A General Mathematical Model of Biomass Devolatilization

Note 1. Lumped kinetic models of cellulose, hemicellulose and lignin.

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Abstract

Main goal of this work, organized in two different notes, is to characterize the pyrolysis and gasification of biomasses with a suitable description of the production of gas and tar components. The chemical characterization of the released species is a relevant aspect towards a consistent design and optimization of different process units where pyrolysis and partial oxidation reactions take place along with the complex physical processes involved in the thermal degradation of biomasses. Biomasses are typically constituted by cellulose, hemicellulose and lignin. Conventional empirical kinetic models are simply derived both on the basis of experimental data and on the basis of semi-detailed kinetic models of devolatilization of the three reference components. The lumped mechanism discussed in this work includes about 15 apparent reactions involving 30 lumped or real species. Together with the formation of CO, CO₂ and H₂O, the model describes the relevant formation of levoglucosan, hydroxycetaldehydes, acetic acid, glyoxal and furfural species from the pyrolysis of cellulose. Similarly, xylose and other oxygenated species characterize the degradation of hemicellulose. Different reference components distinguish softwood and hardwood lignin characteristics and they allow to describe also the release of sinapyl and coumaryl derivatives. The successive evolution in the gas phase of the released tar and gas species is analysed in the second note of this work.

1. Introduction

The interest in the valorization of renewable energy resources has increased worldwide. A recent claim from European government wishes to reach a 20% of energy production from renewable fonts within 2020. The interest of a gradual replacement in specific fields of traditional fossil fuels lies in the possibility of saving the actual reserves and of decreasing the amount of CO₂ emission from energy conversion. One of the alternative is biomass, both coming from agricultural waste and on purpose cultivated. They are widely distributed, easily accessible at relatively low costs and characterized by a reasonable energy content per volume. There are three principal ways to release heat and energy from biomass: direct combustion, gasification and pyrolysis. Pyrolysis results hierarchically the most important, because it is the first step also during both gasification and combustion. These three technologies have different targets and different limitations. Pyrolysis aims to produce liquids and suffers the quite high char residue. Gasification intends to maximize syngas formation (or hydrogen) and tar components are one of the main problem. Combustion’s goal is the direct energy recovery, whilst ashes and unburned hydrocarbons are the critical points. Particle dimensions, formation of sticky materials make difficult the optimal design of these processes. It is then quite evident the role of a proper chemical characterization and kinetic understanding of the process in order to design and identify the operative conditions.

Biomasses are complex structures, formed by different macromolecules. About 90% of biomass weight consists of cellulose, hemicellulose and lignin. Many pyrolysis experiments have been carried out on different biomasses, in order to describe
the rate of weight loss during the primary thermal degradation and/or to model the decomposition process by means of overall kinetic parameters, determined on the basis of the weight loss curves. This work presents three different simplified mechanisms of the main constituents of the biomasses. These models are derived from and take advantage of semi-detailed kinetic schemes [1,2]. This approach allows a better characterization of controlling steps and especially a better description of the main products coming from the decomposition of cellulose, hemicellulose and lignin. These mechanisms, thanks to their limited dimensions, are suitable to be used in quite general tools for the modeling of furnaces and gasifiers and coupled to mechanisms of the gas phase products, as shown in the note II of this work.

2. Lumped kinetic models of biomass devolatilization

2.1. Cellulose

Cellulose is a regular polymer of glucosidic monomers: \((\text{C}_6\text{H}_{10}\text{O}_5)_n\). Pyrolysis of cellulose is a liquid phase molecular and free radical process. A semi-detailed kinetic scheme involving a relatively large set of lumped pseudospecies (40 molecules and 20 radicals) involved in about 400 reactions was already presented and discussed elsewhere [1]. It is widely accepted that the main reaction pathway of cellulose degradation is a chain end depolymerization reaction forming 1,2-anhydro-\(\alpha\)-D-glucopyranose (levoglucosan: LG), relevant reference species of cellulose tar. The unzipping reaction follows a mechanism which starts from the terminal group of the cellulose chain:

As already clearly shown by Suuberg et al. [3], the rate limiting step is the successive vaporization of cellulose tar whose boiling point is about 260 °C. Mass transport resistances in the solid matrix and in the melt phase increase the relative importance of successive degradation and char formation [4,5].

At temperatures higher than 230°C, cellulose pyrolysis follows also a radical process, where the initiation reaction is the cleavage of C-OH bonds. Hydroxyacetaldehyde (HAA), glyoxal (\(\text{C}_2\text{H}_2\text{O}_2\)), \(\text{CH}_3\text{OH}, \text{CH}_2\text{O}, \text{CO}\) and \(\text{CO}_2\) are formed through \(\beta\)-scission reactions with cleavage of C-C bonds inside the polymer backbone and successive radical reactions with a parallel dehydratation. Significant amount of 5-hydroxymethyl-furfural (HMFU) are also observed in the degradation products. Macro-radicals in the liquid phase also propagate the radical reaction chain with radical addition on unsaturated C-C bonds, cross-linking reactions and progressive char formation [4,5]. A lumped kinetic scheme of cellulose degradation is reported in Table 1.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
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</thead>
<tbody>
<tr>
<td>Cellulose (\rightarrow) Active Cellulose</td>
<td>(R=2\times10^{13}\exp\left(-46000/RT\right))</td>
</tr>
<tr>
<td>Active Cellulose (\rightarrow) .72 HAA + .324 (\text{C}_2\text{H}_2\text{O}_2) + .2592 (\text{CH}_3\text{CHO}) + .28 (\text{C}_3\text{H}_6\text{O}) + .25 HMFU</td>
<td>(k = 2\times10^9\exp\left(-30000/RT\right))</td>
</tr>
<tr>
<td>+ .25 (\text{CO}_2) + .1 (\text{CO}) + 1.0229 (\text{H}_2\text{O}) + .1047 (\text{H}_2) + .7036 Char</td>
<td>(k = 2\times T\exp\left(-10000/RT\right))</td>
</tr>
<tr>
<td>Active Cellulose (\rightarrow) Levoglucosane</td>
<td>(k = 2\times T\exp\left(-30000/RT\right))</td>
</tr>
<tr>
<td>Cellulose (\rightarrow) 5 (\text{H}_2\text{O}) + 6 Char</td>
<td>(k = 4\times10^7\exp\left(-32000/RT\right))</td>
</tr>
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</table>

Table 1. Lumped kinetic scheme of cellulose pyrolysis

Figure 1a shows some comparisons between experimental and predicted data of typical TG analysis. The experimental measurements refer to different heating rates and were carried out from different research groups. Some measures refer to the same heating rate, but come from different experiments. This allows to highlight the possible uncertainties of the measures, partially due to the initial sample. A single main degradation step characterizes cellulose
decomposition, the initial weight loss begins at about 250 °C and 400°C respectively at heating rate of 1°C/min and 1000°C/min. The total amount of char residue, usually below 5%, is sensitive to operative condition and experimental devices [3]. The presence of an intermediate as the active cellulose is suggested by many authors since about 30 years [6]. Varhegyi et al. [7] and more recently Capart et al. [8] confuted this assumption, proposing a single step decomposition. Anyway, we preferred to conserve the original model in order to take into account the presence of crosslinked structures observed at relatively low temperatures and in agreement with the propositions of Kilzer and Broido [9].

![Figure 1a. Thermal decomposition of cellulose at different heating rates.](image1)

![Figure 1b. Thermal decomposition of cellulose. Main product formation from isothermal TGA. Comparison between predictions (lines) and experimental measurements [4].](image2)

<table>
<thead>
<tr>
<th></th>
<th>1°C/min</th>
<th>1000°C/min</th>
</tr>
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<tbody>
<tr>
<td>H₂</td>
<td>.0000</td>
<td>.0003</td>
</tr>
<tr>
<td>H₂O</td>
<td>.0725</td>
<td>.0408</td>
</tr>
<tr>
<td>CO</td>
<td>.0003</td>
<td>.0046</td>
</tr>
<tr>
<td>CO₂</td>
<td>.0141</td>
<td>.0180</td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>.0141</td>
<td>.0187</td>
</tr>
<tr>
<td>C₂H₄O₂</td>
<td>.0232</td>
<td>.0308</td>
</tr>
<tr>
<td>HAA</td>
<td>.0058</td>
<td>.0707</td>
</tr>
<tr>
<td>C₃H₆O</td>
<td>.0020</td>
<td>.0266</td>
</tr>
<tr>
<td>HMFU</td>
<td>.0039</td>
<td>.0516</td>
</tr>
<tr>
<td>Levoglucosane</td>
<td>.8534</td>
<td>.7087</td>
</tr>
<tr>
<td>CHAR</td>
<td>.0572</td>
<td>.0292</td>
</tr>
</tbody>
</table>

Table 2. Product distribution (wt) from cellulose pyrolysis at two different heating rates.

Predictions of main products are compared with the measures of Radlein et al. [4] in fig. 1b. These data are carried out in isothermal experiments. Levoglucosan prevails at low temperatures, whilst HAA becomes more important at temperatures higher than 450 °C. HAA does not come from successive reactions of levoglucosan, but directly from cellulose degradation [10]. The competition between cellulose depolymerization and decomposition, can be then properly characterized on the basis of these evidences. This model has been directly derived by using not only the experimental data but also the product distributions as predicted by the semi-detailed kinetic model. In order to give an example of model predictions, Table 2 shows the final degradation products (wt fractions) obtained at two different heating rates. Levoglucosane is always the most abundant product even if the importance of different degradation products increases when rising the heating rates (i.e. at higher degradation temperature).

### 2.2. Hemicellulose

Hemicellulose (HECELL) is present in almost all cell walls along with cellulose and is constituted by a matrix of polysaccharides. While cellulose is crystalline, strong and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength. It is easily devolatilised or hydrolyzed by dilute acid or base as well as myraid hemicellulase enzymes.
Hemicellulose contains many different sugar monomers, while cellulose contains only anhydrous glucose. For instance, besides glucose, sugar monomers in hemicellulose include xylose, mannose, galactose, rhamnose, and arabinose. Hemicelluloses contain most of the D-pentose sugars and occasionally small amounts of L-sugars as well. Xylose is always the sugar monomer present in the largest amount, but mannuronic acid and galacturonic acid also tend to be present.

\[
\begin{align*}
&\text{HECELL} > 0.4 \text{ HCE1} + 0.6 \text{HCE2} & k &= 1.10^{10} \exp \left( -31000/RT \right) \\
&\text{HCE1} > 2.5 \text{H}_2 + \text{CO}_2 + \text{CO} + 0.5 \text{CH}_2 \text{O} + 0.25 \text{CH}_3 \text{OH} + 0.125 \text{C}_5 \text{H}_8 \text{OH} + 0.125 \text{H}_2 \text{O} + 2 \text{Char} & k &= 3.10^9 \exp \left( -27000/RT \right) \\
&\text{HCE1} > \text{Xylose} & k &= 3.10^8 \exp \left( -11000/RT \right) \\
&\text{HCE2} > 1.5 \text{H}_2 + 0.5 \text{GCO}_2 + 0.5 \text{CO}_2 + \text{COH}_2 \text{S} + 0.5 \text{CH}_2 \text{O} + 0.25 \text{CH}_3 \text{OH} + 0.125 \text{C}_5 \text{H}_8 \text{OH} + 0.125 \text{H}_2 \text{O} + 2 \text{Char} & R &= 2.10^9 \exp \left( -33000/RT \right) \quad \text{[HCE2]}^2 \\
&\text{GCO}_2 > \text{CO}_2 & k &= 1.10^9 \exp \left( -24000/RT \right) \\
&\text{COH}_2 \text{S} > \text{CO}_2 + \text{H}_2 & k &= 8 \times 10^{13} \exp \left( -75000/RT \right)
\end{align*}
\]

**Table 3.** Lumped kinetic scheme of hemicellulose pyrolysis

Hemicellulose is here simply considered as a regular polymer of xylose monomers: (C\(_5\)H\(_8\)O\(_4\))\(_n\). The same assumption was made by Williams and Besler [11] when studying the influence of temperature and heating rate on the slow pyrolysis of biomasses. Their experimental data, obtained at 5 and 80 °C/min, are indicating that hemicellulose mainly decomposes between 250 °C and 400 °C with a successive slow weight loss. A semidetailed kinetic model was already developed [12] and it was partially used to derive the lumped kinetic model reported in Table 3. HCE1 and HCE2 represent reaction intermediates in the solid matrix with successive degradation and/or vaporization steps. The successive and final weight loss of hemicellulose is obtained with a proper intermediate (COH\(_2\)S) able to reproduce the slow and final release of H\(_2\) and CO. A detail of the predicted products from hemicellulose pyrolysis is reported in Table 4.

2.3. Lignin

Lignins are complex racemic polymers derived mainly from three hydroxycinnamyl alcohol monomers which differ in their degree of methoxylation. Two main classes of lignin are usually considered: hardwood (dicotyledonous angiosperm) and softwood lignin (gymnosperm). Once again the lumped kinetic scheme reported in Table 5 is derived from a semi-detailed model already discussed elsewhere [2]. The model describes the different
lignins on the basis of three different reference species, reported in Figure 3. Every lignin is
described, according to the elemental composition (C/H/O), in terms of the three
pseudospecies, representative of the different functional groups.

![Lignin Structure](image)

**Figure 3. Reference units in lignin structure**

The simplified kinetic scheme of the lignin decomposition takes into account the different
evolutions of the different components. Figure 4 sketches the different pathways. LIG-O and
LIG-H decompose releasing gases (richer in oxygen in the case of LIG-O and in hydrogen in
the case of LIG-H) and forming the same pseudocomponent (LIG_{OH}). During the first
pyrolysis steps, LIG-C gives rise to a pseudospecies (LIG_{CC}), whilst gases and char are
formed. Both these components decompose to a different pseudospecies (LIG), developing
gas and tar components and some other char. Finally, LIG evolves to CHAR always forming
gas and tar.

![Lignin Decomposition](image)

**Figure 4. Lignin decomposition mechanism**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Kinetic Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIG-C &gt; .325 LIG_{CC} + 8.3925 CHAR + .9825 COH_{S} + .325 COH + .735 H_{2}O + .105 C_{6}H_{10}O_{2} + 0.0385 CH_{3}OH + .0665 C_{6}H_{5}O + .581 H_{2} + .0175 CO</td>
<td>R=4×10^{15} \text{exp}(-46000/RT) [LIG-C]^{2}</td>
</tr>
<tr>
<td>LIG_{CC} &gt; 1.4 H_{2}O + .6 C_{6}H_{10}O_{2} + .4 C_{6}H_{5}O + C_{6}H_{4}O_{2} + 2 H_{2} + 1.2 CH_{4}</td>
<td>k= 2.5×10^{15} \text{exp}(-24000/RT)</td>
</tr>
<tr>
<td>LIG_{CC} &gt; LIG + .75 CH_{3}OH + .875 C_{6}H_{5}O_{2} + 4.25 H_{2} + .25 LIG + 1.5 H_{2}O + .75 CH_{4} + 6 CHAR</td>
<td>R=8×10^{16} \text{exp}(-48000/RT) [LIG-H]^{2}</td>
</tr>
<tr>
<td>LIG-H &gt; LIG_{OH} + C_{6}H_{5}O</td>
<td>k=1.6×10^{16} \text{exp}(-46000/RT)</td>
</tr>
<tr>
<td>LIG-O &gt; LIG_{OH} + CO_{2}</td>
<td>R=4×10^{14} \text{exp}(-25000/RT)</td>
</tr>
<tr>
<td>LIG_{OH} &gt; LIG + H_{2}O + CH_{3}OH + .5 COH + 1.5 COH_{S} + 5 CHAR + .5 H_{2}</td>
<td>k=4×10^{14} \text{exp}(-25000/RT)</td>
</tr>
<tr>
<td>LIG &gt; C_{6}H_{10}O_{2}</td>
<td>R=10^{12} \text{exp}(-5000/RT) [TAR_{OH}]^{2}</td>
</tr>
<tr>
<td>LIG &gt; 1.15 H_{2}O + .5 CH_{3}OH + 1.5 CH_{2}CHO + 1.5 COH + .5 COH_{S} + 7 CHAR + .95 H_{2} + .9 CH_{4} + .1 C_{6}H_{6}O_{2}</td>
<td>k=1×10^{11} \text{exp}(-40000/RT)</td>
</tr>
<tr>
<td>COH_{S} &gt; CO + H_{2}</td>
<td>k=8×10^{13} \text{exp}(-75000/RT)</td>
</tr>
<tr>
<td>COH &gt; CO</td>
<td>k=4×10^{14} \text{exp}(-51000/RT)</td>
</tr>
</tbody>
</table>

**Table 5. Lumped kinetic scheme of lignin pyrolysis**

A very detailed experimental analysis of lignin volatilization was reported by Jakab et al.
[13]. They investigated 16 milled wood lignins isolated from grasses, softwoods and
hardwoods. Figure 5 shows a couple of comparisons with these data, relating to lignins
derived respectively from *liriodendron tulipifera* and from *arachis hypogaea*. In the same
figure it is possible to observe the predictions compared with a different lignin (milled wood)
volatilized at a different heating rate. In this case the agreement is less good, even though
asymptotic values are caught. At this very high heating rate (1000 °C/s) transport phenomena
can occur inside the sample and the effective solid temperature can be consequently affected.
Table 5 reports some detail of the released species.

# 3. Conclusions

Despite the simplicity of the proposed models, they are able to characterize the main features
of the devolatilization of cellulose, hemicellulose and lignin. The peculiarities of the proposed
models lie in their derivation from semi-detailed kinetic mechanisms.
This detail allows not only a wider validation, but mainly the proper prediction of main products and by-products. As a consequence of their simplicity, these schemes are suitable to be included in general models of biomass gasification and combustion, and they also give the possibility of identifying the best operating conditions to optimize yields and performances.

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4. References