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Understanding the torrefaction of woody and agricultural biomasses through their extracted macromolecular components. Part 2: torrefaction model

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Abstract

A new torrefaction model was proposed for predicting solid mass loss in torrefaction as a function of biomass main macromolecular composition and type, as well as on the operating conditions. To do this, solid degradation kinetics were modelled following a 2-successive reaction scheme for each macro-compound and the additive modelling approach through biomass macromolecular component behavior in torrefaction proposed by Nocquet et al. (2014). The use of extracted fractions from different woody and agricultural biomass species (ash-wood, beech, miscanthus, pine and wheat straw) instead of commercial compounds increased the accuracy of the prediction of solid kinetics in biomass torrefaction. The validation of the proposed model with 9 raw biomasses in torrefaction showed an accurate prediction for woods, while the prediction for agricultural biomasses was acceptable.

Highlights

- A torrefaction model of solid kinetics dependent on biomass type was proposed.
- Composition in cellulose, hemicelluloses and lignin were the model parameters.
- Two levels of detail in biomass macromolecule behaviour description were included.
- Accurate prediction achieved for woods in torrefaction.
- Acceptable prediction achieved for agricultural biomasses in torrefaction.

Keywords

- Biomass
- Torrefaction
- Solid kinetics
- Polysaccharides
- Lignin

Abbreviations

E: activation energy (J/mol)

ε_a: mean absolute error

ε_r: mean relative error

F: function minimized by least square fitting for the kinetic parameters determination

k: kinetic constant (s^{-1})

k_0: pre-exponential factor (s^{-1})

R: ideal gas constant (8.314 J mol^{-1} K^{-1})

T: temperature (K)

t_i, T_i: instantaneous values of time and temperature

$m_j(t_i, T_i)$: instantaneous remaining solid mass of *j*, where *j* can be replaced by C («cellulose»), C^I («cellulose I»), C^{II} («cellulose II»), $DMSO_r$ («DMSO residue»), exp (experimental), Glu (glucan), H_1 («hemicelluloses 1»), H_2 («hemicelluloses 2»), H_T («total hemicelluloses»), L («lignin»), mod (model prediction), rb (raw biomass). In all cases $m_j(0\ s, 273\ K) = 1$

$x_{j,k}$: instantaneous mass fraction of *j* in *k* at t = 0, where *j* and *k* can be replaced by C («cellulose»), C^I («cellulose I»), C^{II} («cellulose II»), $DMSO_r$ («DMSO residue»), Glu (glucan), H_1 («hemicelluloses 1»), H_2 («hemicelluloses 2»), H_T («total hemicelluloses»), L («lignin»), rb (raw biomass)

wmf: weight-moisture-free basis

1. INTRODUCTION

Torrefaction is a thermochemical conversion treatment suitable for dry biomasses, occurring between 200 and 300 to 350 ºC under a default-oxygen atmosphere from several tens of minutes to one hour. As a result, a torrefied solid is produced, whose properties are close to those of coal in terms of heating value, flowability, grindability and hydrophobicity. At the same time, gaseous products are released, including permanent gases, water and volatile species [1].

The proportion and the properties of the torrefied solid and the gaseous species produced are mainly dependent on temperature and time [2–4]. Furthermore, biomass main macromolecular composition in cellulose, hemicelluloses and lignin strongly impacts the yield and the nature of the torrefaction products [3,5–7]. The influence of extractives and ash present in biomass still remains controversial in the torrefaction temperature range [8–10]. While extractives are supposed to be mostly released below 200 ºC [11,12], inorganic elements might catalyze thermochemical conversion, but rather at higher temperatures corresponding to pyrolysis or under gasification conditions [13–15].

Up to know, the proposed modelling schemes for pyrolysis and torrefaction were based on a single or several consecutive or parallel reactions, either for biomass or for its macromolecular components [16–20]. A review of the models proposed in literature is provided in Table 1. Mild pyrolysis models were also considered as torrefaction temperature range partly overlaps the lower pyrolysis temperatures [21–23].

First pyrolysis models were focused on cellulose behavior [24,25]. They were based on a first formation step of a called “active cellulose”, whose nature still remains controversial [16]. A recent study has associated the activation of crystalline cellulose to the formation of reducing end groups in this polymer [26]. Shafizadeh and Chin proposed the first biomass pyrolysis model in 1977, which consisted of a global scheme of three competitive parallel reactions, the main products being gas, liquids (tar) and char. Then, Koufopanos et al. modified this model by adding an intermediate mechanism about gas and condensable species formation [27].

Pyrolysis model development was typically based on lumped components, for which kinetic parameters were fitted with experimental data [16]. To do this, a first order reaction rate was typically supposed for a sequence of simultaneous and/or consecutive reactions of known or representative stoichiometry. The kinetic

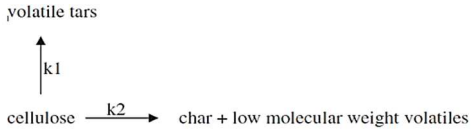
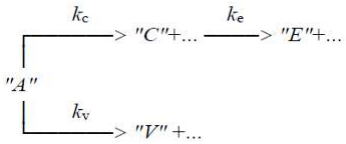
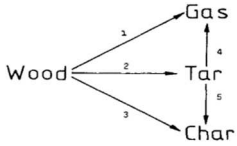
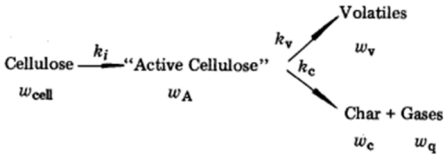
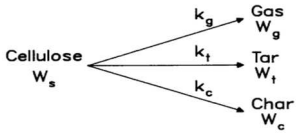
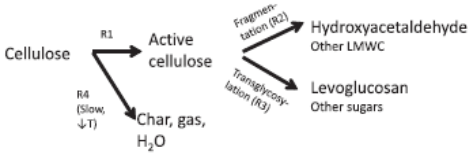
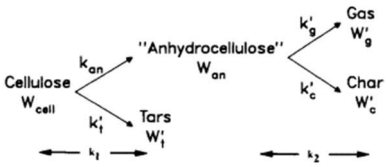
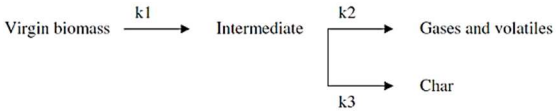
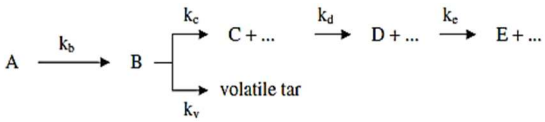
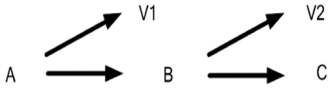
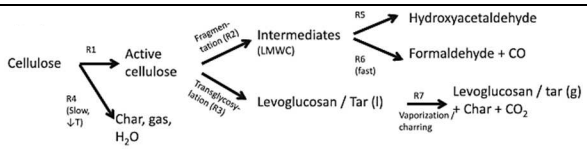
scheme of 2-succesive-step model developed by Di Blasi and Lanzetta [28] was one of the most frequently used. It is based on the competition between the formation of volatiles and solid products at each step of the reaction. Even if it was initially developed for xylan pyrolysis, it was then applied to biomass and other macromolecular components pyrolysis [7,29–32] and torrefaction [7,33]. Bates and Ghoniem proposed to calculate the volatile species composition for each reaction of the Di Blasi scheme for willow [34].

Kinetic pyrolysis models based on lumped components were progressively developed to increase the level of detail of the description of biomass transformation. In this sense, molecular-based kinetic models were developed, in parallel to kinetic models based on lumped components with a higher level of complexity. Thanks to molecular-based models, kinetic parameters can be calculated for each chemical reaction involved in biomass transformation, which contributes in a deep description of the phenomena involved [35]. However, the main challenge to their development is achieving an accurate description of biomass composition, especially in the case of hemicelluloses. A simple but effective description of beech transformation through torrefaction was proposed by Nocquet et al. [29]. His torrefaction model is based the additive behavior in torrefaction of commercial cellulose, xylan and lignin, and showed interesting results in predicting solid mass loss and volatile species composition for beech torrefaction. Molecular-based models that can be applied for torrefaction were developed by Vinu and Broadbelt for fast pyrolysis cellulose and glucose-based carbohydrates [36], by Klein et al. for lignin fast pyrolysis [37] and biomass gasification [38], as well as by Norinaga et al. for cellulose [39], wood [40] and lignin pyrolysis [41]. Even if these models lead to a detailed description of the volatile species formed, they are based either on model molecules or on commercial compounds [42].

Ranzi's group proposed a more detailed approach to pyrolysis (and therefore torrefaction) modelling through lumped stoichiometric reactions. Its model consists of a multicomponent mechanism based on the superposition of the pyrolysis sub-mechanisms of cellulose, hemicellulose and lignin [43,44]. Solid kinetics, as well as the production of volatile species, were predicted for woods by considering their macromolecular and elemental composition [45,46]. However, the main limitations of Ranzi's model were considering xylan as representative of hemicelluloses, neglecting interactions between macromolecular components and inorganic elements in biomass, as they might play a role at the pyrolysis temperature range, as well as secondary charring reactions [16]. Anca-Couce introduced some modifications to Ranzi's model [44,47,48],

in particular the charring reactions description, which is especially relevant for slow processes as torrefaction, and to some extent the influence of the inorganic elements [16,49]. This modified model was applied by Anca-Couce et al. for torrefaction as well as slow and intermediate pyrolysis [49–51]. Later, Dussan et al. contributed to this model by detailing the transformation mechanism of hemicelluloses and lignin. This description was based on five model compounds representing hemicelluloses main sugar units from woody, herbaceous and agricultural biomasses (xylan with acetyl and 4-methyl-D-glucuronic acid groups, arabinoxylan, xyloglucan, glucomannan and β-glucan). As a result, pentose and hexose-based sugar transformation mechanisms were described [52]. Lignin was defined through dimeric pseudo-components with phenolic functionalities based on two of the lignin base units, namely, *p*-hydroxyphenyl, guaiacyl and syringyl groups, linked through β–O–4' aryl ether bonds [53]. Dussan's lignin model accurately described heating rate and temperature influence on the product distribution, as well as monoaromatic content in the volatile fraction.

The objective of the present work is to propose a kinetic model able to predict solid mass loss in torrefaction as a function of the biomass type and its main macromolecular composition of cellulose, hemicelluloses and lignin, as well as of the main operating conditions, namely time and temperature. This model aims to contribute in describing biomass through more representative cellulose, hemicelluloses and lignin fractions, which were extracted from ash-wood, beech, miscanthus, pine and wheat straw, instead of using commercial compounds. However, the detailed chemical reactions involved in the mechanisms of transformation of biomass through torrefaction were not assessed in this work. The experimental results of torrefaction of extracted compounds were presented in the first part of this paper [54] and here kinetics are derived and employed to predict biomass torrefaction. The proposed model, based on the additive experimental behavior of the extracted fractions in torrefaction, was compared to previous models in the literature and then validated with nine additional woody and agricultural biomass samples.

Name	Year	Scheme	Process	T (°C)	Ref.	Used in
Kilzer, Broido	1969 - 1975		Cellulose pyrolysis	370	[55,56]	
Arseneau	1971		Cellulose thermal decomposition	200 - 270	[57]	[58]
Shafizadeh, Chin	1977		Wood torrefaction/ mild pyrolysis	300-400	[59]	[60]
Broido-Shafizadeh and Bradbury	1979		Cellulose torrefaction/ mild pyrolysis	250-340	[61]	
Thurner and Mann (1981), then Kilzer-Broido (1988)	1981 - 1988		Cellulose torrefaction	300-400	[62]	[33,7,28,63–66]
Piskorz	1988		Cellulose pyrolysis	300-800	[67]	
Modified Kilzer-Broido Model by Agrawal	1988		Cellulose torrefaction	250 - 360	[68,69]	
Koufopanos	1989		Biomass pyrolysis	100 - 440	[27]	
Broido-Shafizadeh (reviewed by Várhegyi)	1994		Cellulose pyrolysis	220 - 370	[58]	[23,65]
Di Blasi-Lanzetta	1997		Pyrolysis (developed for hemicelluloses)	200 - 340	[28]	[70,29,65,71]
Banyasz	2001		Cellulose pyrolysis	400 - 800	[72]	
Klinger	2013	$Biomass \xrightarrow{k_{1,i}} R_1 + \sum \alpha_{1,i} P_{1,i}$ $R_{j-1} \xrightarrow{k_{j,i}} R_j + \sum \alpha_{j,i} P_{j,i}$	Unified model torrefaction/ pyrolysis	260 - 425	[73,74]	

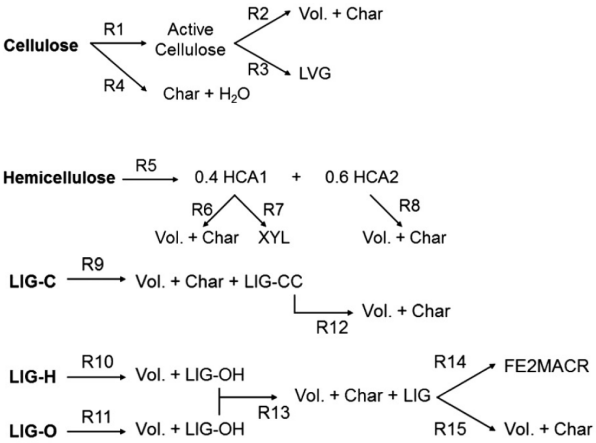
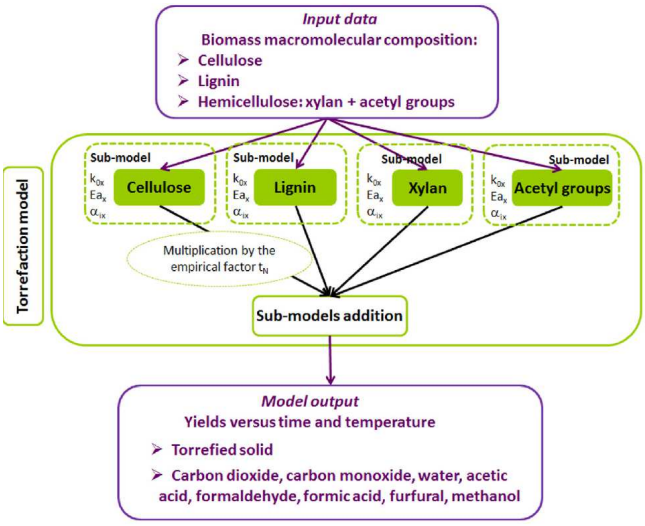
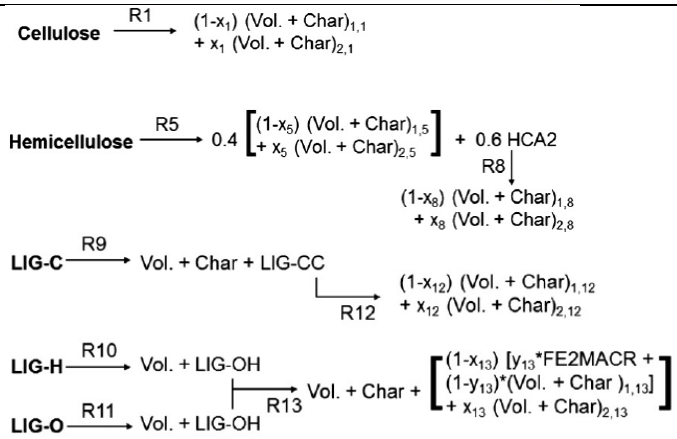
Name	Year	Scheme	Process	T (°C)	Ref.
Ranzi	2008 – 2015		Pyrolysis	150 - 450	[125–127, 129]
Nocquet	2014		Torrefaction	200 – 300	[29]
Ranzi-Anca-Couce (RAC)	2016	 * *Adapted from pyrolysis model proposed by Ranzi (2008)*	Torrefaction	150 - 450	[75]
Dussan	2017	Detailed model for hexose-based and pentose-based sugars in hemicelluloses pyrolysis *(details in* [52]*)*	Pyrolysis	150 - 450	[52]
Dussan	2018	Detailed model for lignin pyrolysis based on β–O–4' linked dimers of lignin base units *(details in* [53]*)*	Pyrolysis	150 - 450	[53]

Table 1. Review of the evolution of main pyrolysis models applicable to torrefaction

2. MODEL DEVELOPMENT

The proposed torrefaction model was based on the additivity of the behavior of cellulose, hemicelluloses and lignin in torrefaction, as suggested by Nocquet et al. [29]. The main difference with Nocquet's model is that extracted fractions from five biomasses were considered, instead of commercial compounds. Two levels were defined in the present model in function of the extracted fractions selected for representing biomass main macromolecular components.

2.1. FIRST-LEVEL MODEL

In this first-level model, the extracted fractions identified as «cellulose II» (C^{II}), «hemicelluloses 1» (H_1) and «lignin» (L) were considered as the representative main macromolecular components for each biomass. The so-called "additive model" is based on the sum of the behavior of these extracted fractions, analyzed in the in part 1, weighted by the proportions of the corresponding main macromolecular components on each raw biomass (Eq. 1, Table 2).

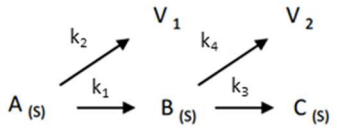
$$m_{rb}(t_i, T_i) = x_{C,rb}\, m_{C^{II}}(t_i, T_i) + x_{H,rb}\, m_{H_1}(t_i, T_i) + x_{L,rb}\, m_L(t_i, T_i) \qquad \text{Eq. 1}$$

$$T_i \in [200,300]°C$$

Macromolecular component	Cellulose	Hemicelluloses	Lignin
Extracted fractions considered for the torrefaction model			
1st level model	C^{II}	H_1	L
2nd level model	C^{I}	H_T	L
Raw biomass composition		**%wmf**	
Ash-wood	43.7	24.9	31.4
Beech	44.3	27.2	28.4
Miscanthus	51.4	25.7	22.9
Pine	41.3	29.3	29.4
Wheat straw	45.8	29.1	25.0

Table 2. Biomass main macromolecular composition as considered for the modelling of the behavior of the five raw biomasses in torrefaction

Kinetics of solid transformation through torrefaction for the extracted fractions were described following the structure of the 2-succesive step kinetic model proposed by Di Blasi and Lanzetta (Eq. 1).



Eq. 2

In this model, A, B and C represent solid species, while V_1 and V_2 corresponds to gaseous species. The kinetic constants of each chemical reaction are represented by k_1, k_2, k_3 and k_4. It was supposed that all reactions order is 1 and that the Arrhenius law governs the kinetics of the 4 reactions of the proposed scheme.

$$k = k_0 \exp\left(\frac{-E}{R\,T}\right) \qquad \text{Eq. 3}$$

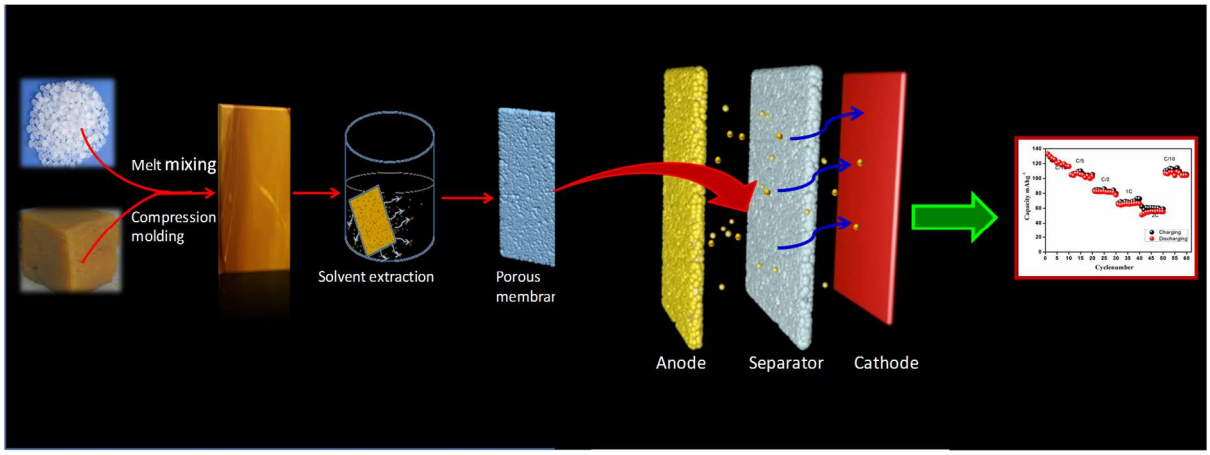
2.1.1. Kinetic parameter calculations

The kinetic parameters of the model were identified with Matlab® for each extracted fraction per biomass by least square fitting (Table 3). To do this, the function F representing the difference between the modelled and the experimental remaining solid mass (Eq. 4) was minimized. The initialization was carried out with the values of the Nocquet's model parameters [29].

$$F = \sum_{t_i,T_i} \left| m_{mod}(t_i,T_i) - m_{exp}(t_i,T_i) \right| \qquad \text{Eq. 4}$$

Mean absolute (ε_a) and relative (ε_r) errors, expressed as the average of the square of relative errors, were calculated (Eq. 5-6).

$$Mean\ \varepsilon_a = \frac{\sum_{i=1}^{n}\left(m_{mod}(t_i,T_i) - m_{exp}(t_i,T_i)\right)^2}{n} \qquad \text{Eq. 5}$$

$$Mean\ \varepsilon_r = \frac{\sum_{i=1}^{n}\left(\frac{m_{mod}(t_i,T_i) - m_{exp}(t_i,T_i)}{m_{exp}(t_i,T_i)}\right)^2}{n} \qquad \text{Eq. 6}$$

Graphical abstract