

Pyrolysis of Energy Cane Bagasse: Investigating Kinetics, Thermodynamics, and Effect of Temperature on Volatile Products

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Supplementary Material

Multicomponent kinetic modeling

For comparison purposes, results of three other classical integral methods, namely the Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), and Starink (STK) have been present in the supplementary material. In contrast to Fridman (FR) method, the integral isoconversional methods, expressed by Equation (S1) to Equation (S3), use numerical approximations to solve $[p(x)]$. The FWO method applies Doyle's approximation [50], the KAS method uses Murray and White's approximation [50], and the STK method uses Starink's approximation [51]. Four isoconversional methods were used to evaluate the coherence of activation energy values employing two distinct calculation algorithms, namely differential and integral methods [31,52].

$$\text{FWO: } \log \beta = \log \left(\frac{AE_a}{Rg(\alpha)} \right) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (\text{S1})$$

$$\text{KAS: } \ln \left(\frac{\beta}{T^2} \right) = \ln \left(\frac{AR}{E_a g(\alpha)} \right) - \frac{E_a}{RT} \quad (\text{S2})$$

$$\text{STK: } \ln \left(\frac{\beta}{T^{1.92}} \right) = \text{Constant} - 1.0008 \frac{E_a}{RT} \quad (\text{S3})$$

The activation energy (E_a) was determined for a constant conversion degree by plotting $\log(\beta)$ vs. $(1/T)$ for the FWO method, $\ln(\beta/T^2)$ vs. $(1/T)$ for the KAS

method and $\ln(\beta/T^{1.92})$ vs. $(1/T)$ for the STK method, as indicated by linearized versions of Equation (S1) to Equation (S3).

Results for activation energy

Figure S1 illustrates the dependence of the activation energy on the extent of conversion for each of the pseudo-components by the FR, FWO, KAS and STK methods. The activation energy dependence on the extent of conversion for the three integral methods shows a similar trend with considerable overlap. However, the activation energy values for the FR differential method varied with the degree of conversion, similar to the integral isoconversional methods, but with a clear overestimation.

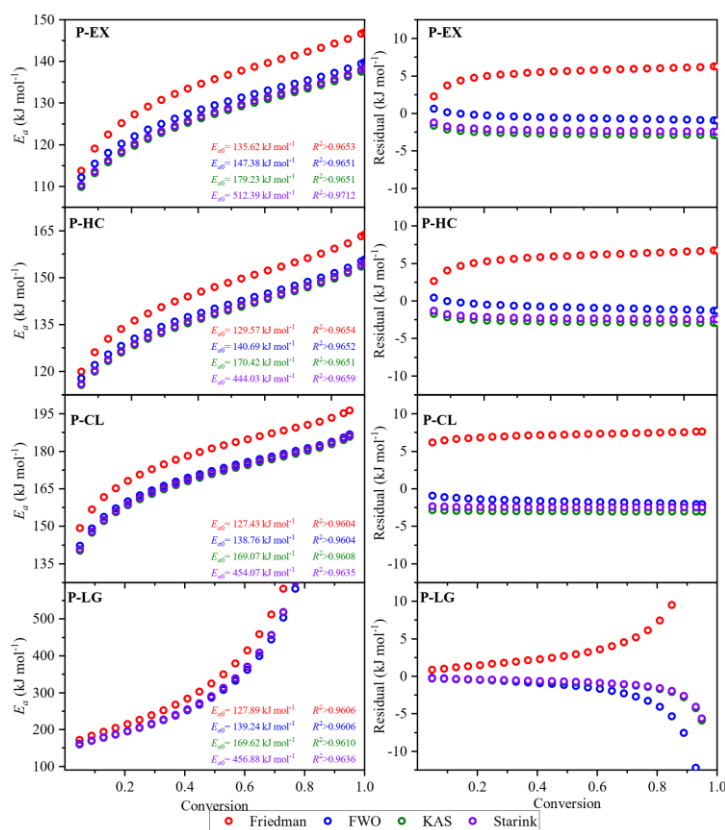


Figure S1. Dependence of the activation energy and residual plots on the extent of conversion for the pyrolysis of energy cane bagasse with four independent parallel reactions for the four isoconversional methods FR, FWO, KAS and STK.

As displayed in Table S1, the activation energy results obtained from FWO, KAS, and STK isoconversional methods exhibited slight deviations attributed to the use of different temperature integral approximations. Also, the FR isoconversional method, which is free of mathematical approximations and utilizes numerical differentiation of nonisothermal thermogravimetry data, is highly sensitive to experimental noise, representing a major drawback of the method [59,62]. The literature indicates that this phenomenon affects activation energy calculations, resulting in the FR isoconversional method typically yielding higher activation energy values than classical integral methods [60,61].

Table S1. Main compounds from TIC chromatogram of the fast pyrolysis of energy cane bagasse.

Isoconversional method	P-EX		P-HL		P-CL		P-LG	
	E_a (kJ mol ⁻¹)	R^2	E_a (kJ mol ⁻¹)	R^2	E_a (kJ mol ⁻¹)	R^2	E_a (kJ mol ⁻¹)	R^2
FR	135.62	0.97	147.38	0.97	179.23	0.97	512.39	0.97
FWO	129.57	0.97	140.69	0.97	170.42	0.97	444.03	0.97
KAS	127.43	0.96	138.76	0.96	169.07	0.96	456.07	0.96
STK	127.89	0.96	139.24	0.96	169.62	0.96	456.88	0.96

Abbreviations: P-EX, pseudo-extractives; P-HC, pseudo-hemicellulose; P-CL, pseudo-cellulose; and P-LG, pseudo-lignin.

Table S2. Thermodynamic parameters with respect to progressing conversions and their respective average values for the pyrolysis of energy cane bagasse with four independent parallel reactions. Units: ΔH and ΔG (kJ mol⁻¹); ΔS (J mol⁻¹ K⁻¹).

α	P-EX			P-HC			P-CL			P-LG		
	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS	ΔH	ΔG	ΔS
0.1	131.45	154.33	-45.57	143.09	161.55	-35.78	171.70	180.45	-15.17	507.49	207.60	508.60
0.2	131.33	154.99	-45.80	142.94	162.18	-36.05	171.56	180.71	-15.41	507.32	197.35	508.32
0.3	131.26	155.39	-45.94	142.85	162.57	-36.22	171.47	180.87	-15.56	507.18	188.59	508.09
0.4	131.20	155.69	-46.04	142.79	162.86	-36.34	171.41	180.99	-15.66	507.03	179.94	507.87
0.5	131.16	155.93	-46.13	142.73	163.10	-36.44	171.36	181.08	-15.74	506.89	170.97	507.64
0.6	131.12	156.14	-46.20	142.68	163.32	-36.53	171.31	181.17	-15.81	506.73	161.57	507.41
0.7	131.09	156.34	-46.26	142.63	163.55	-36.62	171.27	181.24	-15.88	506.56	151.28	507.17
0.8	131.05	156.55	-46.33	142.58	163.79	-36.71	171.23	181.32	-15.94	506.38	140.21	506.91
0.9	131.00	156.81	-46.42	142.50	164.12	-36.84	171.18	181.41	-16.02	506.18	128.05	506.64
Av	131.18	155.80	-46.08	142.76	163.00	-36.39	171.39	181.03	-15.69	506.86	169.51	507.63
SD	0.14	0.79	0.27	0.19	0.81	0.34	0.17	0.31	0.27	0.44	26.63	0.66

Abbreviations: P-EX: pseudo-extractives; P-HC: pseudo-hemicellulose; P-CL: pseudo-cellulose; and P-LG: pseudo-lignin. Av: Average values; SD: Standard Deviation.

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