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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 (Brazilian 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_{biomass} : ~10 mg

Gas: Nitrogen, 50mL/min

Heating rates: 5, 10, 15, 20 $^{\circ}\text{C}/\text{min}$

T range: 25 $^{\circ}\text{C}$ – 900 $^{\circ}\text{C}$



Fig. 2. Cane stem



Fig. 3. Equipment Shimadzu TGA-50

3.2 Mathematical Approach

Normalized mass	$W = \frac{m_t}{m_i}$
Normalized mass rate (DTG)	$\frac{dW}{dt} = \frac{1}{m_i} \frac{dm_t}{dt}$
Experimental conversion	$\alpha_{exp} = \frac{W_i - W_t}{W_i - W_f} \quad (\alpha=0-1)$
Experimental conversion rate	$\left(\frac{d\alpha}{dt}\right)_{exp} = -\frac{1}{(W_i - W_f)} \frac{dW_t}{dt}$

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



Theoretical
Conversion rate

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

Arrhenius Equation

Kinetic parameters

E_a	Isoconv. Methods	Differential	- Friedman (1964), FD
		Integral	- Ozawa-Flynn-Wall (1965, 1966), OFW
		Integral	- Coats-Redfern modified (Braun et al., 1991), CRM
		Integral	- (advanced) Vyazovkin (1997), VZ

$f(\alpha)$ - Master Plots method

A - Linearization method

3.1.1. Isoconversional Methods

Graphical solution

FD

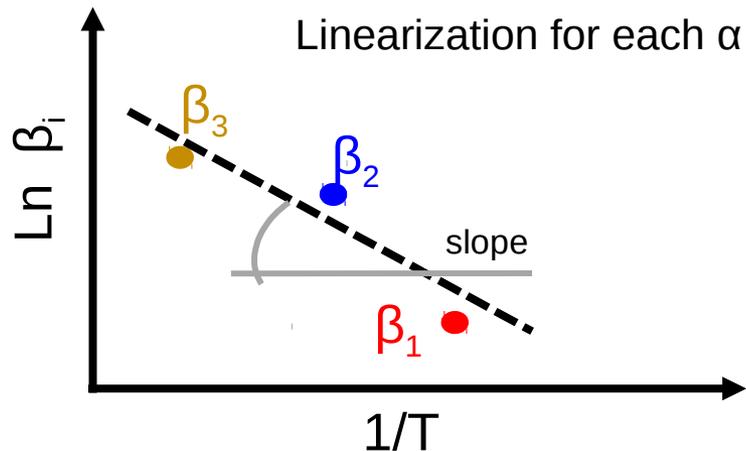
$$\ln \left(\frac{d\alpha}{dt} \right)_{\alpha,\beta} = cte - \frac{E_a}{RT_{\alpha,\beta}} ; E_a = aR$$

CRM

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

OFW

$$\log \beta_i = cte - 0.4567 \frac{E_a}{RT} ; E_a = \frac{aR}{0.4567}$$



Numerical solution

VZ

$$\phi(E_a) =$$

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

$$I(E_{a\alpha}, T_{\alpha,i}) =$$

$$p \left(\frac{E_{a\alpha}}{R \cdot T_{\alpha,i}} \right) \cdot \frac{E_{a\alpha}}{R}$$

Minimization for each α

Pérez-Maqueda;
Criado (2000) $p \left(\frac{E_a}{RT_\alpha} \right)$

3.1.2 Master Plots (mechanism) and Linearization (A) Methods

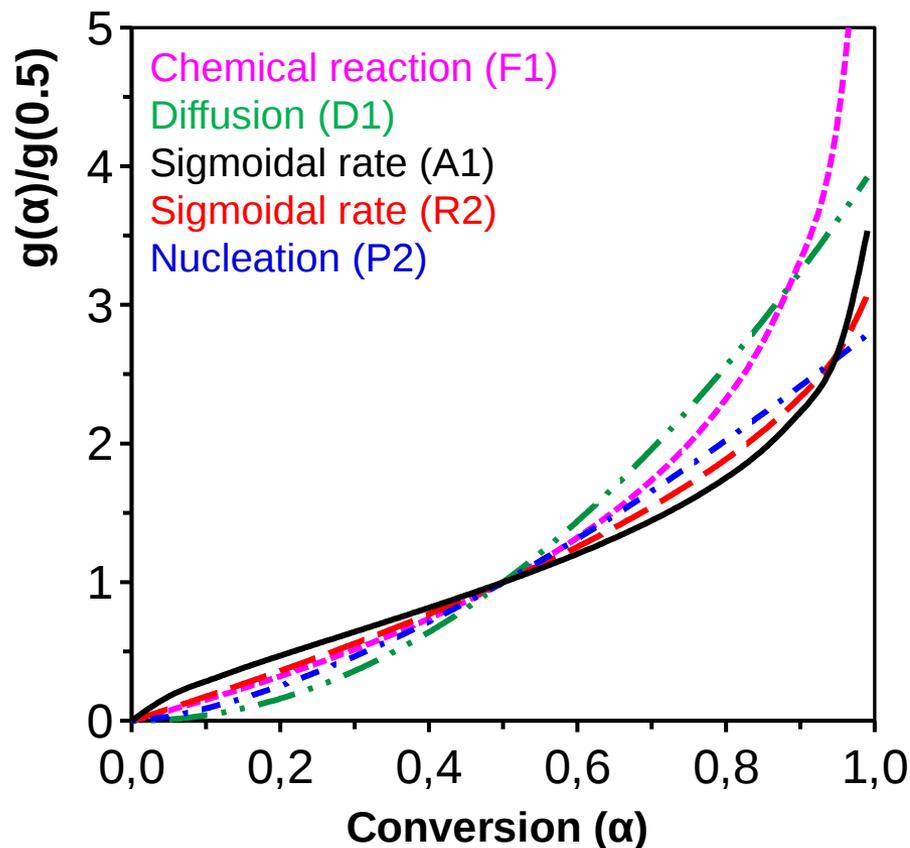


Fig. 4: Decomposition phenomena representation

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

Integral
solution

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

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

Pérez-Maqueda; Criado (2000)

$$p\left(\frac{E_a}{RT\alpha}\right) = \left(\frac{\exp(-x)}{x}\right) * \left(\frac{x^7 + 70x^6 + \dots + 357120}{x^8 + 72x^7 + 2024x^6 + \dots + 403200}\right)$$

3.4 Kinetic Modeling – Multistep reaction model

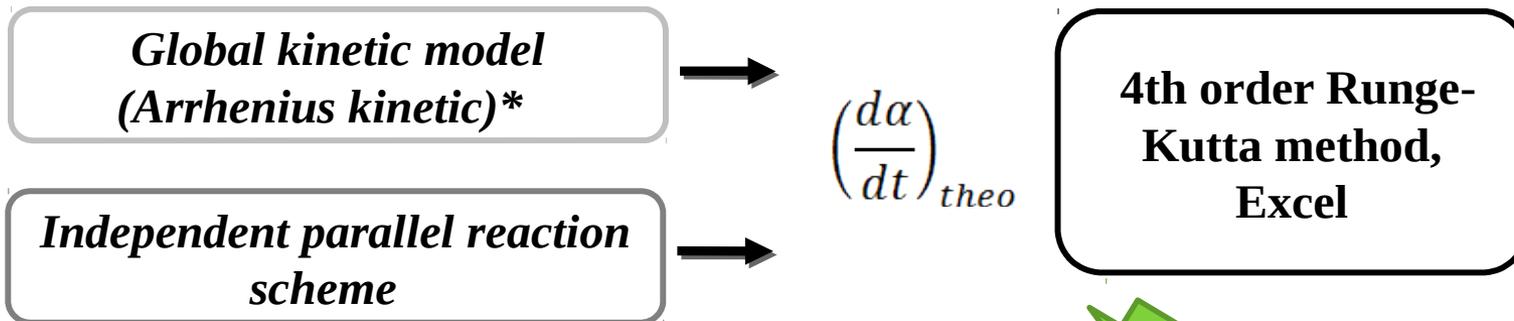
Independent parallel reactions scheme, IPRS



$$\frac{d\alpha_i}{dt} = k_i (1 - \alpha_i)^{n_i} \quad \longrightarrow \quad \frac{d\alpha_i}{dt} = A_i \exp\left(\frac{E_{a_i}}{RT}\right) \underbrace{(1 - \alpha_i)^{n_i}}_{f(\alpha)=Fn}$$

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

3.5 Validation of data modeling



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

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

$$AD(\%) = \left[\frac{\sqrt{\frac{SS}{N}}}{\left(\frac{d\alpha}{dt}\right)_{exp,max}} \right] * 100$$

residual sum of squares

Average deviation, Órfão et al., (1999)

< 5%

4. Results and Discussion

4.1 Thermal decomposition analysis

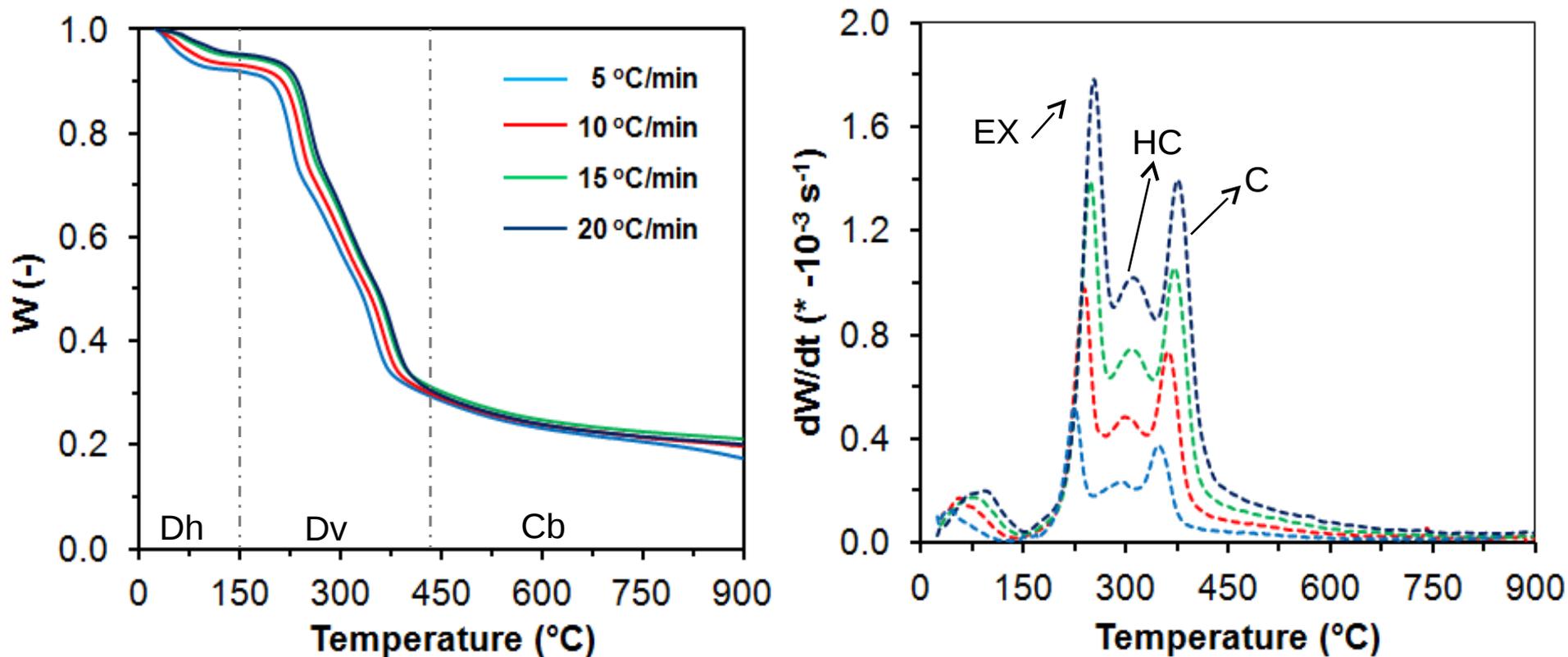
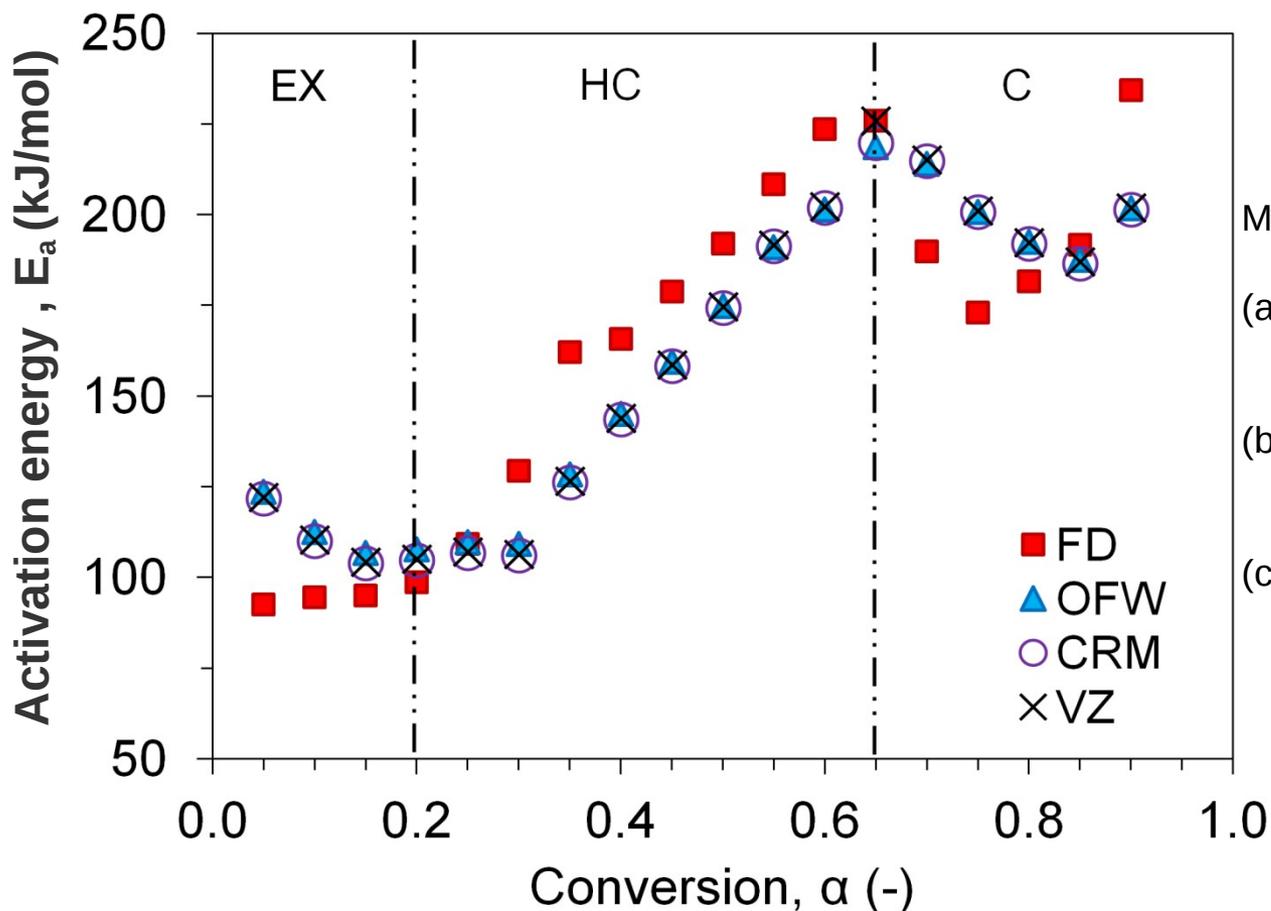


Fig. 5. Normalized mass, W , and its derivative, dW/dt , for four heating rates

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°C

4.3 Determination of reaction mechanism

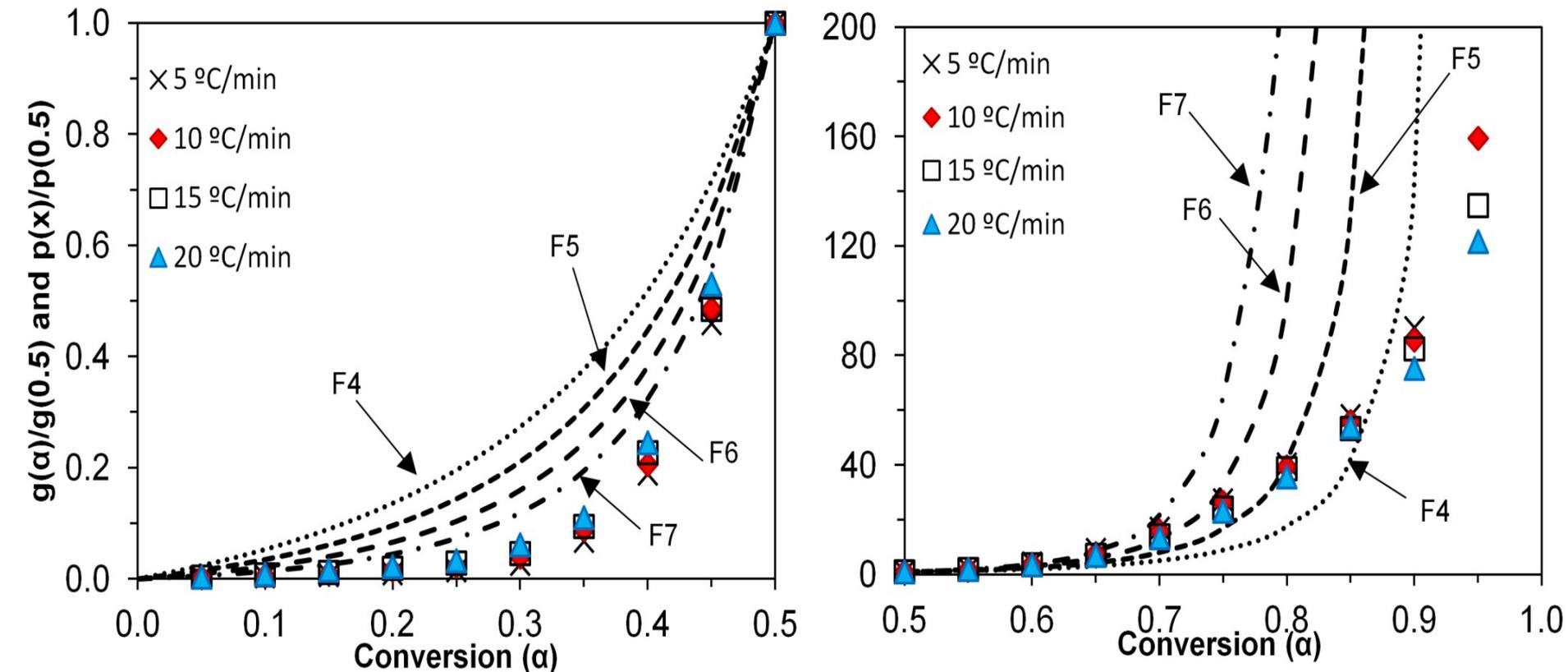


Fig. 7 Comparatives of experimental and theoretical data as a function of conversion

$$E_a \text{ (VZ)}; \alpha = 0.2-0.8 \text{ (} T=180-420^\circ\text{C)} ; F6 = (1-\alpha)^6$$

4.4 Determination of pre-exponential factor

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_A}{RT}\right) f(\alpha)$$



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

$$E_{a_vz} = 165.5 \text{ kJ/mol}$$

$$\text{Difference} = 4.6\%$$

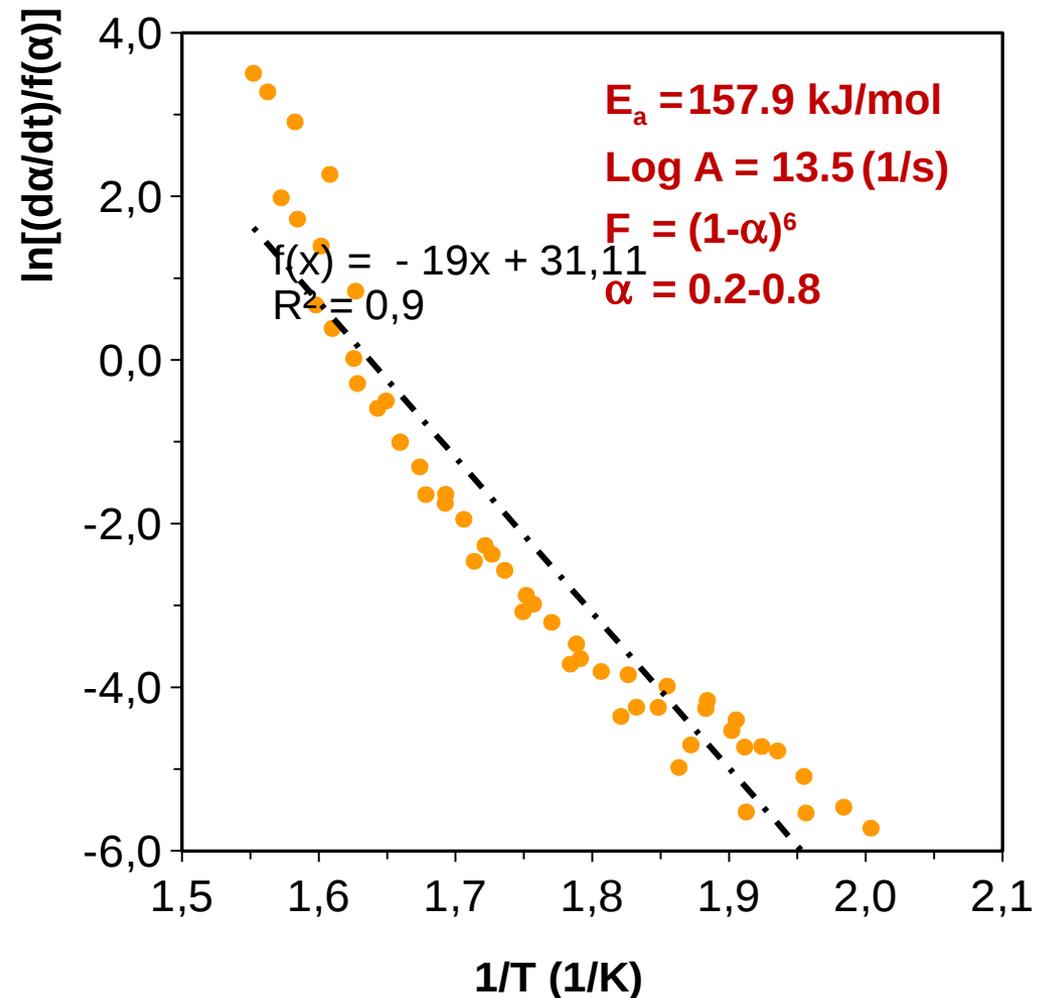


Fig. 8 Linearization of the conversion rate equation as

a function of the inverse of absolute temperature

4.5 Validation of kinetic parameters for both reaction models, 5° C/min

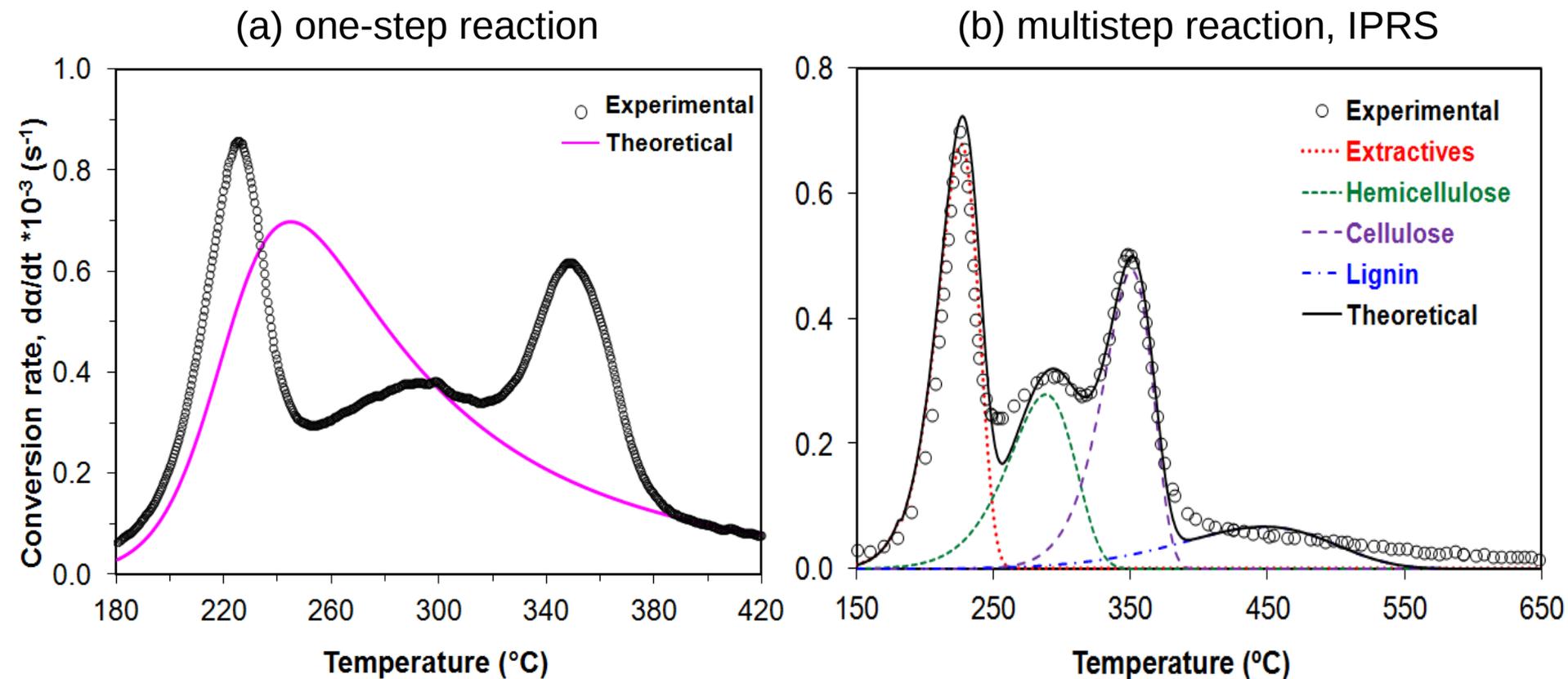


Fig. 9 Comparative between experimental and theoretical conversion rates (a, b) and for each component (b) as a function of temperature

Table 1: Parameters obtained through the reaction models ($\beta=5-20^\circ\text{C}/\text{min}$)

Model	E_a (kJ/mol)	Log A (log s ⁻¹)	Reaction order	volatilized fraction	AD (%)
One-step	152.57	13.03	F6 = (1- α) ⁶		22.64± 1.24
Multistep, IPRS					
Extractives	131.43 ± 1.60	11.39 ± 0.27	1	0.32 ± 0.01	4.61± 0.14
Hemicellulose	103.65 ± 0.50	7.31 ± 0.06	1	0.23 ± 0.01	
Cellulose	174.05 ± 0.06	12.24 ± 0.05	1	0.27 ± 0.01	
Lignin	64.04 ± 2.85	2.09 ± 0.25	1.5	0.18 ± 0.01	

[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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