



Application of a detailed biomass pyrolysis kinetic scheme to hardwood and softwood torrefaction



Andrés Anca-Couce^{a,*}, Ingwald Obernberger^{a,b}

^aInstitute for Process and Particle Engineering, Graz University of Technology, Inffeldgasse 21b, 8010 Graz, Austria

^bBIOS BIOENERGIESYSTEME GmbH, Inffeldgasse 21b, 8010 Graz, Austria

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ABSTRACT

A detailed pyrolysis kinetic scheme is applied in this work for biomass torrefaction, with a focus on hardwood and softwood. The scheme includes secondary charring reactions, relevant for particles of a certain thickness, and sugar formation is avoided due to the catalytic effect of alkali metals in biomass. The release of acetic acid from hardwood and softwood hemicellulose is also considered. Representative initial compositions of hardwood and softwood are proposed in order to correctly predict mass loss in pyrolysis and torrefaction micro-TGA experiments. The predictions for product composition are validated with torrefaction batch experiments conducted in a lab-scale reactor with beech and spruce. The scheme predicts with good accuracy the yields of permanent gases and the main groups in which the condensable species are classified. The amount of secondary charring reactions is higher in the lab-scale than in the micro-TGA experiments, due to the higher particle size. The main discrepancies can be explained by the limitations of the scheme: reactive drying is not included and xylan is considered as representative for hemicellulose, which leads to deviations in the predictions of some products from softwood, e.g. furans. A more precise description of hemicellulose from softwood would include a hemicellulose reaction scheme based on glucomannan.

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1. Introduction

Biomass, as other renewable energy sources, is expected to play a more important role in the energy mix of the future. Torrefaction is a mild pyrolysis process at temperatures ranging from 220 to 350 °C where mainly the hemicellulose fraction decomposes. Torrefaction and its applications were reviewed by Van der Stelt et al. [1] and Tumuluru et al. [2]. In this process biomass loses mass and gets enriched in carbon due to volatiles release. Additionally, torrefaction improves grindability, increases hydrophobicity and reduces biological and thermal degradation, which improves storage and transportation properties. Due to these benefits torrefaction may become an interesting biomass pre-treatment technology.

Torrefaction is usually modelled with a two steps kinetic scheme [3–5] where there is at each step a competition between formation of volatiles and solid products. This scheme is inspired from the one developed for hemicellulose by Di Blasi and Lanzetta [6]. The composition of the volatiles of each reaction was

* Corresponding author. Tel.: +43 (0) 316 873 30432; fax: +43 (0) 316 873 1030432.

E-mail address: anca-couce@tugraz.at (A. Anca-Couce).

calculated by Bates and Ghoniem [7] for a hardwood species (willow), based on the kinetics [3] and analysis of products [8] from Prins et al. The main limitation of this scheme is that it can just be applied for biomass species for which the kinetics and product composition were calculated, i.e. it cannot be generally applied for lignocellulosic biomass. Moreover, the competition between the production of char and volatiles is described with different activation energies for each reaction, not considering other relevant parameters in charring as particle size, pressure or ash content [9].

Biomass pyrolysis kinetics based on the sum of the contributions of the components hemicellulose, cellulose and lignin were also employed to describe mass loss in torrefaction [10,11]. A kinetic scheme which is able to predict biomass pyrolysis should also be valid for biomass torrefaction, as this is just a partial pyrolysis process. The authors of this paper applied a detailed kinetic scheme of biomass pyrolysis [9,12] to predict the product composition of torrefaction of beech (hardwood) chips [13]. The objective of this work is to present a general kinetic scheme which is able to generally predict mass loss evolution and product composition of torrefaction of lignocellulosic biomass. This kinetic scheme will be applied for hardwood and softwood torrefaction in this work. The kinetic scheme is presented in Section 2, mass loss evolution

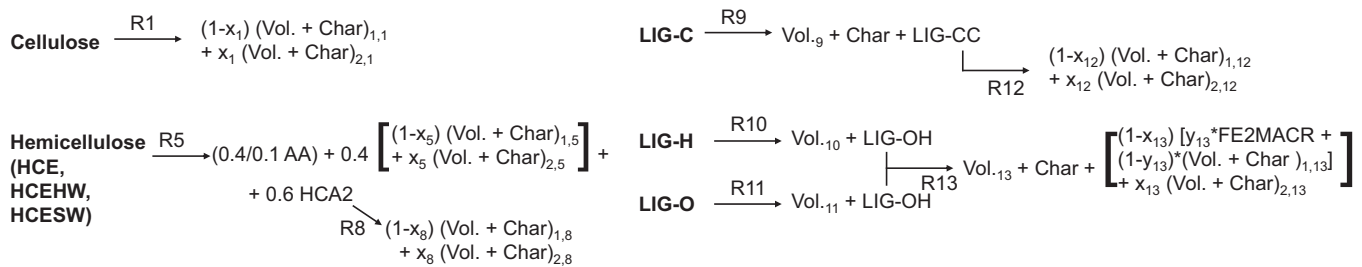


Fig. 1. Summary of the adapted reaction scheme. The release of acetic acid (AA) from hemicellulose is different for hardwood and softwood.

is discussed in Section 3 and product composition in Section 4. Finally, the conclusions are exposed.

2. Kinetic scheme

The pyrolysis kinetic scheme presented in this work to model biomass torrefaction is going to be briefly described. It is based on the scheme developed by Ranzi et al. [12] for pyrolysis of small ash free biomass particles (i.e., primary pyrolysis) called from now on original scheme. A recent update of this scheme, which has not been employed in this work, was presented by Corbetta et al. [14]. Biomass consists of cellulose, hemicellulose and 3 types of lignin which independently decompose and the volatiles are represented by 20 species, including main permanent gases and condensable species. This original scheme was adapted by the authors of this paper [9] to include the presence of secondary char formation reactions, which are relevant for particles of a certain thickness as under typical torrefaction conditions. In these reactions char is produced together with other products, such as H_2O and CO_2 , from the original products of primary pyrolysis. Moreover, in the competition between fragmentation and sugar formation reactions, the catalytic effect of alkali metals in biomass, together with the presence of secondary reactions of the volatiles in particles of a certain thickness, leads to the preference of the fragmentation pathway over sugar formation for both cellulose and hemicellulose in the adaptation.

The employed adapted scheme is summarized in Fig. 1, the reactions are detailed in Table 1 and the list of species is shown in Table 2. Cellulose pyrolysis is described with one reaction representing devolatilization through ring fragmentation plus a secondary reaction representing charring. An adjustable parameter “ x_1 ” represents the amount of the initial fragmentation primary products – $(\text{Vol.} + \text{Char})_{1,1}$, including several low molecular weight compounds such as hydroxyacetaldehyde (HAA), 5-hydroxymethyl-furfural (HMFU), CO_2 or H_2O – that react to form the secondary products – $(\text{Vol.} + \text{Char})_{2,1}$, including char, H_2O , CO_2 and H_2 . The hemicellulose scheme is based on pyrolysis of xylan, which is a good representative of the hemicelluloses of hardwoods. It consists of two successive reactions. The scheme of lignin consists of three different components: LIG-C, LIG-H and LIG-O, which are richer in carbon, hydrogen and oxygen, respectively. Hemicellulose and lignin pyrolysis in the adapted scheme also include adjustable parameters “ x_i ” representing the amount of secondary charring reactions. These parameters should depend on the retention time and partial pressure of the volatiles in the particle, presence of minerals and temperature. A value in the range of 0.3–0.4, constant for all components, provided good results for slow pyrolysis in fixed beds of wood particles with a size of around 1 cm [9].

In this scheme char is not just produced as pure carbon, but also as several $G\{\}$ forms ($G\{\text{CO}_2\}$, $G\{\text{CO}\}$, $G\{\text{COH}_2\}$) and $G\{\text{H}_2\}$) that further react at higher temperatures producing CO_2 , CO or H_2 , but these reactions are not active at typical torrefaction temperatures.

Table 1

List of reactions of the adapted scheme (SW: softwood, HW: hardwood).

Reaction		A (s^{-1})	E (kJ/mol)	
1	CELL	$\rightarrow (1-x_1) * (0.95 \text{ HAA} + 0.25 \text{ GLYOX} + 0.2 \text{ CH}_3\text{CHO} + 0.25 \text{ HMFU} + 0.2 \text{ C}_3\text{H}_6\text{O} + 0.16 \text{ CO}_2 + 0.23 \text{ CO} + 0.9 \text{ H}_2\text{O} + 0.1 \text{ CH}_4 + 0.61 \text{ Char}) + x_1 * (5.5 \text{ Char} + 4 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)$	8×10^{13}	192.5
5	HCE	$\rightarrow 0.4 * [(1-x_5) * (0.75 \text{ G}\{\text{H}_2\} + 0.8 \text{ CO}_2 + 1.4 \text{ CO} + 0.5 \text{ CH}_2\text{O} + 0.25 \text{ CH}_3\text{OH} + 0.125 \text{ ETOH} + 0.125 \text{ H}_2\text{O} + 0.625 \text{ CH}_4 + 0.25 \text{ C}_2\text{H}_4 + 0.675 \text{ Char}) + x_5 * (4.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)] + 0.6 \text{ HCEA2}$	1×10^{10}	129.7
5 (HW)	HCEHW	$\rightarrow 0.4 \text{ AA} + 0.4 * [(1-x_5) * (0.75 \text{ G}\{\text{H}_2\} + 0.8 \text{ CO}_2 + 1.4 \text{ CO} + 0.5 \text{ CH}_2\text{O} + 0.25 \text{ CH}_3\text{OH} + 0.125 \text{ ETOH} + 0.125 \text{ H}_2\text{O} + 0.625 \text{ CH}_4 + 0.25 \text{ C}_2\text{H}_4 + 0.675 \text{ Char}) + x_5 * (4.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)] + 0.6 \text{ HCEA2}$	1×10^{10}	129.7
5 (SW)	HCESW	$\rightarrow 0.1 \text{ AA} + 0.4 * [(1-x_5) * (0.75 \text{ G}\{\text{H}_2\} + 0.8 \text{ CO}_2 + 1.4 \text{ CO} + 0.5 \text{ CH}_2\text{O} + 0.25 \text{ CH}_3\text{OH} + 0.125 \text{ ETOH} + 0.125 \text{ H}_2\text{O} + 0.625 \text{ CH}_4 + 0.25 \text{ C}_2\text{H}_4 + 0.675 \text{ Char}) + x_5 * (4.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)] + 0.6 \text{ HCEA2}$	1×10^{10}	129.7
8	HCEA2	$\rightarrow (1-x_8) * (0.2 \text{ CO}_2 + 0.5 \text{ CH}_4 + 0.25 \text{ C}_2\text{H}_4 + 0.8 \text{ G}\{\text{CO}_2\} + 0.8 \text{ G}\{\text{COH}_2\} + 0.7 \text{ CH}_2\text{O} + 0.25 \text{ CH}_3\text{OH} + 0.125 \text{ ETOH} + 0.125 \text{ H}_2\text{O} + \text{Char}) + x_8 * (4.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + \text{H}_2)$	1×10^{10}	138.1
9	LIG-C	$\rightarrow 0.35 \text{ LIG-CC} + 0.1 \text{ pCOUMARYL} + 0.08 \text{ PHENOL} + 0.41 \text{ C}_2\text{H}_4 + \text{H}_2\text{O} + 0.495 \text{ CH}_4 + 0.32 \text{ CO} + \text{G}\{\text{COH}_2\} + 5.735 \text{ Char}$	4×10^{15}	202.9
10	LIG-H	$\rightarrow \text{LIG-OH} + \text{C}_3\text{H}_6\text{O}$	2×10^{13}	156.9
11	LIG-O	$\rightarrow \text{LIG-OH} + \text{CO}_2$	1×10^9	106.7
12	LIG-CC	$\rightarrow (1-x_{12}) * (0.3 \text{ pCOUMARYL} + 0.2 \text{ PHENOL} + 0.35 \text{ C}_3\text{H}_4\text{O}_2 + 0.7 \text{ H}_2\text{O} + 0.65 \text{ CH}_4 + 0.6 \text{ C}_2\text{H}_4 + \text{G}\{\text{COH}_2\} + 0.8 \text{ G}\{\text{CO}\} + 6.4 \text{ Char}) + x_{12} * (14.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + 4 \text{ H}_2)$	5×10^6	131.8
13	LIG-OH	$\rightarrow \text{H}_2\text{O} + \text{CH}_3\text{OH} + 0.45 \text{ CH}_4 + 0.2 \text{ C}_2\text{H}_4 + 1.4 \text{ G}\{\text{CO}\} + 0.6 \text{ G}\{\text{COH}_2\} + 0.1 \text{ G}\{\text{H}_2\} + 4.15 \text{ Char} + [(1-x_{13}) * (y_{13}/100 * \text{FE2MACR} + (1-y_{13}/100) * (\text{H}_2\text{O} + 0.5 \text{ CO} + 0.2 \text{ CH}_2\text{O} + 0.4 \text{ CH}_3\text{OH} + 0.2 \text{ CH}_3\text{CHO} + 0.2 \text{ C}_3\text{H}_6\text{O} + 0.6 \text{ CH}_4 + 0.65 \text{ C}_2\text{H}_4 + \text{G}\{\text{CO}\} + 0.5 \text{ G}\{\text{COH}_2\} + 5.5 \text{ Char})) + x_{13} * (10.5 \text{ Char} + 3 \text{ H}_2\text{O} + 0.5 \text{ CO}_2 + 3 \text{ H}_2)]$ $y_{13} = -3.6800\text{E}-11 * T^5 + 8.2619\text{E}-08 * T^4 - 6.8901\text{E}-05 * T^3 + 2.6124\text{E}-02 * T^2 - 4.5911 * T + 4.0398\text{E} + 02; T \text{ in } [^\circ\text{C}]$	3×10^8	125.5
16	$\text{G}\{\text{CO}_2\}$	$\rightarrow \text{CO}_2$	1×10^5	100.4
17	$\text{G}\{\text{CO}\}$	$\rightarrow \text{CO}$	1×10^{13}	209.2
18	$\text{G}\{\text{COH}_2\}$	$\rightarrow \text{CO} + \text{H}_2$	5×10^{11}	272.0
19	$\text{G}\{\text{H}_2\}$	$\rightarrow \text{H}_2$	5×10^{11}	313.8

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