Combustion Kinetics of Biomass Materials in the Kinetic Regime

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Keywords: Wheat straw, willow; wood; sewage sludge; thermogravimetry; distributed activation energy model; combustion; char burn-off; pyrolysis; kinetic regime.

Scope of this document: The kinetic evaluation was illustrated by two experiments for each sample in the figures of our article. Figures S1 - S6 of the present Supporting Information show series of 10 experiments that were evaluated simultaneously. Besides, details are given on the autocatalytic (self-accelerating) kinetics of the oxidative decomposition of the cellulose in the wood sample of the study in Figure S7 and Table S1.

Textual information in Figures S1 - S6: The first row below each figure contains the name of the sample and a brief description of the experimental conditions. The second row lists the fit quality for the given experiment (fit1) and for the whole series (fit10). The further rows display parameters for the partial processes.

Colors and line types in Figures S1 - S6:

○○○○ DTG curves normalized by the initial sample mass

—— normalized mass loss rate curves calculated from the model (-dm_{calc}/dt)

—— rate of the biomass devolatilization (-dm_{ur}/dt or c_{other} d\alpha_{other}/dt)

- - - - rate of the cellulose devolatilization (when present in the model, c_{cell} d\alpha_{cell}/dt)

•••••• rate of the char formation and/or char burn-off (-dm_{char}/dt or c_{char} d\alpha_{char}/dt)

××××× ash formation rate

The last figure (Figure S7) displays f(\alpha_{cell}) functions, where \alpha_{cell} is the reacted fraction of the cellulose in the wood sample and f(\alpha_{cell}) is an empirical function describing an autocatalytic oxidative devolatilization. The notations of Figure S7 are explained in the table of parameters (Table S1) in the same page.
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Figure S1. Evaluation of the wheat straw experiments by a model of successive devolatilization and char burn-off reactions

Wheat straw, 4°C/min, [O2]=0.04
fit1=4.16%, fit10=3.99%
1: \( E_0=157.0 \) \( \log_{10} A=12.24 \) \( \sigma(E)=5.55 \) \( \nu=0.431 \) yield=0.323
2: \( E_0=151.0 \) \( \log_{10} A=9.56 \) \( \sigma(E)=0 \) \( \nu=0.498 \) yield=0.309

Wheat straw, 20°C/min, [O2]=0.04
fit1=4.52%, fit10=3.99%
1: \( E_0=157.0 \) \( \log_{10} A=12.24 \) \( \sigma(E)=5.55 \) \( \nu=0.431 \) yield=0.323
2: \( E_0=151.0 \) \( \log_{10} A=9.56 \) \( \sigma(E)=0 \) \( \nu=0.498 \) yield=0.309

Wheat straw, 40°C/min, [O2]=0.04
fit1=5.25%, fit10=3.99%
1: \( E_0=157.0 \) \( \log_{10} A=12.24 \) \( \sigma(E)=5.55 \) \( \nu=0.431 \) yield=0.323
2: \( E_0=151.0 \) \( \log_{10} A=9.56 \) \( \sigma(E)=0 \) \( \nu=0.498 \) yield=0.309
Figure S1. Evaluation of the wheat straw experiments by a model of successive devolatilization and char burn-off reactions.
**Figure S1.** Evaluation of the wheat straw experiments by a model of successive devolatilization and char burn-off reactions

**Wheat straw, 40°C/min, [O2]=0.2**

<table>
<thead>
<tr>
<th>Time [min]</th>
<th>-dm/dt [s⁻¹] × 10³</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>2: E₀=151.0 log₁₀ A=9.56 σ(E)=0 ν=0.498 yield=0.309</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Wheat straw, stepwise 1, [O2]=0.2**

<table>
<thead>
<tr>
<th>Time [min]</th>
<th>-dm/dt [s⁻¹] × 10³</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>2: E₀=151.0 log₁₀ A=9.56 σ(E)=0 ν=0.498 yield=0.309</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Wheat straw, stepwise 2, [O2]=0.2**

<table>
<thead>
<tr>
<th>Time [min]</th>
<th>-dm/dt [s⁻¹] × 10³</th>
<th>Temperature [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>2: E₀=151.0 log₁₀ A=9.56 σ(E)=0 ν=0.498 yield=0.309</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure S2. Evaluation of the sewage sludge experiments by a model of successive devolatilization and char burn-off reactions
Figure S2. Evaluation of the sewage sludge experiments by a model of successive devolatilization and char burn-off reactions
Sewage sludge, 40°C/min, [O2]=0.2

$E_0=142.8 \quad \log_{10} A=10.98 \quad \sigma(E)=14.3 \quad \nu=0.541 \quad \text{yield}=0.657$

$E_0=120.2 \quad \log_{10} A=7.03 \quad \sigma(E)=0 \quad \nu=0.646 \quad \text{yield}=0.785$

Figure S2. Evaluation of the sewage sludge experiments by a model of successive devolatilization and char burn-off reactions
Figure S3. Evaluation of the willow experiments assuming two devolatilization reactions and a successive devolatilization and char burn-off
**Figure S3.** (Continued)

**Willow, stepwise 1, \([O_2]=0.04\)**

\[
\begin{align*}
E_0 &= 165.9 & \log_{10} A &= 13.05 & \sigma(E) &= 11.2 & \nu &= 0.366 & \text{yield} &= 0.231 \\
E_0 &= 145.0 & \log_{10} A &= 10.66 & \sigma(E) &= 0 & \nu &= 0.611 & \text{yield} &= 0.208 \\
E_0 &= 168.9 & \log_{10} A &= 10.66 & \sigma(E) &= 0 & \nu &= 0.624 & \text{yield} &= 0.200 \\
\end{align*}
\]

**Willow, stepwise 2, \([O_2]=0.04\)**

\[
\begin{align*}
E_0 &= 165.9 & \log_{10} A &= 13.05 & \sigma(E) &= 11.2 & \nu &= 0.366 & \text{yield} &= 0.231 \\
E_0 &= 145.0 & \log_{10} A &= 10.66 & \sigma(E) &= 0 & \nu &= 0.611 & \text{yield} &= 0.208 \\
E_0 &= 168.9 & \log_{10} A &= 10.66 & \sigma(E) &= 0 & \nu &= 0.624 & \text{yield} &= 0.200 \\
\end{align*}
\]

**Willow, 4°C/min, \([O_2]=0.2\)**

\[
\begin{align*}
E_0 &= 165.9 & \log_{10} A &= 13.05 & \sigma(E) &= 11.2 & \nu &= 0.366 & \text{yield} &= 0.231 \\
E_0 &= 145.0 & \log_{10} A &= 10.66 & \sigma(E) &= 0 & \nu &= 0.611 & \text{yield} &= 0.208 \\
E_0 &= 168.9 & \log_{10} A &= 10.66 & \sigma(E) &= 0 & \nu &= 0.624 & \text{yield} &= 0.200 \\
\end{align*}
\]

**Willow, 20°C/min, \([O_2]=0.2\)**

\[
\begin{align*}
E_0 &= 165.9 & \log_{10} A &= 13.05 & \sigma(E) &= 11.2 & \nu &= 0.366 & \text{yield} &= 0.231 \\
E_0 &= 145.0 & \log_{10} A &= 10.66 & \sigma(E) &= 0 & \nu &= 0.611 & \text{yield} &= 0.208 \\
E_0 &= 168.9 & \log_{10} A &= 10.66 & \sigma(E) &= 0 & \nu &= 0.624 & \text{yield} &= 0.200 \\
\end{align*}
\]

**Evaluation of the willow experiments assuming two devolatilization reactions and a successive char burn-off**
Figure S3. (Continued)
**Figure S4.** Evaluation of the wheat straw experiments by an approximate model of two parallel reactions
**Figure S4.** Evaluation of the wheat straw experiments by an approximate model of two parallel reactions
**Figure S4.** Evaluation of the wheat straw experiments by an approximate model of two parallel reactions
**Figure S5.** Evaluation of the sewage sludge experiments by an approximate model of two parallel reactions
Figure S5. (Continued)
Figure S5. (Continued)
Figure S6. Evaluation of the willow experiments by an approximate model of three parallel reactions.
**Figure S6.** Evaluation of the willow experiments by an approximate model of three parallel reactions.
Willow, 40°C/min, [O2]=0.2

$E_0=165.9 \quad \log_{10} A=13.06 \quad \sigma(E)=11.2 \quad \nu=0.366$

$E_0=145.0 \quad \log_{10} A=10.66 \quad \sigma(E)=0 \quad \nu=0.611$

$E_0=168.9 \quad \log_{10} A=10.66 \quad \sigma(E)=0 \quad \nu=0.625$

Willow, stepwise 1, [O2]=0.2

$E_0=165.9 \quad \log_{10} A=13.06 \quad \sigma(E)=11.2 \quad \nu=0.366$

$E_0=145.0 \quad \log_{10} A=10.66 \quad \sigma(E)=0 \quad \nu=0.611$

$E_0=168.9 \quad \log_{10} A=10.66 \quad \sigma(E)=0 \quad \nu=0.625$

Willow, stepwise 2, [O2]=0.2

$E_0=165.9 \quad \log_{10} A=13.06 \quad \sigma(E)=11.2 \quad \nu=0.366$

$E_0=145.0 \quad \log_{10} A=10.66 \quad \sigma(E)=0 \quad \nu=0.611$

$E_0=168.9 \quad \log_{10} A=10.66 \quad \sigma(E)=0 \quad \nu=0.625$

Figure S6. Evaluation of the willow experiments by an approximate model of three parallel reactions
Table S1. Parameters of the \(f(\alpha_{\text{cell}})\) functions\(^a\)

<table>
<thead>
<tr>
<th>Devolatilization of the non-cellulosic part</th>
<th>DAEM</th>
<th>DAEM</th>
<th>DAEM</th>
<th>DAEM</th>
<th>DAEM</th>
<th>n-order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Char burn-off</td>
<td>successively 1(^{\text{st}}) order(^a)</td>
<td>successively 1(^{\text{st}}) order(^a)</td>
<td>parallel 1(^{\text{st}}) order(^a)</td>
<td>parallel 1(^{\text{st}}) order(^a)</td>
<td>parallel DAEM(^b)</td>
<td>successive parallel 1(^{\text{st}}) order(^a)</td>
</tr>
<tr>
<td>Line style and color of the corresponding curve in Figure S7</td>
<td>black</td>
<td>red</td>
<td>blue</td>
<td>green</td>
<td>blue</td>
<td>dark magenta</td>
</tr>
<tr>
<td>(n)</td>
<td>0.87</td>
<td>0.87</td>
<td>0.88</td>
<td>0.88</td>
<td>0.88</td>
<td>0.86</td>
</tr>
<tr>
<td>(a)</td>
<td>2.89</td>
<td>2.98</td>
<td>3.21</td>
<td>3.24</td>
<td>3.21</td>
<td>4.86</td>
</tr>
<tr>
<td>(z)</td>
<td>1.02</td>
<td>1.06</td>
<td>1.16</td>
<td>1.18</td>
<td>1.16</td>
<td>2.55</td>
</tr>
</tbody>
</table>

\(^a\) The parameters of the \(f(\alpha_{\text{cell}})\) functions do not have physical meaning of their own. Their physical meaning lies in the shape of the corresponding \(f(\alpha_{\text{cell}})\) curves, which are shown in Figure S7, below. The maximum curves shown there correspond to self-accelerating (autocatalytic) kinetics. The curves practically coincide with each other; only the dashed dark magenta curve (belonging to the last column in the table) differs from the others.

\(^b\) The two evaluations denoted by blue color gave identical results because the DAEM for char burn-off converged to a simple first order reaction (\(\alpha_{\text{char}}=0\)).

Figure S7. \(f(\alpha_{\text{cell}})\) functions. (See the explanation in the footnotes of Table S1.)