Pyrolysis Kinetics Modeling of the Hybrid Sugarcane IACSP95-5000

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Presentation Outline

1. Introduction
2. Objectives
3. Materials and methods
4. Results and discussion
5. Conclusions

Acknowledgements
1. Introduction

**Fig. 1.** Cutting cross-section of different sugarcane stems

**Hybrid sugarcane** SP-95-5000 (2013) - Agronomic Institute of Campinas (IAC), SP, Brazil: genetically modified from Sac. officinarum and spontaneum.

**EX>HC≈C>L** (Lima, 2016).

**Advantages:** higher sugar production, better water independence, and higher biomass productivity in the dried areas (Brazillian cerrado).
2. Objectives

Evaluate the thermal decomposition kinetics of hybrid sugarcane, SP95-5000, by thermogravimetric analysis in an inert atmosphere applying one-step (isoconversional methods) and multistep (independent parallel reactions scheme) reaction models, providing the viability of this biomass as a source for pyrolysis processes.
3. Materials and Methods

3.1 Thermogravimetric Analysis, TGA

Material: hybrid sugarcane (18 month)
Treatment: Dried, ground/knife mill, sieved (250 μm)

\[ M_{\text{biomass}} : \sim 10 \text{ mg} \]

Gas: Nitrogen, 50mL/min

Heating rates: 5, 10, 15, 20 °C/min

T range: 25 °C – 900 °C

Fig. 2. Cane stem

Fig. 3. Equipment Shimadzu TGA-50
### 3.2 Mathematical Approach

<table>
<thead>
<tr>
<th>Normalized mass</th>
<th>$W = \frac{m_t}{m_i}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normalized mass rate (DTG)</td>
<td>$\frac{dW}{dt} = \frac{1}{m_i} \frac{dm_t}{dt}$</td>
</tr>
<tr>
<td>Experimental conversion</td>
<td>$\alpha_{exp} = \frac{W_i - W_t}{W_i - W_f}$ \hspace{1cm} ((\alpha = 0-1))</td>
</tr>
<tr>
<td>Experimental conversion rate</td>
<td>$\left(\frac{d\alpha}{dt}\right)_{exp} = -\frac{1}{(W_i - W_f)} \frac{dW_t}{dt}$</td>
</tr>
</tbody>
</table>

$m_i / W_i$: the mass/normalized mass at the beginning; $m_t$ mass at the time; $W_f$: normalized mass at the end of the pyrolysis range, for each heating rate
3.3 Kinetic Modeling – One-step reaction model

\[ \text{Biomass} \xrightarrow{k} \text{Solid + Volatile} \]

Theoretical Conversion rate

\[ \left( \frac{d\alpha}{dt} \right)_{\text{theo}} = k(T)f(\alpha) = A \left[ \exp \left( -\frac{E_a}{RT} \right) \right] f(\alpha) \]

**Arrhenius Equation**

**Kinetic parameters**

- **Differential**
  - Friedman (1964), FD

- **Integral**
  - Ozawa-Flynn-Wall (1965, 1966), OFW
  - Coats-Redfern modified (Braun et al., 1991), CRM
  - (advanced) Vyazovkin (1997), VZ

- **f(\alpha)** - Master Plots method

- **A** - Linearization method
3.1.1. Isoconversional Methods

Graphical solution

FD

\[
\ln \left( \frac{d\alpha}{dt} \right)_{\alpha,\beta} = \text{cte} - \frac{E_a}{RT_{\alpha,\beta}} ; \ E_a = aR
\]

CRM

\[
\ln \left( \frac{\beta_i}{T^2} \right) = \text{cte} - \frac{E_a}{RT} ; \ E_a = aR
\]

OFW

\[
\log \beta_i = \text{cte} - 0.4567 \frac{E_a}{RT} ; \ E_a = \frac{aR}{0.4567}
\]

Linearization for each \( \alpha \)

\[
\phi(E_a) = \sum_{i=1}^{n} \sum_{j \neq i}^{n} \frac{I(E_{a,\alpha}, T_{\alpha,i}) \cdot \beta_j}{I(E_{a,\alpha}, T_{\alpha,j}) \cdot \beta_i}
\]

\[
I(E_{a,\alpha}, T_{\alpha,i}) = p \left( \frac{E_{a,\alpha}}{R \cdot T_{\alpha,i}} \right) \cdot \frac{E_{a,\alpha}}{R}
\]

Minimization for each \( \alpha \)

Pérez-Maqueda; Criado (2000)

\[
p \left( \frac{E_a}{RT_{\alpha}} \right)
\]
3.1.2 Master Plots (mechanism) and Linearization (A) Methods

\[
\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = A \exp\left(-\frac{E_A}{RT}\right) f(\alpha)
\]

\[
g(\alpha) = \frac{AE_a}{\beta R} p(x)
\]

\[
\left. \frac{g(\alpha)}{g(\alpha_{0.5})} \right|_{\text{theo}} = \left. \frac{p(x)}{p(x_{0.5})} \right|_{\text{exp}}
\]

Pérez-Maqueda; Criado (2000)

\[
p\left(\frac{E_a}{RT_\alpha}\right) = \left(\exp\left(-\frac{x}{x}\right) \right) \times \left(\frac{x^7 + 70x^6 + \cdots 357120}{x^8 + 72x^7 + 2024x^6 + \cdots 403200}\right)
\]

Fig. 4: Decomposition phenomena representation
3.4 Kinetic Modeling – Multistep reaction model

Independent parallel reactions scheme, IPRS

Biomass → EX \( k_1 \) → Solid + Volatile (I)

Biomass → HC \( k_2 \) → Solid + Volatile (II)

Biomass → C \( k_3 \) → Solid + Volatile (III)

Biomass → L \( k_4 \) → Solid + Volatile (IV)

\[
\frac{d\alpha_i}{dt} = k_i (1 - \alpha_i)^{n_i}
\]

\[
\frac{d\alpha_i}{dt} = A_i \exp\left(\frac{E_{a,i}}{RT}\right)(1 - \alpha_i)^{n_i}
\]

\[
\frac{d\alpha}{dt}_{\text{total}} = x_E \left( \frac{d\alpha}{dt} \right)_E + x_{HC} \left( \frac{d\alpha}{dt} \right)_{HC} + x_C \left( \frac{d\alpha}{dt} \right)_C + x_L \left( \frac{d\alpha}{dt} \right)_L
\]

150<T<900°C
3.5 Validation of data modeling

Global kinetic model (Arrhenius kinetic)*

Independent parallel reaction scheme

\[ \frac{d\alpha}{dt}_{\text{theo}} \]

4th order Runge-Kutta method, Excel

\[ *E_a, A, \text{ and } f(\alpha); E_{ai}, A_i, x_i, \text{ and } n_i \]

\[ SS = \sum_{i=0}^{N} \left[ \left( \frac{d\alpha}{dt} \right)_{i,\text{exp}} - \left( \frac{d\alpha}{dt} \right)_{i,\text{theo}} \right]^2 \]

\[ AD(\%) = \left[ \frac{\sqrt{SS}}{N} \right] \times 100 \]

residual sum of squares

Average deviation, Órfão et al., (1999)

< 5%
4. Results and Discussion

4.1 Thermal decomposition analysis

Fig. 5. Normalized mass, W, and its derivative, dW/dt, for four heating rates
4.2 Determination of activation energy

Main decomposition components:

(a) **Low conversions (EX):**
92.5-125 kJ/mol

(b) **Intermediate conversions (HC):**
106-225 kJ/mol

(c) **High conversions (C):**
173-234 kJ/mol

Fig. 6. Activation energy profiles as a function of conversion
\( \alpha = 0.05-0.90, 180-420^\circ C \)
4.3 Determination of reaction mechanism

Fig. 7 Comparatives of experimental and theoretical data as a function of conversion

\[ E_a \text{ (VZ); } \alpha = 0.2-0.8 \text{ (T=180-420}^{\circ}\text{C) ; F6} = (1-\alpha)^6 \]
4.4 Determination of pre-exponential factor

\[
\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha)
\]

\[
\ln\left[\left(\frac{d\alpha}{dt}\right)/f(\alpha)\right] = \ln A - \frac{E_a}{RT}
\]

\[E_a = 157.9 \text{ kJ/mol}\]

\[\log A = 13.5 (1/s)\]

\[F = (1-\alpha)^6\]

\[\alpha = 0.2-0.8\]

\[E_{a_{\text{VZ}}} = 165.5 \text{ kJ/mol}\]

Difference = 4.6%

Fig. 8 Linearization of the conversion rate equation as a function of the inverse of absolute temperature
4.5 Validation of kinetic parameters for both reaction models, 5° C/min

(a) one-step reaction

(b) multistep reaction, IPRS

Fig. 9 Comparative between experimental and theoretical conversion rates (a, b) and for each component (b) as a function of temperature
Table 1: Parameters obtained through the reaction models ($\beta=5-20^\circ\text{C/min}$)

<table>
<thead>
<tr>
<th>Model</th>
<th>$E_a$ (kJ/mol)</th>
<th>Log $A$ (log s$^{-1}$)</th>
<th>Reaction order</th>
<th>volatilized fraction</th>
<th>$AD$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-step</td>
<td>152.57</td>
<td>13.03</td>
<td>F6 = (1-$\alpha$)$^6$</td>
<td></td>
<td>22.64± 1.24</td>
</tr>
<tr>
<td><strong>Multistep, IPRS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Extractives</strong></td>
<td>131.43 ± 1.60</td>
<td>11.39 ± 0.27</td>
<td>1</td>
<td>0.32 ± 0.01</td>
<td></td>
</tr>
<tr>
<td><strong>Hemicellulose</strong></td>
<td>103.65 ± 0.50</td>
<td>7.31 ± 0.06</td>
<td>1</td>
<td>0.23 ± 0.01</td>
<td></td>
</tr>
<tr>
<td><strong>Cellulose</strong></td>
<td>174.05 ± 0.06</td>
<td>12.24 ± 0.05</td>
<td>1</td>
<td>0.27 ± 0.01</td>
<td></td>
</tr>
<tr>
<td><strong>Lignin</strong></td>
<td>64.04 ± 2.85</td>
<td>2.09 ± 0.25</td>
<td>1.5</td>
<td>0.18 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>

$[E_a$: Energy canes and sugarcane residues from literature]: Extractives (100-110 kJ/mol); Hemicellulose (100-200 kJ/mol), Cellulose (180-250 kJ/mol), Lignin (40-100 kJ/mol)
5. Conclusions

✓ Thermal decomposition (devolatilization) of the hybrid cane showed three main components: extractives, hemicellulose, and cellulose;

✓ Isoconversional methods/One-step reaction model presented higher average deviation, however, the activation energy can be used as initial guesses for each component in the multiple reactions scheme;

✓ Total conversion rates were better described considering four reactions (AD < 5%), indicating that these kinetic parameters could be used for future process modeling involving the hybrid sugarcane;

✓ Similarities with residues and energy cane show possibility possible to mix them to use industrially with the current technologies for sugar and energy productions.
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Coordination for the improvement of higher level Personnel

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