Supplementary Materials

Kinetic Modeling of Co-Pyrogasification in Municipal Solid Waste (MSW) Management: Towards Sustainable Resource Recovery and Energy Generation

S1. Kinetic modeling

The reaction rate for a single-step mechanism can be expressed by the differential equation:

$$\frac{d\alpha}{dt}=k(T)f(\alpha) \tag{S1.1}$$

where α is the conversion of the solid reactant that can be defined as a function of mass loss, as follows:

$$\alpha=\frac{m_0-m_t}{m_0-m_\infty} \tag{S1.2}$$

assigning m_0 to the initial mass, m_t to the mass at time t, and m_∞ to the residual mass after the heating process finishes. The term $f(\alpha)$ in Eq. (S1.1) corresponds to the kinetic model, which is an exclusive function of the conversion. On the other hand, k is the specific rate constant, which can be defined according to the empirical Arrhenius equation:

$$k(T)=A\exp\left(\frac{-E}{RT}\right) \tag{S1.3}$$

The main objective of the kinetic analysis is to determine the kinetic triplet: E, A and $f(\alpha)$, to enable prediction of the decomposition rate of MSW by pyrogasification. For non-isothermal determinations, Eq. (S1.1) can be rewritten as follows:

$$\frac{d\alpha}{dT}\frac{dT}{dt}=k(T)f(\alpha) \tag{S1.4}$$

If the heating rate is constant, then $dT/dt = \beta$. Combining Eqs. (S1.3) and (S1.4) yields:

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{S1.5}$$

By taking the derivative of Eq. (S1.2):

$$\frac{d\alpha}{dt}=\frac{-1}{m_0-m_\infty}\frac{dm}{dt} \tag{S1.6}$$

dm/dt is the derivative thermogravimetric (DTG) data, which is obtained through numerical differentiation with Lagrange's second order numerical operator.

For a multi-step mechanism, such as independent parallel reactions, Eq. (S1.5) can be rewritten considering that each reaction, i, partially contributes to the total mass loss in a fraction, y_i, so that the global conversion is given by:

$$\alpha=\sum_{i=1}^{N} y_i\alpha_i \tag{S1.7}$$

The derivative form of Eq. (S1.7) leads to:

$$\frac{d\alpha}{dT}=\sum_{i=1}^{N} y_i\frac{d\alpha_i}{dT} \tag{S1.8}$$

For each independent reaction, the conversion rate can be written as follows:

$$\frac{d\alpha_i}{dT}=\frac{A_i}{\beta}\exp\left(\frac{-E_i}{RT}\right)f_i(\alpha_i) \tag{S1.9}$$

Finally, by combining Eqs. (S1.8) and (S1.9), an expression analogous to Eq. (S1.5) for multi-step mechanisms is obtained:

$$\frac{d\alpha}{dT} = \sum_{i=1}^{N} y_i \frac{A_i}{\beta} \exp\left(\frac{-E_i}{RT}\right) f_i(\alpha_i) \tag{S1.10}$$

S2. Kinetic parameters

S2.1 Isoconversional methods

Integral isoconversional methods are used to determine activation energy. They are obtained from the integrated form of Eq. (S1.5):

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_{T_0}^T \frac{A}{\beta} \exp\left(\frac{-E}{RT}\right) dT = \frac{AE}{\beta R} [P(u) - P(u_0)] \tag{S2.1}$$

where $u_0 = E/R\,T_0$, $u = E/RT$ and $P(u)$ is the approximation of the temperature integral. Depending on the function $P(u)$ used to approximate the integral, various integral isoconversional methods arise, among which the FWO (Flynn-Wall-Ozawa), KAS (Kissinger-Akahira-Sunose) and Starink methods stand out [43].

$$\text{FWO: } \ln\beta_j = \text{Const} - 1.0516 \left(\frac{E_\alpha}{RT}\right) \tag{S2.2}$$

$$\text{KAS: } \ln\left(\frac{\beta_j}{T^2}\right) = \text{Const} - \frac{E_\alpha}{RT} \tag{S2.3}$$

$$\text{Starink: } \ln\left(\frac{\beta_j}{T^{1.92}}\right) = \text{Const} - 1.0008 \frac{E_\alpha}{RT} \tag{S2.4}$$

The activation energy can be determined from the slope of the regression analysis line in any of the three integral methods by plotting $\ln(\beta_j/T^m)$ vs $1/T$, where $j = 1 \dots J$, with J being the number of heating rates used in the experiment.

The dependence between activation energy and degree of conversion is important to determine whether it is necessary to model the kinetics of the pyrolysis chemical reaction considering a single step for a mechanism of multiple steps, since a significant variation of the activation energy with conversion could mean the existence of complex kinetic processes, such as the occurrence of multiple parallel reactions [44].

S2.2 Compensation Effect

For a series of closely similar reactions, different authors have reported the existence of the kinetic compensation effect (KCE), which can be seen when there is a linear

relationship between the logarithm of the pre-exponential factor and the activation energy [45].

$$\ln A = a + bE \qquad (S2.5)$$

The physical origin of the KCE are not entirely certain, although it is believed to be related to the thermodynamic or enthalpy-entropy compensation (EEC) through the transition state theory, since the activation energy and the pre-exponential factor are related to these thermodynamic parameters [46].

$$A = k^{\ddagger} \exp\left(\frac{\Delta S}{R}\right) \qquad (S2.6)$$

$$E = \Delta H + RT \approx \Delta H \qquad (S2.7)$$

Where ΔS and ΔH represent the entropy and enthalpy change between reactants and the transition state, and $k^{\ddagger} = \frac{k_B T}{h}$ according to Eyring's theory (k_B being Boltzmann's constant and h being Planck's constant). The compensation effect can thus be expressed in terms of the change in enthalpy and entropy:

$$\Delta H = m + n\Delta S \qquad (S2.8)$$

In any case, it is possible to determine the pre-exponential factor by making use of the compensation effect considering different kinetic models, $f(\alpha)$, which represent the different closely similar reactions [44]. From the Coats and Redfern linear approximation [47] it is possible to calculate the activation energy and pre-exponential factor corresponding to different kinetic models.

$$\ln\left(\frac{g_z(\alpha_i)}{T^2}\right) = \ln\left(\frac{A_{i,z}R}{\beta E_{i,z}}\right) - \frac{E_{i,z}}{RT} + \ln\left(1 - \frac{2RT}{E_{i,z}}\right) \qquad (S2.9)$$

Since $2RT/E_{i,k}$ is usually much lower than one, $\ln\left(1 - \frac{2RT}{E_{i,z}}\right) \rightarrow 0$, and therefore:

$$\ln\left(\frac{g_z(\alpha_i)}{T^2}\right) = \ln\left(\frac{A_{i,z}R}{\beta E_{i,z}}\right) - \frac{E_{i,z}}{RT} \qquad (S2.10)$$

In Eq. (B.10), the subscript z represents the reaction model used. Using multiple kinetic models, g_z, (see Table S2.1), it is possible to perform a linear regression analysis to find, from slope and intersect, the pair ($E_{i,z}$; ln $A_{i,z}$) from Eq. (S2.10). The pairs obtained from each model are plotted in a scatter diagram and linear regression analysis is performed to obtain the compensation parameters a and b of Eq. (S2.5). Thus,

$$A_i=\exp(a\overline{E}_i+b) \tag{S2.11}$$

with $\overline{E}_i$ being the mean value of the activation energy found by the isoconversional methods previously described.

Table S2.1. Conversion function, $f(\alpha)$, and integral rate, $g(\alpha)$, for different reaction models

Reaction Model	$f(\alpha)$	$g(\alpha)=\int_0^\alpha \dfrac{d\alpha}{f(\alpha)}$
Reaction Order		
F1. First Order	$(1-\alpha)$	$-\ln(1-\alpha)$
F2. Second Order	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
F3. Third Order	$(1-\alpha)^3$	$(1/2)[(1-\alpha)^{-2}-1]$
Fn. N-Order	$(1-\alpha)^n$	$[1-(1-\alpha)^{1-n}](1-n)^{-1}$
Diffusional		
D1. One-dimensional diffusion	$1/2\,\alpha^{-1}$	α^2
D2. Two-dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
D3. Three-dimensional diffusion (Jander)	$\dfrac{3}{2}(1-\alpha)^{\frac{2}{3}}\left[1-(1-\alpha)^{\frac{1}{3}}\right]^{-1}$	$\left[1-(1-\alpha)^{\frac{1}{3}}\right]^2$
D4. Ginstling-Brounshtein	$3\left[2\left((1-\alpha)^{-1/3}-1\right)\right]^{-1}$	$1-(2/3)\alpha-(1-\alpha)^{2/3}$
Nucleation		
P2. Power Law	$2\alpha^{1/2}$	$\alpha^{1/2}$
P3. Power Law	$3\alpha^{2/3}$	$\alpha^{1/3}$
P4. Power Law	$4\alpha^{3/4}$	$\alpha^{1/4}$
P2/3. Power Law	$2/3\,\alpha^{-1/2}$	$\alpha^{3/2}$
A2. Avrami-Erofeev	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3. Avrami-Erofeev	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A4. Avrami-Erofeev	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
Contracting Geometry		
R2. Contracting Area	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R3. Contracting Volume	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

S2.3 Master-plots

Considering that u >> u0 and therefore P(u) >> P(u0), the integrated rate equation (Eq. (B.1)) can be rewritten as:

$$g(\alpha)=\int_0^\alpha \frac{d\alpha}{f(\alpha)} \approx \frac{AE}{\beta R}P(u) \qquad (S2.12)$$

Doyle's approximation can be used for the temperature integral $P(u)$:

$$P(u)=0.0048e^{-1.0516u} \qquad (S2.13)$$

Evaluating $\alpha=0.5$ in Eq. (S2.12):

$$g(0.5)=\frac{AE}{\beta R}P(u_{0.5}) \qquad (S2.14)$$

Dividing Eq. (S2.12) by Eq. (S2.14):

$$\frac{g(\alpha)}{g(0.5)}=\frac{P(u)}{P(u_{0.5})} \qquad (S2.15)$$

The term on the left of Eq. (S2.15) represents the theoretical plot, while the term on the right represents the experimental plot. The function $g(\alpha)$ (and therefore, $f(\alpha)$) will be the adequate model if it approximates the experimental values verifying as best as possible the exact form of Eq. (S2.15).

S3. Activation energy through isoconversional methods results for a multi-step mechanism

Table S3.1. Activation energy (including statistical parameters) from isoconversional methods, for PW pyrogasification

α	FWO				KAS				Starink			
	E [kJ/mol]	R^2	MSE	AAD	E [kJ/mol]	R^2	MSE	AAD	E [kJ/mol]	R^2	MSE	AAD
0.15	18.38	0.876	2.999×10^{-02}	4.553×10^{-02}	14.83	0.9625	3.055×10^{-02}	4.595×10^{-03}	21.15	0.9636	2.999×10^{-02}	4.553×10^{-02}
0.20	17.96	0.921	1.909×10^{-02}	3.695×10^{-02}	14.34	0.9522	1.969×10^{-02}	3.753×10^{-03}	25.13	0.9537	1.909×10^{-02}	3.695×10^{-02}
0.25	17.49	0.963	1.239×10^{-02}	3.004×10^{-02}	13.81	0.9532	1.298×10^{-02}	3.075×10^{-02}	26.25	0.9547	1.239×10^{-02}	3.004×10^{-02}
0.30	17.85	0.972	9.025×10^{-03}	2.574×10^{-02}	14.15	0.9439	9.552×10^{-03}	2.648×10^{-04}	24.38	0.9458	9.025×10^{-03}	2.574×10^{-02}
0.35	18.88	0.989	6.785×10^{-03}	2.236×10^{-02}	15.20	0.9461	7.214×10^{-03}	2.306×10^{-03}	21.43	0.9481	6.785×10^{-03}	2.236×10^{-02}
0.40	19.88	0.989	2.691×10^{-03}	1.412×10^{-02}	16.21	0.9456	2.953×10^{-03}	1.479×10^{-02}	20.43	0.9477	2.691×10^{-03}	1.412×10^{-02}
0.45	19.59	0.996	8.194×10^{-04}	7.785×10^{-03}	15.87	0.9474	9.745×10^{-04}	8.489×10^{-03}	18.88	0.9496	8.194×10^{-04}	7.785×10^{-03}
0.50	19.50	0.998	2.618×10^{-04}	4.395×10^{-03}	15.74	0.9503	3.543×10^{-04}	5.112×10^{-03}	17.84	0.9525	2.618×10^{-04}	4.395×10^{-03}
0.55	19.12	0.999	1.845×10^{-05}	1.162×10^{-03}	15.31	0.9483	2.504×10^{-06}	4.282×10^{-02}	17.13	0.9507	1.845×10^{-05}	1.162×10^{-03}
0.60	20.07	0.999	1.922×10^{-06}	3.755×10^{-04}	16.27	0.9529	1.273×10^{-06}	3.055×10^{-04}	15.62	0.9552	1.922×10^{-06}	3.755×10^{-04}
0.65	21.35	0.999	1.890×10^{-04}	3.712×10^{-03}	17.56	0.9643	1.330×10^{-04}	3.115×10^{-03}	13.24	0.9662	1.890×10^{-04}	3.712×10^{-03}
0.70	20.60	0.993	1.540×10^{-03}	1.051×10^{-02}	16.76	0.9999	1.371×10^{-03}	9.918×10^{-03}	12.71	0.9999	1.540×10^{-03}	1.051×10^{-02}
0.75	25.60	0.999	2.373×10^{-03}	1.321×10^{-03}	21.88	0.9903	4.303×10^{-05}	1.778×10^{-03}	14.68	0.9906	2.373×10^{-03}	1.321×10^{-03}
0.80	20.56	0.994	1.373×10^{-03}	9.936×10^{-03}	16.62	0.9902	1.026×10^{-03}	9.309×10^{-03}	19.45	0.9908	1.373×10^{-03}	9.936×10^{-03}
0.85	25.42	0.999	1.301×10^{-04}	3.082×10^{-03}	21.61	0.9804	9.388×10^{-05}	2.618×10^{-03}	21.92	0.9820	1.301×10^{-04}	3.082×10^{-03}
Average	19.88				16.13				19.01			

Table S3.2. Activation energy (including statistical parameters) from isoconversional methods, for PP – PC1 pyrogasification

α	FWO				KAS				Starink			
	E [kJ/mol]	R^2	MSE	AAD	E [kJ/mol]	R^2	MSE	AAD	E [kJ/mol]	R^2	MSE	AAD
0.15	16.50	0.846	3.740×10^{-02}	4.616×10^{-02}	13.15	0.759	1.785×10^{-02}	3.635×10^{-02}	9.27	0.612	1.782×10^{-02}	3.633×10^{-02}
0.20	18.94	0.909	2.211×10^{-02}	3.720×10^{-02}	15.61	0.861	2.238×10^{-02}	4.068×10^{-02}	11.63	0.777	2.235×10^{-02}	4.065×10^{-02}
0.25	19.81	0.910	2.178×10^{-02}	3.697×10^{-02}	16.46	0.865	2.150×10^{-02}	3.989×10^{-02}	12.43	0.786	2.147×10^{-02}	3.985×10^{-02}
0.30	19.35	0.907	2.262×10^{-02}	3.757×10^{-02}	15.93	0.857	2.530×10^{-02}	4.323×10^{-02}	11.85	0.771	2.526×10^{-02}	4.320×10^{-02}
0.35	20.34	0.928	1.751×10^{-02}	3.358×10^{-02}	16.91	0.891	2.378×10^{-02}	4.193×10^{-02}	12.79	0.825	2.374×10^{-02}	4.189×10^{-02}
0.40	20.24	0.907	2.257×10^{-02}	3.754×10^{-02}	16.76	0.859	2.368×10^{-02}	4.184×10^{-02}	12.58	0.777	2.362×10^{-02}	4.179×10^{-02}
0.45	21.16	0.940	1.466×10^{-02}	3.100×10^{-02}	17.69	0.909	2.240×10^{-02}	4.070×10^{-02}	13.48	0.855	2.234×10^{-02}	4.065×10^{-02}
0.50	21.05	0.943	1.385×10^{-02}	3.021×10^{-02}	17.53	0.913	2.084×10^{-02}	3.927×10^{-02}	13.29	0.861	2.078×10^{-02}	3.922×10^{-02}
0.55	21.24	0.965	8.390×10^{-03}	3.392×10^{-02}	17.69	0.948	2.123×10^{-02}	3.964×10^{-02}	13.41	0.914	2.117×10^{-02}	3.958×10^{-02}
0.60	22.61	0.961	9.374×10^{-03}	3.521×10^{-02}	19.10	0.943	1.886×10^{-02}	3.737×10^{-02}	14.78	0.910	1.879×10^{-02}	3.730×10^{-02}
0.65	22.85	0.980	4.887×10^{-03}	1.848×10^{-02}	19.29	0.970	1.394×10^{-02}	3.213×10^{-02}	14.92	0.953	1.388×10^{-02}	3.206×10^{-02}
0.70	23.57	0.987	3.173×10^{-03}	1.499×10^{-02}	19.99	0.981	1.455×10^{-06}	3.245×10^{-04}	15.57	0.971	9.042×10^{-07}	2.558×10^{-04}
0.75	23.31	0.995	1.097×10^{-03}	8.894×10^{-03}	19.66	0.994	4.683×10^{-03}	1.859×10^{-02}	15.17	0.991	4.672×10^{-03}	1.856×10^{-02}
0.80	23.38	1.000	2.652×10^{-06}	4.413×10^{-04}	19.62	1.000	3.299×10^{-03}	1.523×10^{-02}	15.04	1.000	3.339×10^{-03}	1.532×10^{-02}
0.85	16.50	0.846	6.178×10^{-04}	6.757×10^{-03}	13.15	0.759	5.115×10^{-03}	1.887×10^{-02}	9.27	0.612	5.201×10^{-03}	1.902×10^{-02}
Average	21.37				17.86				13.61			

Table S3.3. Activation energy (including statistical parameters) from isoconversional methods, for PP – PC2 pyrogasification

α	FWO	KAS	Starink

	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD
0.15	42.67	0.994	3.740×10^{-03}	4.616×10^{-02}	40.24	0.992	1.785×10^{-03}	1.046×10^{-02}	35.95	0.990	1.516×10^{-03}	1.060×10^{-02}
0.20	37.75	0.995	2.211×10^{-03}	9.867×10^{-03}	34.92	0.993	2.238×10^{-03}	1.006×10^{-02}	30.51	0.990	1.416×10^{-03}	2.069×10^{-02}
0.25	36.71	0.977	2.178×10^{-03}	2.030×10^{-02}	33.72	0.969	2.150×10^{-03}	32.050×10^{-02}	29.21	0.959	5.799×10^{-03}	3.985×10^{-02}
0.30	35.64	0.975	2.262×10^{-03}	2.099×10^{-02}	32.52	0.967	2.530×10^{-03}	2.121×10^{-02}	27.94	0.955	6.214×10^{-03}	2.677×10^{-02}
0.35	33.32	0.975	1.751×10^{-03}	3.201×10^{-02}	30.03	0.966	2.378×10^{-03}	2.188×10^{-02}	25.40	0.952	6.293×10^{-03}	3.165×10^{-02}
0.40	32.92	0.942	2.257×10^{-03}	3.754×10^{-02}	29.53	0.921	2.368×10^{-02}	2.638×10^{-02}	24.83	0.890	1.455×10^{-02}	2.136×10^{-02}
0.45	33.00	0.974	1.466×10^{-02}	3.100×10^{-02}	29.59	0.964	2.240×10^{-03}	4.070×10^{-02}	24.87	0.948	3.248×10^{-02}	9.697×10^{-02}
0.50	30.79	0.962	1.385×10^{-03}	3.021×10^{-02}	27.22	0.946	2.084×10^{-02}	3.927×10^{-02}	22.46	0.921	2.214×10^{-03}	3.114×10^{-02}
0.55	29.83	0.947	8.390×10^{-03}	3.392×10^{-02}	26.15	0.924	2.123×10^{-02}	3.964×10^{-02}	21.33	0.889	1.333×10^{-03}	3.958×10^{-02}
0.60	27.61	0.945	9.374×10^{-03}	3.521×10^{-02}	23.76	0.918	1.886×10^{-02}	3.737×10^{-02}	18.90	0.874	3.187×10^{-02}	3.730×10^{-02}
0.65	27.35	0.951	4.887×10^{-03}	1.848×10^{-02}	23.43	0.927	1.394×10^{-02}	3.213×10^{-02}	18.51	0.885	1.398×10^{-02}	3.206×10^{-02}
0.70	27.28	0.943	3.173×10^{-03}	1.499×10^{-02}	23.31	0.914	1.455×10^{-06}	3.245×10^{-04}	18.34	0.865	1.240×10^{-02}	3.361×10^{-04}
0.75	26.85	0.929	1.097×10^{-03}	8.894×10^{-03}	22.76	0.893	4.683×10^{-03}	1.859×10^{-02}	17.71	0.832	3.007×10^{-02}	1.856×10^{-02}
0.80	26.00	0.931	2.652×10^{-06}	4.413×10^{-04}	21.77	0.892	3.299×10^{-03}	1.523×10^{-02}	16.63	0.826	3.251×10^{-02}	3.567×10^{-02}
0.85	25.31	0.960	6.178×10^{-04}	6.757×10^{-03}	20.89	0.942	5.115×10^{-03}	1.241×10^{-03}	15.61	0.913	1.690×10^{-02}	3.492×10^{-03}
Average	31.16	0.994			27.59	0.992			22.82	0.990		

Table S3.4. Activation energy (including statistical parameters) from isoconversional methods, for PO – PC1 pyrogasification

α	FWO				KAS				Starink			
	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD
0.15	21.59	0.980	4.885×10^{-03}	4.616×10^{-02}	18.32	0.968	1.785×10^{-03}	3.635×10^{-02}	14.28	0.946	1.782×10^{-03}	3.633×10^{-02}
0.20	21.51	1.000	2.211×10^{-05}	3.720×10^{-03}	18.13	0.999	2.238×10^{-04}	4.068×10^{-03}	13.98	0.998	2.235×10^{-04}	4.065×10^{-03}
0.25	19.97	0.996	2.178×10^{-04}	3.697×10^{-03}	16.38	0.993	2.150×10^{-03}	3.989×10^{-03}	12.13	0.986	2.147×10^{-03}	3.985×10^{-03}

α	E [kJ/mol]	R^2	MSE	AAD	E [kJ/mol]	R^2	MSE	AAD	E [kJ/mol]	R^2	MSE	AAD
0.30	20.18	1.000	2.262×10^{-05}	3.757×10^{-03}	16.53	1.000	2.530×10^{-05}	4.323×10^{-03}	12.21	0.999	2.526×10^{-05}	4.320×10^{-03}
0.35	23.12	0.992	1.751×10^{-03}	3.358×10^{-02}	19.49	0.987	2.378×10^{-03}	4.193×10^{-02}	15.04	0.977	2.374×10^{-03}	4.189×10^{-02}
0.40	19.80	1.000	2.257×10^{-05}	3.754×10^{-03}	15.99	1.000	2.368×10^{-06}	4.184×10^{-04}	11.54	1.000	4.113×10^{-07}	1.735×10^{-04}
0.45	19.54	0.999	1.466×10^{-04}	3.100×10^{-03}	15.66	0.998	2.240×10^{-04}	4.070×10^{-03}	11.17	0.998	2.234×10^{-04}	4.065×10^{-03}
0.50	19.79	0.999	1.385×10^{-04}	3.021×10^{-03}	15.87	0.999	2.084×10^{-04}	3.927×10^{-03}	11.32	0.999	9.275×10^{-05}	3.922×10^{-03}
0.55	19.77	0.997	8.390×10^{-04}	3.392×10^{-02}	15.80	0.996	2.123×10^{-04}	3.964×10^{-03}	11.20	0.994	2.179×10^{-04}	3.958×10^{-03}
0.60	18.96	0.998	9.374×10^{-04}	3.521×10^{-03}	14.89	0.998	1.886×10^{-04}	3.737×10^{-03}	10.23	0.997	1.879×10^{-04}	3.730×10^{-03}
0.65	19.40	0.994	4.887×10^{-04}	1.848×10^{-02}	15.30	0.991	1.394×10^{-04}	3.213×10^{-03}	10.60	0.984	1.388×10^{-03}	8.766×10^{-03}
0.70	19.10	0.992	3.173×10^{-03}	1.499×10^{-02}	14.90	0.988	1.455×10^{-03}	3.245×10^{-02}	10.12	0.978	1.406×10^{-03}	1.003×10^{-02}
0.75	18.52	0.991	1.097×10^{-03}	8.894×10^{-02}	14.20	0.985	4.683×10^{-03}	1.859×10^{-02}	9.35	0.971	1.671×10^{-03}	1.092×10^{-02}
0.80	18.72	0.985	2.652×10^{-03}	4.413×10^{-02}	14.30	0.975	3.299×10^{-03}	1.523×10^{-02}	9.34	0.948	2.949×10^{-03}	1.442×10^{-02}
0.85	18.63	0.987	6.178×10^{-03}	6.757×10^{-02}	14.02	0.979	5.115×10^{-03}	1.124×10^{-02}	8.88	0.954	2.374×10^{-03}	1.297×10^{-02}
Average	19.87	0.994			15.96	0.990			11.40	0.982		

Table S3.5. Activation energy (including statistical parameters) from isoconversional methods, for PO – PC2 pyrogasification

α	FWO				KAS				Starink			
	E [kJ/mol]	R^2	MSE	AAD	E [kJ/mol]	R^2	MSE	AAD	E [kJ/mol]	R^2	MSE	AAD
0.15	13.87	0.886	3.740×10^{-02}	4.616×10^{-02}	10.45	0.795	1.785×10^{-02}	3.635×10^{-02}	9.27	0.604	1.782×10^{-02}	3.633×10^{-02}
0.20	14.77	0.894	2.211×10^{-02}	3.720×10^{-02}	11.28	0.811	2.238×10^{-02}	4.068×10^{-02}	11.63	0.641	2.235×10^{-02}	4.065×10^{-02}
0.25	15.65	0.942	2.178×10^{-02}	3.697×10^{-02}	12.15	0.894	2.150×10^{-02}	3.989×10^{-02}	12.43	0.787	2.147×10^{-02}	3.985×10^{-02}
0.30	16.13	0.957	2.262×10^{-02}	3.757×10^{-02}	12.60	0.921	2.530×10^{-02}	4.323×10^{-02}	11.85	0.837	2.526×10^{-02}	4.320×10^{-02}
0.35	16.68	0.971	1.751×10^{-02}	3.358×10^{-02}	13.14	0.947	2.378×10^{-02}	4.193×10^{-02}	12.79	0.889	2.374×10^{-02}	4.189×10^{-02}
0.40	17.26	0.989	2.257×10^{-02}	3.754×10^{-02}	13.70	0.978	2.368×10^{-02}	4.184×10^{-02}	12.58	0.953	2.362×10^{-02}	4.179×10^{-02}

α	E	R²	MSE	AAD	E	R²	MSE	AAD	E	R²	MSE	AAD
0.45	17.80	0.987	1.466×10^{-02}	3.100×10^{-02}	14.22	0.975	2.240×10^{-02}	4.070×10^{-02}	13.48	0.948	2.234×10^{-02}	4.065×10^{-02}
0.50	18.92	0.996	1.385×10^{-02}	3.021×10^{-02}	15.38	0.992	2.084×10^{-02}	3.927×10^{-02}	13.29	0.982	2.078×10^{-02}	3.922×10^{-02}
0.55	19.27	1.000	8.390×10^{-03}	3.392×10^{-02}	15.73	1.000	2.123×10^{-02}	3.964×10^{-02}	13.41	1.000	2.117×10^{-02}	3.958×10^{-02}
0.60	20.10	0.999	9.374×10^{-03}	3.521×10^{-02}	16.55	0.999	1.886×10^{-02}	3.737×10^{-02}	14.78	0.998	1.879×10^{-02}	3.730×10^{-02}
0.65	19.47	0.992	4.887×10^{-03}	1.848×10^{-02}	15.86	0.988	1.394×10^{-02}	3.213×10^{-02}	14.92	0.980	1.388×10^{-02}	3.206×10^{-02}
0.70	20.00	0.977	3.173×10^{-03}	1.499×10^{-02}	16.36	0.964	1.455×10^{-06}	3.245×10^{-04}	15.57	0.939	9.042×10^{-07}	2.558×10^{-04}
0.75	20.29	0.982	1.097×10^{-03}	8.894×10^{-03}	16.59	0.972	4.683×10^{-03}	1.859×10^{-02}	15.17	0.951	4.672×10^{-03}	1.856×10^{-02}
0.80	23.61	0.857	2.652×10^{-06}	4.413×10^{-04}	20.02	0.795	3.299×10^{-03}	1.523×10^{-02}	15.04	0.703	3.339×10^{-03}	1.532×10^{-02}
0.85	20.63	0.851	6.178×10^{-04}	6.757×10^{-03}	16.72	0.773	5.115×10^{-03}	1.143×10^{-02}	9.27	0.643	5.201×10^{-03}	1.902×10^{-02}
Average	18.46	0.952			14.89	0.920			13.61	0.857		

Table S3.6. Activation energy (including statistical parameters) from isoconversional methods, for PO – PC3 pyrogasification

α	FWO				KAS				Starink			
	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD
0.15	16.50	0.846	3.740×10^{-02}	4.616×10^{-02}	13.15	0.759	3.733×10^{-02}	3.635×10^{-02}	9.27	0.612	3.727×10^{-02}	4.608×10^{-02}
0.20	25.90	0.791	2.211×10^{-02}	3.720×10^{-02}	21.98	0.710	5.099×10^{-02}	4.068×10^{-02}	17.13	0.597	5.124×10^{-02}	5.728×10^{-02}
0.25	26.88	0.742	2.178×10^{-02}	3.697×10^{-02}	22.84	0.651	6.286×10^{-02}	3.989×10^{-02}	17.83	0.532	2.147×10^{-02}	3.985×10^{-02}
0.30	27.29	0.786	2.262×10^{-02}	3.757×10^{-02}	23.17	0.704	2.530×10^{-02}	4.323×10^{-02}	18.07	0.590	2.526×10^{-02}	4.320×10^{-02}
0.35	26.46	0.800	1.751×10^{-02}	3.358×10^{-02}	22.20	0.716	2.378×10^{-02}	4.193×10^{-02}	17.02	0.596	2.374×10^{-02}	4.189×10^{-02}
0.40	27.75	0.849	2.257×10^{-02}	3.754×10^{-02}	23.50	0.783	2.368×10^{-02}	4.184×10^{-02}	18.26	0.683	2.362×10^{-02}	4.179×10^{-02}
0.45	26.63	0.879	1.466×10^{-02}	3.100×10^{-02}	22.26	0.819	2.240×10^{-02}	4.070×10^{-02}	16.96	0.722	2.234×10^{-02}	4.065×10^{-02}
0.50	24.75	0.890	1.385×10^{-02}	3.021×10^{-02}	20.19	0.827	2.084×10^{-02}	3.927×10^{-02}	14.80	0.717	2.078×10^{-02}	3.922×10^{-02}
0.55	26.13	0.915	8.390×10^{-02}	3.392×10^{-02}	21.61	0.866	2.123×10^{-02}	3.964×10^{-02}	16.20	0.781	2.117×10^{-02}	3.958×10^{-02}

α	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD
0.60	26.47	0.930	9.374×10^{-02}	3.521×10^{-02}	21.91	0.889	1.886×10^{-02}	3.737×10^{-02}	16.45	0.815	1.879×10^{-02}	3.730×10^{-02}
0.65	26.18	0.957	4.887×10^{-02}	1.848×10^{-02}	21.54	0.928	1.394×10^{-02}	3.213×10^{-02}	16.01	0.874	1.388×10^{-02}	3.206×10^{-02}
0.70	25.25	0.959	3.173×10^{-03}	1.499×10^{-02}	20.48	0.931	1.455×10^{-02}	3.245×10^{-02}	14.88	0.872	9.042×10^{-02}	2.558×10^{-02}
0.75	25.30	0.962	9.305×10^{-03}	2.612×10^{-03}	20.43	0.934	9.778×10^{-03}	2.678×10^{-02}	14.73	0.875	1.022×10^{-03}	1.856×10^{-02}
0.80	25.08	0.974	6.417×10^{-03}	2.175×10^{-04}	20.08	0.952	6.851×10^{-03}	2.248×10^{-02}	14.27	0.905	7.264×10^{-03}	2.315×10^{-02}
0.85	25.11	0.984	3.960×10^{-03}	1.712×10^{-03}	19.93	0.969	4.334×10^{-03}	1.791×10^{-02}	13.96	0.934	4.692×10^{-03}	1.863×10^{-02}
Average	26.16	0.884			21.71	0.829			16.35	0.740		

Table S3.7. Activation energy (including statistical parameters) from isoconversional methods, for PO – PC4 pyrogasification

α	FWO				KAS				Starink			
	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD	E [kJ/mol]	R²	MSE	AAD
0.15	51.86	1.000	3.740×10^{-05}	4.616×10^{-02}	50.66	1.000	2.083×10^{-05}	1.237×10^{-03}	47.06	1.000	1.782×10^{-02}	3.633×10^{-02}
0.20	39.20	0.949	2.211×10^{-02}	3.720×10^{-02}	37.10	0.938	1.228×10^{-02}	4.068×10^{-02}	33.28	0.925	2.235×10^{-02}	4.065×10^{-02}
0.25	37.53	0.982	2.178×10^{-03}	3.697×10^{-02}	35.10	0.977	4.385×10^{-03}	3.989×10^{-02}	31.06	0.971	2.147×10^{-02}	3.985×10^{-02}
0.30	32.33	0.960	2.262×10^{-03}	3.757×10^{-02}	29.45	0.949	2.530×10^{-03}	4.323×10^{-02}	25.25	0.932	2.526×10^{-02}	4.320×10^{-02}
0.35	30.70	0.981	1.751×10^{-03}	3.358×10^{-02}	27.57	0.973	2.378×10^{-03}	4.193×10^{-02}	23.22	0.961	2.374×10^{-02}	4.189×10^{-02}
0.40	27.86	1.000	2.257×10^{-06}	3.754×10^{-02}	24.42	1.000	2.368×10^{-08}	4.184×10^{-05}	19.91	1.000	2.362×10^{-02}	4.179×10^{-02}
0.45	22.37	0.906	1.466×10^{-02}	3.100×10^{-02}	18.50	0.858	2.240×10^{-02}	4.070×10^{-02}	13.87	0.774	2.234×10^{-02}	4.065×10^{-02}
0.50	21.05	0.887	1.385×10^{-02}	3.021×10^{-02}	16.96	0.822	2.084×10^{-02}	3.927×10^{-02}	12.19	0.707	2.078×10^{-02}	3.922×10^{-02}
0.55	20.30	0.919	8.390×10^{-02}	3.392×10^{-02}	15.99	0.866	2.123×10^{-02}	3.964×10^{-02}	11.05	0.759	2.117×10^{-02}	3.958×10^{-02}
0.60	19.10	0.942	9.374×10^{-02}	3.521×10^{-02}	14.58	0.899	1.886×10^{-02}	3.737×10^{-02}	9.51	0.796	1.879×10^{-02}	3.730×10^{-02}
0.65	19.24	0.855	4.887×10^{-02}	1.848×10^{-02}	14.60	0.755	1.394×10^{-02}	3.213×10^{-02}	9.40	0.562	1.388×10^{-02}	3.206×10^{-02}
0.70	19.30	0.943	3.173×10^{-02}	1.499×10^{-02}	14.40	0.896	1.455×10^{-02}	3.245×10^{-04}	8.98	0.777	9.042×10^{-07}	2.558×10^{-04}

0.75	18.34	0.931	1.097×10^{-02}	8.894×10^{-03}	13.17	0.867	1.609×10^{-02}	1.859×10^{-02}	7.53	0.689	4.672×10^{-03}	1.856×10^{-02}
0.80	19.35	0.940	2.652×10^{-02}	4.413×10^{-04}	13.91	0.884	1.394×10^{-02}	1.523×10^{-02}	7.98	0.724	3.339×10^{-03}	1.532×10^{-02}
0.85	19.84	0.947	1.279×10^{-02}	6.757×10^{-03}	14.12	0.896	1.216×10^{-02}	1.887×10^{-02}	7.91	0.740	5.201×10^{-03}	1.902×10^{-02}
Average	25.13	0.943			21.21	0.905			16.40	0.821		

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