfection of the experimental assessment of the bio-components content of beechwood (in Part 1). The experimental analyses of the beech wood did not include the measurement of extractives nor assess the detailed (bio)chemical composition of the lignin fractions in beech wood. This subsequently led to inaccuracies in the model.^{13, 16, 90} Similarly, with respect to char yield, the model-predicted elemental compositions were least accurate for the T1 scenarios, and the model prediction accuracy increased with conversion temperature. Figure 2 shows a visible trend of overestimation of the hydrogen content in char for scenarios T1-T4 (on average, 1.1 ± 0.4 wt.%) despite the hydrogen being underestimated in the initial feedstock material. The model, for both particle lengths, also noticeably overestimated the carbon (by 6.3 ± 1.3 wt.%) and underestimated the oxygen content (by 5.7 ± 1.2 wt.%) for scenario T5 ($T_G = 840$ °C). It is suspected that for such a high temperature of conversion as in scenario T5, the uncertainty related to the initial wood elemental composition did not have a high impact on the overestimation. Therefore, it is presumed that the overestimation at T5 is more related to the implemented kinetic scheme of the primary degradation.

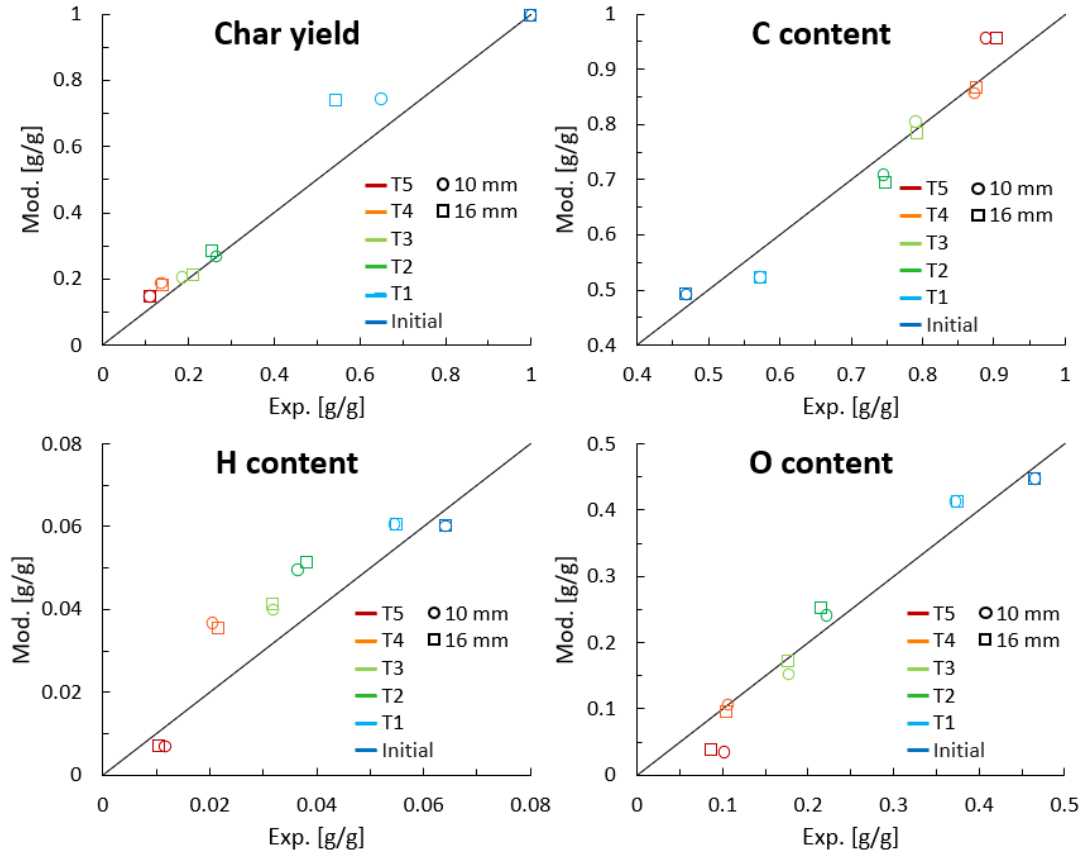


Figure 2. Comparison of char yield and char elemental composition between modeled (SHR) and experimental data for both particle lengths and all investigated scenarios.

The geometric deformation of particles as a function of conversion extent (equal to remaining solid mass in wt.%) is presented in Figure 3. The dashed lines represent both particle lengths since the deformation factors had the same values for the 10 mm and 16 mm particle. Additionally, the presented “Radial (simul.)” points (green), were obtained as an average between the experimentally obtained “Radial” points (yellow) and “Tangential” points (blue) since the presented model accounted for only 2 dimensions.

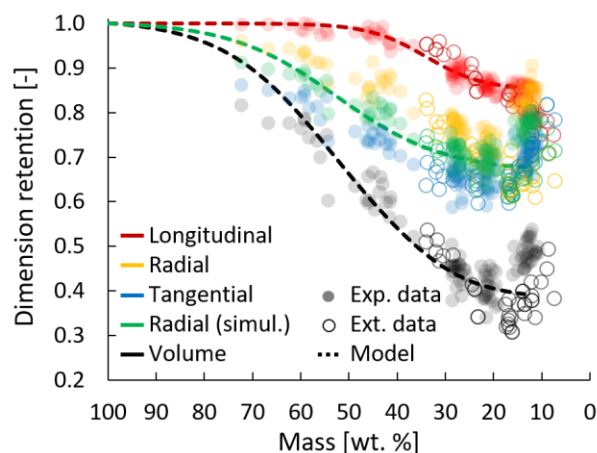


Figure 3. Dimensional (longitudinal and recalculated radial) and volume changes as a function of mass loss predicted by model (SHR model) compared to the data from Part 1 (Exp. data) and data from Davidsson and Peterson (Ext. data).⁸³

Geometrical deformation in specific directions (i.e., longitudinal, radial) followed the implemented functions to a great extent. That led to a good match with the volumetric changes assessed experimentally. Moreover, the function derived from this study data fits well with the external data from Davidsson and Pettersson, which indicates the reliability of the presented approach.⁸³ A slight deviation between the datasets (Exp. and Ext.) can be noticed. It is presumed that they were caused mainly by the difference in the shape of particles used for conversion (cylinders versus cubes) and the difference in bio-composition between species tested (beech versus birch). Additionally, the specific structure of the used species or the impact of the heating conditions could add to the deviation between datasets. More details on the subject are provided in Section S1.7.

The dimensional reduction and volume reduction in the initial phase of the conversion (remaining solid mass between 100 wt.% and 70 wt.%) were slightly lower than experimentally assessed, especially at the end of the range. The experimentally assessed dimensions increased in the final

phase of conversion (remaining solid mass between 20 wt.% and 10 wt.%). Additionally, in Figure 3, it can be noticed that the external data is also burdened with an increase in particle dimensions (and volume) when mass drops to ca. 20 wt.%. As was pointed out in Part 1, such an outcome was caused by the layering of the char structure and the appearance of cracks. Therefore, since such a phenomenon was assessed as non-volumetric, it was not included in the geometry deformation description.

Figure 4 presents the model-predicted average bulk density as a function of conversion (remaining solid mass in wt.%) for the NO_SHR and SHR model for all scenarios with comparison to the experimentally obtained data. The trend was the same for particles of both lengths, so only one trend line was presented for each model. In the initial mass change (up to 70 wt.%), the experimental average bulk density profile matches the trend obtained from the NO_SHR model. The match to the NO_SHR model results is related to minor volumetric changes during the initial phase of the conversion. With further conversion, i.e., below 70 wt.% remaining mass, the trend obtained with the SHR model started to show a better match to the experimental trend than the data from the NO_SHR model. Both trends, obtained with the SHR model and experimental data, showed a plateau for averaged bulk density for a conversion between 70 wt.% and 30 wt.%. The cause of its appearance was related to similar rates of mass and volume reduction. When volume and mass loss occur at a similar rate, a balance is established, which leads to net-zero bulk density changes. Nonetheless, this net-zero change is only artificial since the bulk density has been averaged over the entire particle volume.

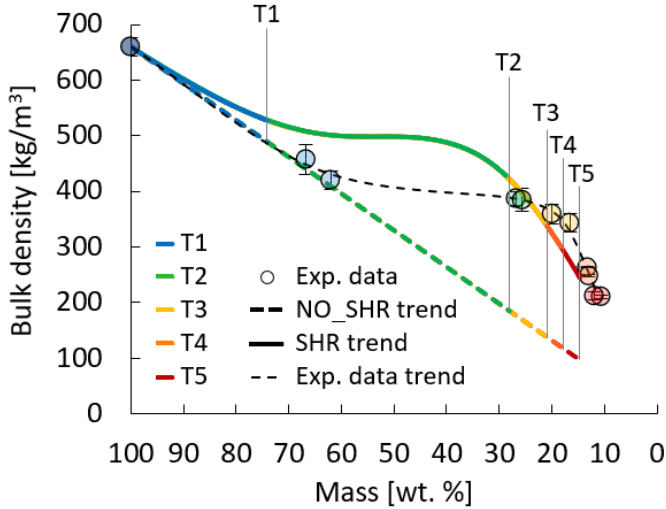


Figure 4. Average bulk density as a function of mass obtained with NO_SHR and SHR model with comparison to experimental data (from Part 1).

The obtained trends indicate that for scenarios T2-T5 (conversion temperatures between ca. 400 °C and 840 °C), the SHR model predicted very accurately the final average bulk density (difference on average, $31 \pm 15 \text{ kg/m}^3$). However, the prediction for T1 scenarios of the average bulk density was far from satisfactory, with a difference of $90 \pm 25 \text{ kg/m}^3$. The implemented volumetric change in the initial phase of the conversion was lower than experimentally assessed. Therefore, it should lead to a lower value of bulk density predicted by the model in comparison to experimental data. The leading cause of the poor prediction of averaged bulk density in scenario T1 can be assigned to the more considerable differences between the modeled and experimental mass change (for both particle lengths). For this scenario, the mass reduction in the model started faster, but at the final temperature, it led to a higher remaining mass than experimentally observed (see Figure 1).

Figure 5 shows a comparison between the modeled porosity from the SHR model and experimentally measured values for the 10 mm and 16 mm particle for all scenarios. As can be observed, the modeled porosity was in very good agreement with the experimental data. The model-predicted porosity matched very accurately experimental data for scenarios T2-T5 (the

average difference to experimental data, 1.8 ± 1.1 vol.%). The less accurate porosity prediction was obtained for scenario T1 (4.4 ± 1.2 vol.%), which, as mentioned above, was related to the inaccurate prediction of bulk density by the model. The porosity in the presented model was a derivative of bulk density (cell mass and volume change), but also a function of true density with temperature (see eq. 1, Section 2.2). The obtained results indicate that the implemented function of the true density was also accurate and resembled the real changes in the material properties well.

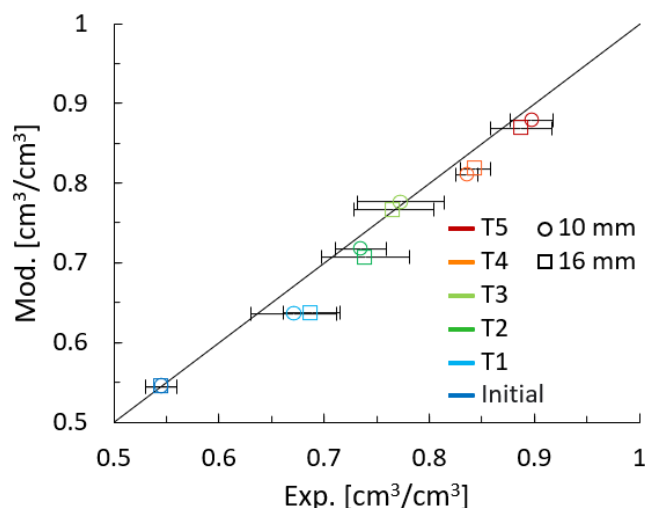


Figure 5. Comparison of porosity between results from the SHR model and experimental data for both particle lengths and all investigated scenarios.

3.2. Yields of vapors and release profiles

In this section, the FT-IR results from Part 1 were used as experimental data. This dataset did not contain a complete assessment of the heavy tar group (T). Therefore, for comparison, the combined CD + T group was shown, where CD (i.e., condensable fraction) was obtained experimentally, and the T (tars) group was calculated by difference. A comparison of yields for main product groups (char, PG, and CD+T) between SCR, SCR_R, and experimental results is presented in Figure 6. The results from the NO_SCR model were not included in the comparison since the difference

between results from the NO_SCR and the SCR model were minor. The elaboration on the impact of the intrinsic secondary reactions of vapors on yields is provided in more detail in Section 3.3.

As shown in Figure 6, the SCR model for all scenarios (temperature and particle length) showed worse accuracy than the SCR_R model, even in scenarios where the effect of the secondary reactions of vapors was presumed not to be strongly influential (i.e., at lower conversion temperatures, $< 500\text{ }^{\circ}\text{C}$). It can be concluded that omitting the implementation of the secondary vapor reactions in the reactor zone leads to the inability of the model to predict the lumped pyrolysis product yields accurately. Therefore, for any future modeling studies of single particle conversion, the reactions occurring within the reactor zone must also be considered.

The results from the SCR_R model predicted well the PG yields and CD+T yields between T2 and T4, with an average difference for both particle lengths of $4.1 \pm 1.9\text{ wt.}\%$ and $6.5 \pm 3.3\text{ wt.}\%$, respectively. The poor prediction in the T1 scenarios ($T_G = 300\text{ }^{\circ}\text{C}$) was related to inaccurate prediction of biomass conversion, which resulted in an overprediction of the char yield and an underprediction of the yield of vapors. The SCR_R model started to overpredict PG yield at the expense of the CD+T yields from scenario T4 ($T_G = 680\text{ }^{\circ}\text{C}$) onwards. The effect is very strongly distinguishable at T5 ($T_G = 840\text{ }^{\circ}\text{C}$), where the PG overprediction was accounted as $16.1 \pm 2.9\text{ wt.}\%$ and CD+T underprediction as $23.1 \pm 1.3\text{ wt.}\%$ (on average, for both particles). It is presumed that such an effect was related to the implementation of a very basic secondary reaction scheme of vapors, which did not distinguish between specific compounds (all vapors had the same kinetic parameters of degradation). Additionally, in the applied secondary reaction scheme, the products of the reactions were mainly PG and soot. The literature indicates that the mono- or polyaromatic hydrocarbons are formed from vapors at temperatures corresponding to scenario T5 ($T_G = 840^{\circ}\text{C}$).^{17, 45} When formed, those compounds would be added to the T group, and reduce the

underprediction of CD+T yield. Therefore, the omission of their formation in the secondary kinetic scheme was presumably one of the reasons for the large inaccuracy in predicting the vapor yields in the T5 scenario.

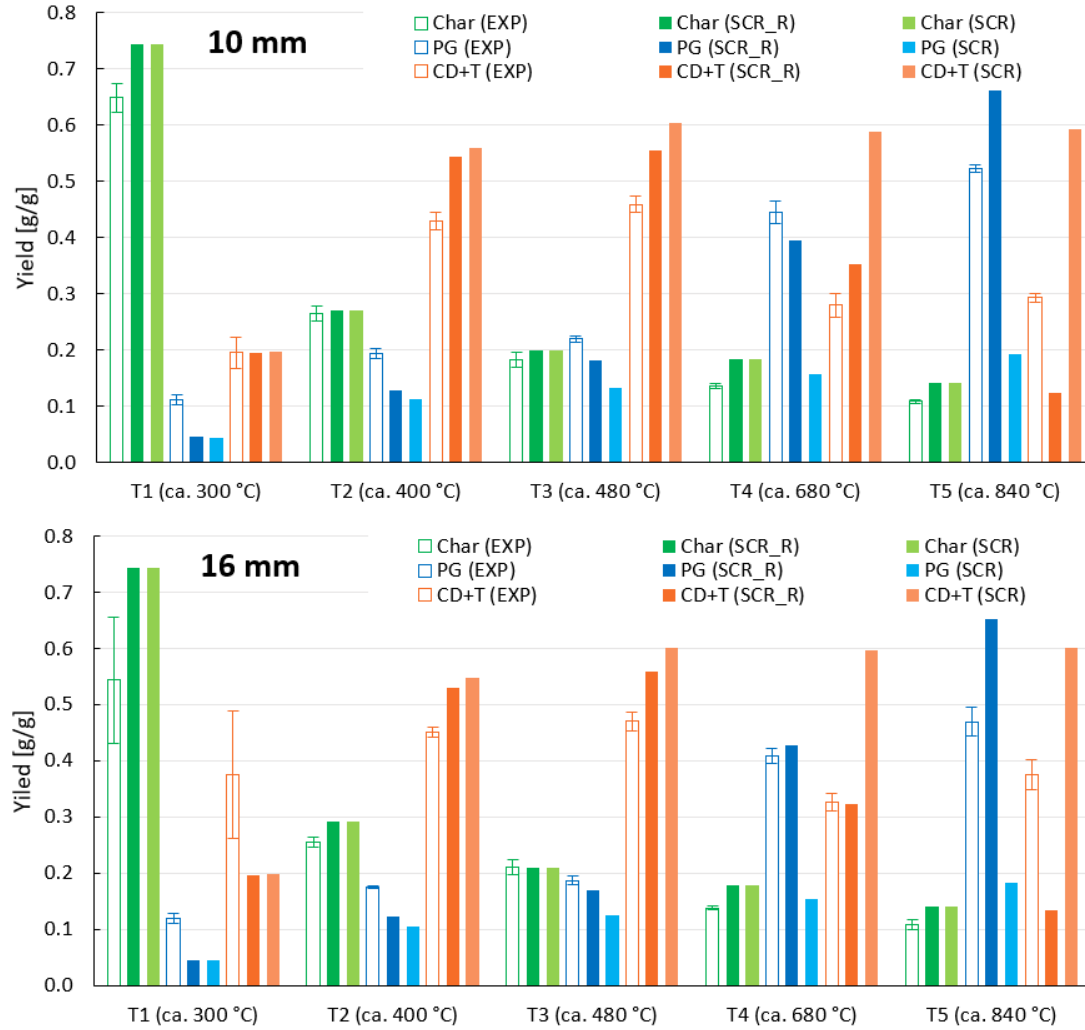


Figure 6. Comparison of the modeled lumped product yield (SCR and SCR_R model) with experimental results (from Part 1) for all investigated scenarios (top – 10 mm, bottom – 16 mm).

The modeled final center temperature for a specific scenario, between 10 mm and 16 mm particles, differed on average by 11 ± 7 °C, while in the experimental results, it differed on average by 7 ± 5 °C (in both cases, mostly in favor for 10 mm particle). Therefore, it was assumed that the

difference in final center temperature was insufficient to induce the observed effects of particle length on yields. It was assumed that the cooling effect related to particle length and the formation of the “outer thermal layer” at higher temperatures, were factors inducing the differences in yields.^{11, 29, 43, 58} Nonetheless, the effect of the factors related to the heat transfer had only a minor influence on the modeled yields (up to 1.5 wt.%), which seems reasonable considering that particles differed in length and not in radius. More details about heat transfer and its possible effect on yields can be found in Section S5 and Figure S8. The heating rate distribution at half of the conversion and its comparison to the distribution of other conversion-related parameters for scenarios T3-T5, for the 16 mm particle are presented in Section S8.

In the literature, an elaboration on the formation of specific compounds during pyrolysis of primary biomass constituents can be found.^{9, 91, 92} Therefore, a detailed discussion on the subject will be omitted, and the focus will be devoted to the performance of the model. Figure 7 presents yields of specific compounds for both particle lengths and for all scenarios from the SCR_R model with the comparison to experimental data. As it can be observed in Figure 7, the model maintains the magnitude of the yield of specific compounds well. Additionally, it can be observed that the trends related to the temperature and particle length match between experimental and modelled results. Overall, the precision of the obtained model with the prediction of the yield of specific compounds was satisfactory.

As shown in Figure 6, the SCR_R model had a satisfactory accuracy in the prediction of PG group compounds up to scenario T3 ($T_G = 480$ °C) for both particle lengths. Above that temperature, the model lost its accuracy. As observed in Figure 7, this was related primarily to inaccurate prediction of the yield of CO and CH₄ in scenarios T4 and T5. A general trend can be derived from Figure 7, where the yield of the compounds included in the CD group was overpredicted up to T3, and with

a further temperature rise, the accuracy of their yield prediction increased. The latter is related to the global effect of secondary reactions of vapors in the reaction zone. It led to a straightforward reduction of the CD yield since all compounds included in this group were susceptible to degradation in the implemented scheme and degraded to PG compounds with the same kinetic parameters. Therefore, the observed effect of improved CD yield predictions above T3 is rather generic than specific for a given compound. Overall, the accuracy losses by the model up to T3 were suspected to be related to imperfections in the applied primary kinetic scheme, while above T3, inaccuracies were suspected to be related to the applied secondary kinetic scheme. However, the latter should also be considered as a derivative of the primary kinetic scheme rather than an imperfection of the secondary scheme alone.

The model strongly overpredicted CO₂ at T5 ($T_G = 840$ °C) for both particles (almost double the experimentally obtained yield). It was a strong overprediction, especially considering that the experimental yield was already elevated in comparison to other studies (details in Part 1). Such a high overestimation was not obtained in a similar study.²² In the mentioned study, LVG and XYL formation reaction was suppressed, and CD compound formation was enhanced instead. In the applied secondary reaction scheme used in this work (see Table S4), the main product of secondary degradation of LVG and XYL was CO₂, while the main product of the CD compounds degradation was CO. Therefore, higher LVG and XYL formation and proportionally lower formation of CD compounds led to elevated formation of CO₂, hence to strong overprediction of its yield. As presented in the study by Ranzi et al., the secondary degradation of carbohydrates should lead to the formation of CO/CO₂ in a ratio of ca. 6 to 1 (from 700 °C onwards).¹⁷ Therefore, it can be stated that the secondary reaction scheme proposed by Mellin et al., is invalid for the representation of secondary reactions of carbohydrates above 500 °C.⁸⁵

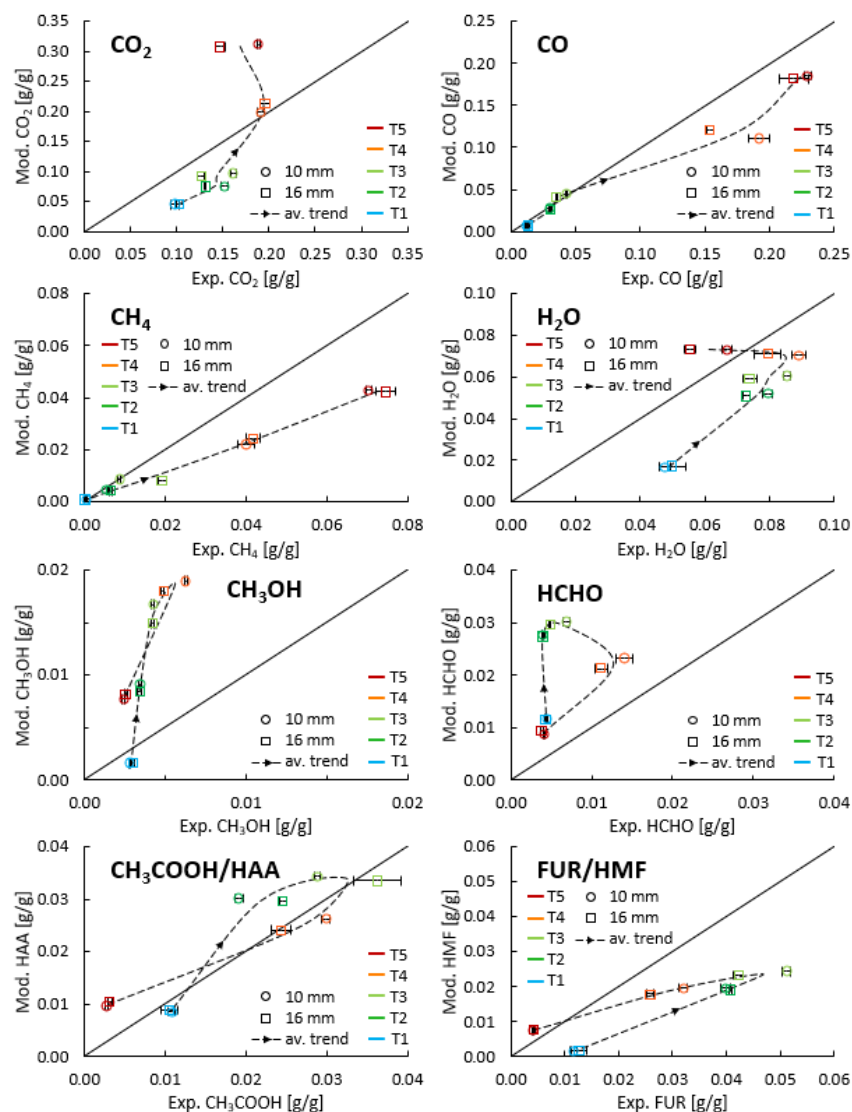


Figure 7. Comparison of yields of specific compounds (CO_2 , CO , CH_4 , H_2O , CH_3OH , HCHO , $\text{CH}_3\text{COOH}/\text{HAA}$, and furfural/HMF) between modeled (SCR_R) and experimental data for both particle lengths and all investigated scenarios.

The H_2O yield predicted by the model for scenarios T1-T4 was much lower than indicated by the experimental results. Such results were obtained despite the implementation of the secondary charring reactions into the model, which increase the H_2O yield (see Table S3). Moreover, as discussed in Part 1, the experimentally obtained H_2O yields could be underestimated compared to other studies. Therefore, it can be stated that the implemented primary kinetic scheme led to a

severe underprediction of H₂O yields. The yield of CO₂ and H₂O between T4 and T5 showed a similarity in trend. In both cases, the experimental data indicated a reduction of their yield at higher temperatures, while the model indicated an increase. Therefore, it is suspected that additional reactions, e.g., gasification with CO₂ and H₂O, may be required to be implemented at T5 ($T_G = 840^\circ\text{C}$) to increase the accuracy of the model prediction. The presence of H₂O gasification reactions would agree with the experimental data where H₂O yield was reduced between the T4 and T5 scenarios (significantly higher reduction for the 16 mm particle than the 10 mm one). The yield reduction observed in the experimental data could also be assigned to the consecutive reaction of CO₂ and H₂O with other vapors in the reactor zone, instead of reacting with the carbonaceous solids. A conclusive statement would need to be derived from a more detailed study. Figures S9 and S10 present modeled and experimental time release profiles of selected compounds for all scenarios, for the 10 mm and the 16 mm particle. The most noticeable difference between modeled and experimental release profiles is the premature start of the modeled release of vapors, which occurred in all scenarios. The results were in agreement with the premature start of mass loss in the modeled results shown in Figure 1 and Figure S7. The obtained release profiles matched fairly well with the experimentally obtained profiles. However, the shape and magnitude of the release profile of specific compounds in scenarios T1-T3 differed noticeably between modeled and experimental results. Therefore, aside from the premature conversion start and inaccuracy induced by the secondary reaction scheme, the modeled release profiles and total yields indicated inaccuracy in the prediction of the release of specific vapors. This is suspected to be caused by imperfections in the primary reaction scheme, as a similar suspicion can be found in other studies.²²

3.3. Intrinsic secondary reactions

The simulation of the particle conversion in scenarios T4 and T5 was conducted for temperatures exceeding 500 °C. Therefore, it was presumed that the impact of secondary reactions on vapor yields and composition would be very clear. The comparison of differences between the PG yield obtained with the NO_SCR and SCR models is presented in Figure 8. From the results, it can be observed that the effect of the intrinsic secondary reactions on the yields is noticeable. However, on average, for both particles and all scenarios, the secondary reactions caused an increase of PG by ca. 0.3 wt.% with a corresponding reduction of CD+T yield. Therefore, besides being noticeable, the outcome of the intrinsic secondary reactions cannot be assessed as severe. Additionally, the effect of particle length on the secondary vapor reactions was even less pronounced despite being noticeable. A clear trend was observed only between scenarios T4 and T5, where the PG yield was higher, on average, by 0.02 wt.% for the 16 mm particles, which is a very minor value (if not negligible).

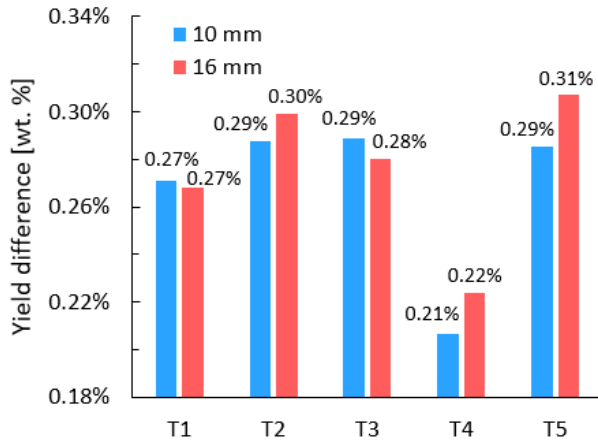


Figure 8. Comparison of difference between PG yield obtained with NO_SCR model and SCR model for both particles and all investigated scenarios.

In Figure 8, aside from scenarios T4 and T5, the intrinsic secondary effects were also present for scenarios T1-T3, where it was suspected that the secondary effect would not be effective given the low conversion temperature (< 500 °C). Such a result seems to be in contradiction to the

experimental studies on secondary vapor reactions.¹⁷ In Figure 9, the modeled masses of soot for both particles and all scenarios obtained with the SCR model are presented. The masses of formed secondary carbon/soot indicate the cumulative effect of the secondary reactions of vapors within the particle. Intuitively, it was suspected that soot would not form below 500 °C, and above that temperature, an elevated soot content should be observed. As can be observed in Figure 9, the modeled results also indicate the formation of secondary carbon/soot at temperatures significantly below 500 °C, like in scenario T1, where the temperature of conversion was close to 300 °C. However, Figures S11-S13, which present the distribution of the conversion-related parameters, and Figure S14, which presents the distribution of soot (carbon originated in secondary reactions) in 16 mm particles for scenarios T3-T5, show otherwise. It was also suspected that the favorable conditions for secondary reaction occurrence would be present in the zone close to the top/bottom surface of the particle. Nonetheless, the modeled results showed a substantial soot accumulation in the outer layer of particles for scenarios T4 and T5, while for scenario T3, the soot was more homogeneously distributed. From the figures, it can be derived that for scenarios T4 and T5, the conversion took place in a layered manner, so with a rapid formation of vapors along an elevated vapor velocity (see Figures S12 and S13). This also resulted in the formation of a strong cooling effect, which reduced temperature in post-conversion parts of the particle.

To further investigate the formation of soot in relation to the implemented secondary reaction scheme, a CFD-based analysis of vapor retention time for scenarios T3-T5 for the 16 mm particle was provided in Figure S15. For scenarios T4 and T5, the post-conversion area had an insufficient temperature and along with the short RT in those areas, did not allow for an extensive conversion of vapors in the secondary reactions. For scenarios T1-T3, the release of vapors was slower, with a weaker cooling effect due to a lower and more evenly distributed heating rate. Less pronounced

convective transport of vapors caused an elevation of the RT in post-conversion areas. However, in scenarios T1-T3, the temperature in the post-conversion areas did not exceed 500 °C, which is considered as a threshold value for secondary reactions of vapors to occur.

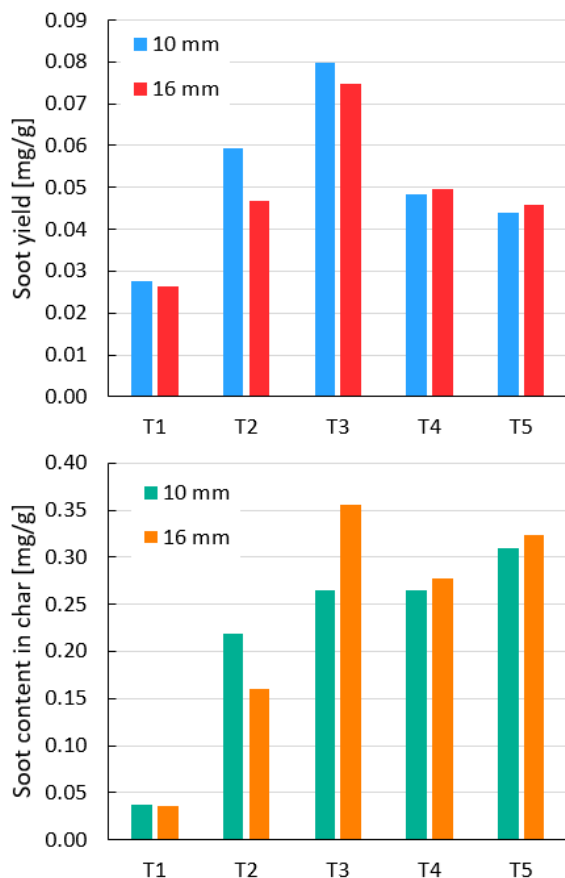


Figure 9. Modelled results of soot formation in SCR model for both particles and all investigated scenarios, top – soot yield per initial biomass, bottom – soot content in the final chars.

It must be pointed out that in the implemented secondary reaction scheme, soot is formed only from the lignin-originated vapors and not via the polyaromatic hydrocarbon route. Therefore, further elaboration will be made in relation to lignin degradation and the fate of vapors derived from it. In the implemented primary kinetic scheme, conversion of lignin starts from ca. 260 °C, while it finishes at ca. 500 °C. From the implemented secondary reaction scheme, it can be derived

that 80 wt.% conversion of volatiles susceptible to undergo secondary reactions can be obtained for a residence time of 0.5 s at 840 °C (T5), 10 s at 500 °C (T3), and 320 s at 300 °C (T1). For scenarios T1-T3, the release of lignin-derived vapors was stretched over time, which led to lower velocities of lignin-derived vapors within the particle. Then, despite the lower temperature, the vapors in relation to the implemented secondary reaction had a sufficient RT to undergo conversion into soot. The latter was suspected to be the main cause of the higher and more homogeneous soot distribution, e.g., in scenario T3 ($T_G = 480^\circ\text{C}$) in comparison to scenarios T4 and T5 (see Figures S11-S14). The modeling results indicated that in the investigated scenarios, the intrinsic secondary reactions of vapors did not take place similarly to flow-through catalytic reactors where the char in the hot, post-conversion zone works as a “catalyst”. Therefore, the modeled mechanism of soot formation for conversions above 500 °C was different than expected. As shown in Figure S15, in scenarios T4 and T5, the release of the lignin-derived vapors, especially around 400 °C, was very rapid. It led to their efficient evacuation with a short RT (weak secondary conversion of vapors to soot). Then, the residual conversion of lignin derivatives did not evolve a vast amount of vapors, which did not induce their high velocity and corresponding cooling effect. The outcome of such a situation was the acceleration of the heating rate in post-conversion zones. In the end, the residual lignin-derived vapors had a sufficient RT and temperature to undergo the conversion in secondary reactions. Considering that the final temperatures were higher for scenario T5 than T4, the rapid release of vapors in scenario T5 was more profound than in scenario T4. That was the suspected cause of the lower soot yield (per initial biomass) in scenario T5 than in scenario T4.

The modeled results of soot formation can be generalized into a statement that with the presence of a sufficiently high heating rate, so with layered conversion (like for the T4 and T5 scenario),

the high rate of vapor release will not allow for a high extent of intrinsic secondary vapor reactions (due to high velocity of the vapors and the corresponding cooling effect). That is especially true for sufficiently small particles. Contrarily, in conversion with a homogeneously distributed heating rate (like in the T1-T3 scenario), the release of the vapors is steadier, leading to higher vapor RT within the particle. Then, if the temperature is sufficiently high, the secondary reactions are more likely to occur within a particle. At the end of the conversion, regardless of the form of conversion (homogeneous or layered), a part of the vapors stays in the particle. The late-stage vapor formation does not induce enough overpressure to create sufficiently high convection, resulting in incomplete evacuation of vapors from the inner part of the particle. In such a case, the residual vapors can escape from the particle only via a diffusion mechanism. However, it is suspected that when temperature conditions are favorable and residual vapors, susceptible to secondary reactions, will most probably undergo secondary degradation prior to diffusion-driven release.

3.4. Effect of permeability

The effect of the model's permeability description on the outcome of the simulation was more visible for the 16 mm particle model than for the 10 mm one, so further discussion will relate to the 16 mm particle only. In Figure 10, presents the modeled volume-averaged permeabilities in the longitudinal (z) and radial (r) directions for CP, VP, and VPT models is presented for scenarios T3-T5 and for the 16 mm particle.

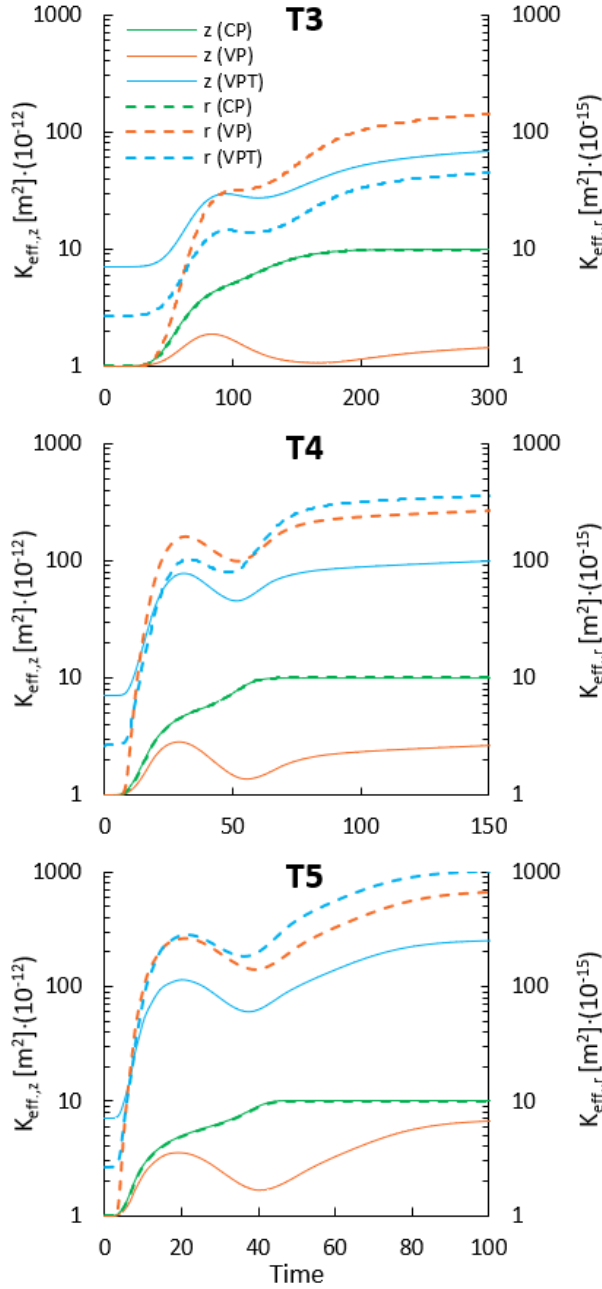


Figure 10. Comparison of modeled volume-averaged longitudinal and radial permeability in a 16 mm particle for scenarios T3-T5 obtained with CP, VP, and VPT models.

The permeability description implemented into a model significantly affected the final, effective values of permeability despite the similarity in the initial value. The permeability in the CP model depended on conversion only, so aside from the magnitude, profiles of changes in permeability

with conversion in longitudinal and radial directions were the same. The Kozeny-Carman equation was implemented in both VP and VPT models, but the models differed in initial values of the pore diameter (wood and char) and in variables on which pore size change depended (conversion and temperature, respectively). As it can be noticed in Figure 10, VP and VPT models show very similar profiles of permeability in the radial direction. However, the models differed significantly with the profiles in the longitudinal direction (especially magnitude). Therefore, it can be stated that the difference in pore size description had a noticeably lower influence on the final permeability in the radial direction than in the longitudinal direction. In general, correlating the permeability with porosity and pore size (VP and VPT model) led to lower final longitudinal permeability and much higher radial permeability for all scenarios in comparison to results from the CP model (e.g., for scenario T5, the VP model resulted in the $\times 0.68$ lower longitudinal permeability and $\times 70$ higher radial permeability than the CP model).

The total release of vapors for CP, VP, and VPT models, for scenarios T3-T5 and for the 16 mm particle are presented in Figure 11. Differences in the permeability description affected the profiles, but their influence was not strong. The effect of the permeability description was more noticeable for scenarios T4 and T5, so when the cooling effect was more profound. The release profiles from the CP and VPT models were very similar despite the Kozeny-Carman equation being implemented only in the latter model, and the overall magnitude of the permeability in both directions being different. Only profiles from the VP model showed noticeable differences to the CP and VPT model, where the latter had a similar permeability description as the VP model. In Figure 11, it can be observed that the description applied in the VP model led to a prolonged, model-predicted, release of vapors in the late stage of conversion in comparison to the CP and VPT models.

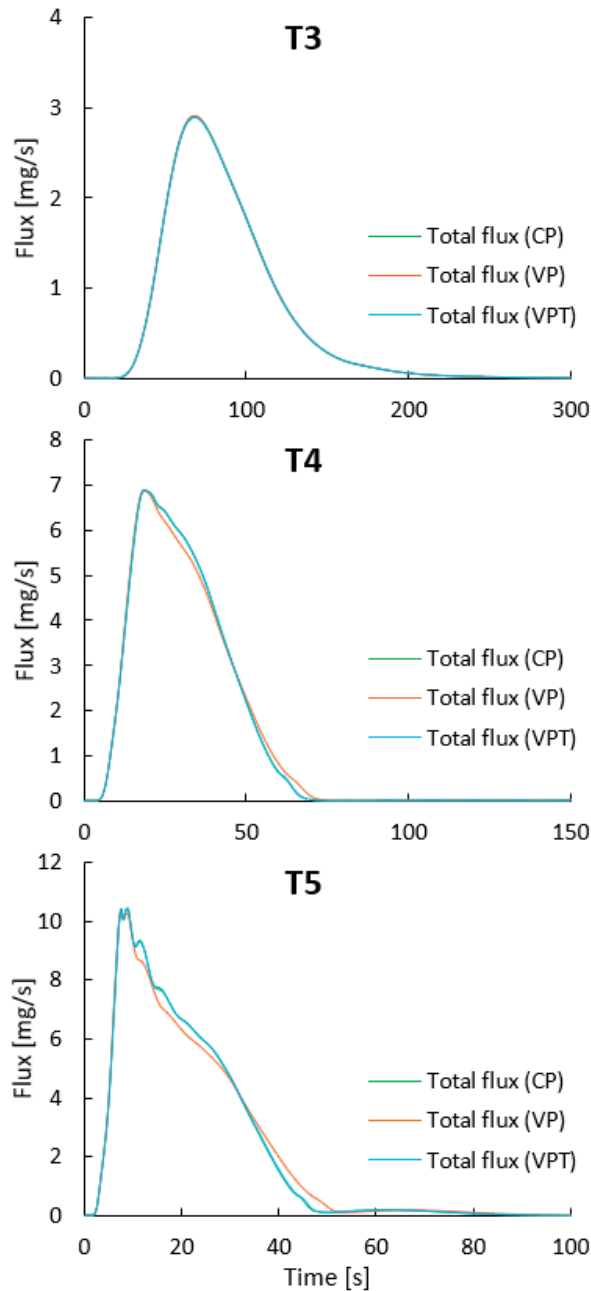


Figure 11. Comparison of modeled profiles of the total release of vapors in the 16 mm particle for scenarios T3-T5 obtained with CP, VP, and VPT models.

Figure 12 presents the TC, TST, and pressure profiles for models CP, VP, and VPT for scenarios T3-T5 for the 16 mm particle. Similarly to the total release profiles, the TC and TST profiles were more affected by the permeability when the cooling effect was more profound (scenarios T4 and

T5). The lower longitudinal permeability in the VP model than in the CP and VPT models, in scenarios T4 and T5 led to a slower increase of the center temperature. For the VP model, a weaker and delayed impact of the cooling effect can also be observed, especially for scenario T5. Despite the hardly noticeable differences in the release profile (Figure 11), the pressure profiles at the particle center were affected by all descriptions as presented in Figure 12. The difference between the CP and VPT models was minor, especially regarding the maximum pressure reached in the center of the particle. The greatest difference in the peak pressure was observed in VP model results, where the peak pressure was ca. 2 times higher than in the results from CP and VPT models (in scenario T5). In the VP model, the cause of an elevated pressure buildup, as well as a weaker cooling effect, was related to lower permeability during the conversion. Moreover, lower permeability had an impeding effect on the heating rate of the particle (opposite to assumed acceleration due to weaker cooling effect). It is suspected that such an outcome was related to an accumulation of the vapors within the particle, which resulted in an elevated value of the averaged specific heat.

The modeled results of the soot content in chars in relation to the permeability description for scenarios T4 and T5 for both particles (10 mm and 16 mm) are presented in Figure S16. As it can be noticed in Figure S16, the permeability description also had an impact on the soot formation. While for scenario T4, the effect of permeability description was negligible, the effect was well visible for scenario T5, regardless of the particle length. This indicates that the severity of the conversion in the layered mode enhances the effect of the permeability on the soot formation. For both particle lengths, the VP model in scenario T5 resulted, on average, in higher soot concentration by 0.022 ± 0.004 mg per g of char than the CP and VPT models. As it can be noticed in Figure 11, the VP model is characterized by the lower longitudinal permeability among other

investigated models, so in the direction of the highest release of vapors from the particle. Reduction in permeability hinders the release of vapors from particles, which is the main cause of the reduction of the vapor flux (Figure 12). Such an effect has as a consequence as the accumulation of the vapors within the particle, so the formation of elevated pressure and less pronounced cooling effect (and, possibly, less rapid heating rate in the center of the particle), which can be observed in Figure 13. Along with the accumulation, the RT of vapors within the particle increases, which has an accelerating effect on the conversion of vapors in secondary reactions. As less pronounced in investigated cases, but still significant, especially for the longer particle, is the impact of the lower permeability on the cooling effect. When the post-conversion zone of a particle is not drastically cooled due to convection (hindered by low permeability, especially of char), it may achieve a sufficiently high temperature to allow for a rapid vapor conversion. Then, the high temperature of the post-conversion zone, along with a low velocity of released vapors, may allow for extensive secondary reactions within the particle, so an elevated soot formation.

The obtained results show that the changes in the permeability implementation have a non-negligible effect on vapor retention time and consecutive phenomena related to it. In the investigated scenarios, the particles were relatively short, which resulted in quantitatively low modeled amounts of soot. This may lead to a presumption of the low relevance of observed results. However, it is suspected that with the increase in particle length, the impact of permeability and its description will have a more profound effect. This could be especially true when the permeability affects the temperature of the post-conversion zone and leads to a temperature above 500 °C while the biopolymers still degrade in the particle center. The conducted study does not allow for an objective confirmation of the postulated hypotheses. Therefore, such confirmation will need to be obtained in consecutive studies.

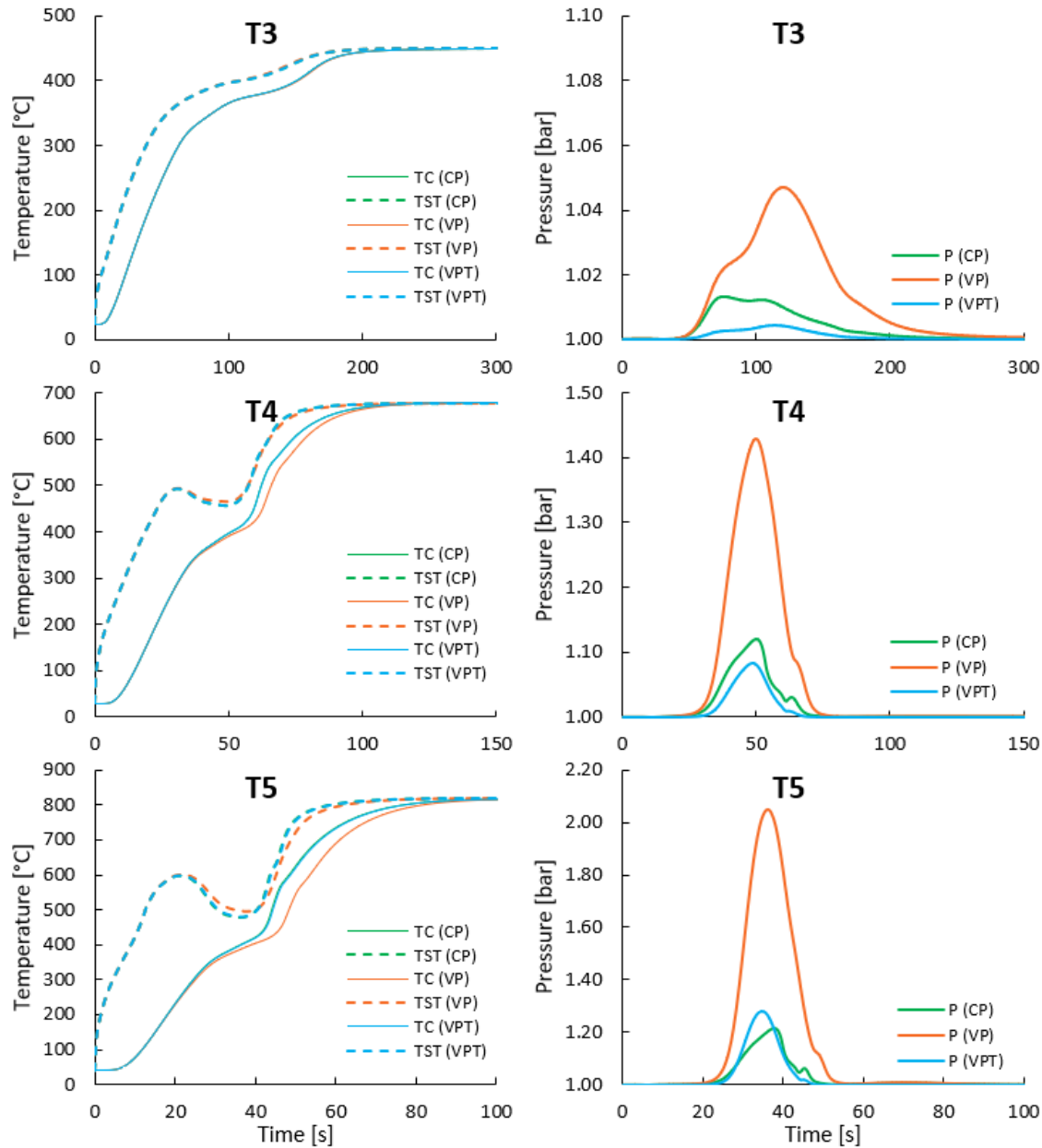


Figure 12. Comparison of profiles of the 16 mm particle for scenario T3-T5 obtained with the CP, VP, and VPT models; left – TC and TST; right – pressure at the center of the particle.

Another observation from the study is that longitudinal permeability may have a limiting effect on the movement of vapors, but only to a certain threshold value. The longitudinal permeability in the CP and VPT models differed, while both were significantly higher than in the VP model. Also,

both CP and VPT models for all scenarios showed a high similarity in model-predicted profile change of resulting parameters, especially for pressure. Therefore, it is suspected that the vapor formation rate is the only limiting effect on vapor velocity when the longitudinal permeability is sufficiently high. Contrarily, when the longitudinal permeability is sufficiently low (under a certain threshold value), it significantly affects convective vapor movement. It is presumed that the range from which the effect of the permeability will become relevant depends on the conversion rate (e.g., lower for scenario T3 than T5), since it still is a leading factor causing pressure evolution.

3.5. Insights from the study

The implementation of the geometric deformation had a low, almost negligible, effect on the model-predicted profiles of center temperature and mass, hence the conversion route (see Figure 1). Presumably, that was the main cause of a wrong assessment of the importance of the geometric deformation effect in the study by Maziarka et al.¹¹ As obtained results show, the phenomenon had a significant effect on the temperature distribution within the particle domain via affecting the cooling effect. More importantly, not implementing geometric deformation led to an inaccurate prediction of bulk density and porosity. In general, in the established model, geometry deformation was considered to be a volumetric phenomenon. However, it is not certain that the phenomenon occurs in such a manner, especially when conversion occurs in a layered way.^{39, 40} If geometric deformation occurs in a layered way, that significantly impacts the dynamic changes of parameters in that specific point of the particle domain (i.e., where layering occurs). In the end, the dynamic changes of parameters may lead to the same final value, but via a different route, and since the conversion is time-dependent, it will influence the overall outcome. Therefore, without geometry deformation, it is not possible to accurately represent changes in the thermal conductivity and

vapor permeability. Contrarily, if the deformation is appropriately implemented, the precision of the outcome of the model will increase due to a more accurate representation of heat transfer and vapor transport.

One of the apparent factors leading to an imperfection of this study is the possible incompatibility between real thermal conductivity parameters and those implemented in the model since the latter were sourced from literature. In this area, the factor that could introduce the strongest uncertainty was the thermal conductivity of the char, whose values are rarely reported in the literature. As observed, the mass change profile did not perfectly match the experimental results (premature start). The model-predicted results for scenario T1 (ca. 300 °C) especially show the greatest inaccuracy due to a premature start. In other modeling studies, such an effect can also be observed.^{29, 41} Additionally, despite the model's implementation of low values of the secondary charring reactions, the model overpredicted the char yield. The cause of this inaccuracy can be related to the use of uncertain values of bio-component concentration in the feedstock and the neglect of the influence of extractives. However, a recent study by Lu et al. suggests that omitting LIGC or TANN components in the primary reaction scheme may improve the accuracy of predicting the char yields.⁹⁰ Regardless, the model showed an overall high accuracy in the prediction of the char yield and its elemental composition. It was observed that, to some extent, the model overpredicted the carbon content and underpredicted the oxygen content of chars obtained above 500 °C, which is less likely related to the feedstock's initial composition. Similarly to this study, inaccurate prediction of the elemental composition of char above 500 °C was observed in the study by Debiagi et al.²¹ It is suspected that this is related to an improper description of the degradation of lignin derivatives and metaphase in the primary kinetic scheme.¹¹

In general, the applied primary kinetic scheme can be pointed out as another factor which adds to the accuracy loss of the model, as it was already indicated in other studies (especially TGA-based foundations of the CRECK scheme and simplification in the included species).^{22, 29} The problem is visible since none of the previous single-particle models showed an accurate prediction of yields of specific compounds regardless of using the CRECK or RAC scheme.^{22, 29, 41, 43, 90} Even a very recent study, supported by the CRECK modeling group, indicates the need for an improvement in the scheme.⁹³ Therefore, it is critically important (especially for new researchers of the subject) not to assume that a model theoretically unburdened with biases related to an inaccurate description of thermo-physical changes will lead to an accurate prediction of vapor release profiles (and other profiles). In that regard, an improvement to the primary kinetic scheme should be strongly considered. Nonetheless, it should be highlighted that the scheme in the current state shows satisfactory predictions of the yield of lumped product groups or even specific compounds.^{43, 90} Therefore, it can be stated that the CRECK scheme and its derivatives can work satisfactorily in basic investigations where accurate release profiles or yields of specific organic compounds are not of particular interest.

The imperfections induced by the primary degradation scheme transfer to the shortcomings of the secondary vapor reaction schemes. However, the imperfection of the implemented secondary reaction scheme itself can have a much more substantial impact on the precision of the results (for both, low-temperature and high-temperature simulations). The POLIMI kinetic mechanism of secondary pyrolysis reactions, developed by the CRECK research group, which is deeply embedded in chemistry (chain radical reactions), presents a more comprehensive option than the relatively straightforward scheme presented by Mellin et al. (implemented in this study).^{22, 85} However, there is a trade-off between those two approaches since the POLIMI scheme is based on

a vast number of intermediate compounds, hence a corresponding number of equations.¹⁷ Implementing such a complex chemical scheme will lead to an elevated computational burden for the CFD model, especially considering the relation between vapors and convection-induced effects. However, without the use of detailed and accurate kinetic schemes, the knowledge about the relation between secondary vapor reaction effects and structure development will not advance. When development in the area of intrinsic primary reaction schemes is provided, and the model is equipped with the detailed scheme of secondary reactions (along with all other components), then an attempt to conduct its validation should be made. Assessing it with newly obtained comprehensive experimental data would be very beneficial. However, it can be suggested to use this study data (Part 1) or the study of Anca-Couce et al.²² for a comprehensive assessment of model performance and Gauthier et al.²³ for a detailed validation of the performance of the implemented kinetics (for both, primary and secondary reactions).

Moreover, the implementation of the POLIMI scheme will allow for an in-depth study of the PAH formation and soot deposition, which is very relevant to the investigation of structural development. Here, it needs to be pointed out that only secondary reactions that occur within the particle are relevant for soot deposition. Additionally, future studies should be strongly considered to distinguish between soot formation and its deposition. It is suggested to treat the formation of soot as a reaction in the gas phase only, and the soot deposition (and its incorporation into the carbonaceous structure) as a heterogeneous, gas-solid phase reaction. So far, an elegant description of the soot formation and deposition within the structure is missing, so in the future, it may be beneficial to find such a description and try to couple it with the structural development of chars. Despite the imperfection of the Mellin et al. scheme presented in this study, its results related to the secondary reactions of vapors obtained were deemed useful for suggesting further development

of the reaction scheme. As observed, the implemented kinetic scheme led to model-predicted secondary reactions of vapors at low temperatures (below 500 °C). It may be crucial for anhydrosugars, which evolve at lower temperatures and constitute the major share of the primary pyrolysis vapors. It is well proven that an increase of the particle size leads to elevated char formation at the expense of the condensable products.⁴⁻⁶ In the RAC kinetic scheme, this relation is represented via the secondary charring factors (“ x ”), which are usually calibrated to the investigated model. However, uncoupling the RAC scheme from the adjustable charring factors may be beneficial, as was already suggested by Anca-Couce et al.²² However, instead of coupling the reactions to the bio-components, it is proposed to introduce a general kinetic scheme with a low-temperature (long retention time) degradation of evolved heavy vapors such as levoglucosan, by e.g. cross-reticulation and condensation reactions.¹⁷ In such a scheme, the low-temperature secondary reactions would be directly coupled with the concentration of the vapors, so it would be indirectly coupled with the heating rate, as was also already postulated.⁹ It cannot be omitted that in future development, the catalytic effect of the inorganics (potassium) should also be accounted for.⁹ That may be especially relevant when vapors escape through post-conversion zones where the inorganic concentration is elevated. Overall, it should be pointed out that the POLIMI scheme accounts only for the reactions in the gas phase. Therefore, even when implemented, the phenomena related to the gas-solid reactions and the influence of the inorganics will still be missing in the model.

Another observation that was made from the result obtained with the Mellin et al. scheme was the presumed impact of vapors on the structure. As shown in Part 1, the 16 mm particle showed a lower pore volume in the micropores range (0.35 nm – 2 nm) for all investigated scenarios, including temperatures in the 300 °C and 400 °C range. The low-temperature degradation of vapors

could be indicated as a factor that led to the obtained experimental result. Conversion of the 16 mm particle produced a higher absolute amount of evolved vapors than the 10 mm particle. Additionally, the vapor retention time in the 16 mm particle was longer than the 10 mm particle due to particle length but also due to lower heating rate. Since the soot in the implemented secondary reaction scheme is only formed from the lignin-derived vapors and not from anhydrosugars, the provided hypothesis needs to be validated in additional studies.

The external secondary reactions (in the reactor area) were shown to be necessary to be implemented into the model for an accurate prediction of the conversion yields in investigations where the temperature exceeds 500 °C. The obtained results confirm that intrinsic secondary reactions of vapors, including soot formation at higher temperatures, critically depend on their transport within particles. Since the permeability is directly coupled with the retention time of vapors, the appropriate description of permeability in the modeling studies is highly significant. As shown in this study, tuning the permeability led to a different outcome in terms of the soot yield. Therefore, the selection of the most accurate permeability model is very relevant to achieve the required precision of the effect of the secondary reactions of vapors. Additionally, the study indicated that permeability has a non-negligible effect on temperature distribution, hence the primary degradation in specific scenarios (when layered conversion occurs). In general, the objective assessment of improvement or loss in accuracy due to the implemented description of permeability cannot be made with an appropriate validation dataset, which has to be obtained experimentally. In the literature, information about experimentally assessed pressure profiles and char permeability with a distinction of conversion temperature is scant. Since permeability is a resultant property derived from the wood structure, it is influenced by all structure-related parameters (i.e., species, type of tissue, location, and growth condition). As shown in this study,

using the Kozeny-Carman equation alone (a more refined approach than direct implementation of values) did not significantly change the model-predicted vapor movement. This was true even when the parameters implemented into the Kozeny-Carman equation were derived from experimental measurements (via mercury porosimetry). Studies that advanced the understanding of the structural changes of wood with the conversion temperature can be found in the literature.^{27, 36, 56-58} An excellent approach was shown in a recent study by Crowley et al., who estimated the structural parameters of wood and its chars from 3D X-ray computed tomography (XCT) results.⁵⁹ However, more fundamental research still needs to be conducted to provide a reliable and repeatable relation between wood/char structural changes and corresponding permeability changes during conversion.⁵⁸ When successful, such studies should allow for the identification of critical parameters of vapor transport and the development of a mechanical model. Another step would be to provide a relatively simple measurement/correlation for the permeability parameters to allow for the wide use of the mechanistic model, which may not be an easy task (if possible).

4. Conclusions

The models presented in this study are based on and validated with a very comprehensive dataset obtained in Part 1 of this study. The established models allowed for a very accurate prediction not only of the yield of lumped groups of products, but also the yields of specific compounds and solid product composition with satisfactory accuracy. The average prediction error for temperatures between 400 °C and 840 °C for char was 2.8 ± 1.1 wt.%, for the condensable fraction was 6.5 ± 3.3 wt.%, and for the pyrolysis gas was 4.1 ± 1.9 wt.%. The single particle models where the conversion is conducted at a temperature sufficient to induce secondary vapor reactions must include the conversion in the reactor zone. Otherwise, the prediction of vapor composition

becomes inaccurate. The model indicated an elevated CO₂ formation at temperatures exceeding 500 °C. Additionally, it was identified that the cause of such an outcome was related to the imperfection of the applied secondary reaction model, in detail, with an inappropriate indication of the products of the cracking of the anhydrosugars.

The established single particle model, possibly for, as the first, was able to prove a very accurate prediction of the relevant structural properties of the wood-derived chars (e.g., bulk density and porosity). The average prediction error over the mentioned temperature range of bulk density was $31 \pm 15 \text{ kg/m}^3$, and porosity was $1.8 \pm 1.1 \text{ vol.}\%$. The presented model correctly simulated the evolution of structural parameters over a wide range of conversion temperatures. It unlocked the identification of the problems related to the formulation and implementation of other parameters that are relevant for future accuracy improvements. It was shown that geometric deformation is an inseparable feature of the model since it has a major effect on implementing the more developed thermal conductivity and permeability descriptions.

Various descriptions of permeability changes (e.g., use of the Kozeny–Carman equation) had a minor influence on the vapor outflux. However, the changes in the description had a non-negligible effect on the soot formation, especially at 840 °C. The results indicate a need for further improvement of the primary degradation model to increase the accuracy of the effect of soot formation on the char structure.

Improvement of the primary biomass degradation scheme is critically necessary since the one used in this study may be only suitable for accurately estimating the lumped product groups, not the individual vapor-phase compounds. Also, a detailed investigation of the PAH and soot formation is not possible with a basic secondary vapor reaction scheme. For that reason, in future studies, more advanced reaction schemes like the POLIMI kinetic mechanism should be applied. However,

the issue related to the reliable implementation of the permeability changes should be addressed before, since this feature impacts the residence time of vapors and consequently their secondary reactions.

A general outlook from the obtained results and literature survey is that further fundamental studies are strongly advised. The imperfections of the established kinetic and single particle models have already been indicated to a large extent, so the route to be taken is known. It has to be highlighted that future studies should not start from scratch but from already established models. Therefore, using a few, selected software environments would be beneficial. In view of the increase in the demand for tailor-made bio-based products, high accuracy of prediction of only basic parameters may become insufficient in the near future. So, the next models should focus on precisely predicting more parameters instead of bulk assessments of a few.

ASSOCIATED CONTENT

Supporting Information 1 – CFD model details and applied equations, derivation of newly proposed auxiliary equation, additional modeling results (PDF)

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Notes

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