Supporting information

Critical issues for the deployment of plastic waste pyrolysis

Kinetic constant parameters (pre-exponential factor and activation energy) are usually obtained by fitting experimental results of thermogravimetric analysis (TGA) from isothermal and/or dynamic decomposition. During dynamic TGA, temperature is increased at a constant heating rate ($\beta = dT/dt$) and the following general form for the rate equation is used:

$$\frac{d\alpha}{dt} = \beta \cdot \frac{d\alpha}{dT} = k_0 \cdot exp\left(-\frac{E}{RT}\right) \cdot f(\alpha) \tag{1}$$

$f(\alpha)$ is the so called "reaction model": the mathematical function accounting for the conversion dependence. The estimation of the sole activation energy could be done without any assumption of $f(\alpha)$ (isoconversional methods). Several methods (differential and integral) can be found in the open literature. Friedman method follows a differential approach, while other methods like Ozawa-Flynn-Wall (OFW), Kissinger-Akahira-Sunnose (KAS) and advanced isoconversional (AIC) are based on numerical integration. On the contrary by assuming the form of $f(\alpha)$ (reaction model method), the pre-exponential factor (for each conversion) can be determined using TGA experimental results. Table S1 reports the most common models used in reaction methods.

Table S1. Main reaction models for solid materials decomposition.

Reaction model	Model code	*f(α)*
First order	F1	$1 - \alpha$
Second order	F2	$(1 - \alpha)^2$
Third order	F3	$(1 - \alpha)^3$
One-dimensional diffusion	D1	$\left(\frac{1}{2}\right)\alpha^{-1}$
Two-dimensional diffusion	D2	$[-ln(1 - \alpha)]^{-1}$
Three-dimensional diffusion	D3	$\frac{3}{2}(1 - \alpha)^{\frac{2}{3}}\left(1 - (1 - \alpha)^{\frac{1}{3}}\right)^{-1}$
Ginstling-Brounshtein	D4	$\frac{3}{2}\left[(1 - \alpha)^{-\frac{1}{3}} - 1\right]$
Two-dimensional nucleation	A2	$2(1 - \alpha)[-ln(1 - \alpha)]^{\frac{1}{2}}$
Three-dimensional nucleation	A3	$3(1 - \alpha)[-ln(1 - \alpha)]^{\frac{2}{3}}$
Four-dimensional nucleation	A4	$4(1 - \alpha)[-ln(1 - \alpha)]^{\frac{3}{4}}$
One-dimension phase boundary	R1	1
Contracting sphere	R2	$2(1 - \alpha)^{\frac{1}{2}}$
Contracting cylinder	R3	$3(1 - \alpha)^{\frac{2}{3}}$
Power law	P2	$2\alpha^{\frac{1}{2}}$
Power law	P3	$3\alpha^{\frac{2}{3}}$
Power law	P4	$4\alpha^{\frac{3}{4}}$

Table S2. Results from kinetic investigation works on plastics thermal pyrolysis available in the open literature.

Plastic	Method	E (kJ/mol)	Notes	Reference
LDPE	AIC, Criado	170-231		1
LDPE	Coats-Redfern, Criado	171	Reported E from Coats-Redfern	2
LDPE	Friedman, KAS, OFW, Coats-Redfern, Criado	214	Reported E from Coats-Redfern	3
HDPE	AIC, Criado	143-233		1
HDPE	Friedman, KAS, OFW, Coats-Redfern, Criado	248	Reported E from Coats-Redfern	3
PP	AIC	133-173		1
PP	Friedman, KAS, OFW, Coats-Redfern, Criado	187	Reported E from Coats-Redfern	3
PP	OFW	183		4
PS	KAS	193	Averaged value	5
PS	Coats-Redfern	151 - 199	Activation energy affected by the involved inert gas	6
PS	OFW	145		7
PS	OFW	169		4
PVC	Coats-Redfern, Criado	47 (First stage)		2
	Coats-Redfern, Criado	119 (Second stage)		
PVC	KAS, FWO, FR, Criado	152 (First stage)	Reported E is the averaged value from different methods	8
	KAS, FWO, FR, Criado	294 (Second stage)		
PVC	OFW, Coats-Refern	141 (First stage)	Averaged values from OFW	9
PVC	OFW, Coats-Refern	235 (Second stage)		
PET	Friedman	193, 223	Two values: the first for conversion up to 80%.	10
PET	KAS	208	Reported E is averaged value	11
PET	KAS	198	Reported E is averaged value	5

Table S3. Results from kinetic investigation works on plastics catalytic pyrolysis available in the open literature.

Plastic	Catalyst	Method	E (kJ/mol)	Notes	Reference
LDPE	Y-zeolite	Isoconversional	169		12
LDPE	Ni on Y-zeolite	first order power law	72		13
LDPE	HY	OFW	79	Conv. = 0.6	14
LDPE	MCM-41	OFW	167	Conv. = 0.6	14
UHMWPE	ZSM-23 (AZ-PYR)	OFW	74		15
HDPE	Y-zeolite	Isoconversional	87		12
HDPE	ZSM-5	First order power-law	60		16
HDPE	SAPO-11	OFW, AIC, Vyazovkin, Coats-Redfern	175	E from Coats-Redfern	17
HDPE	Ni on zeolite Y	first order power-law	69		13
PP	Y-zeolite	Isoconversional	113		12
PP	Al-MCM-41	Model-fitting method	129	First order model	18
PP	FCC	OFW	87		19
PP	HUSY	OFW	76		19
PP	ZSM-5	OFW	72		19
PP	Silicalite	OFW	143		19
PP	MOR	Kissinger	51		20
PP	BEA	Kissinger	59		20
PP	ZSM-5	Kissinger	62		20
PP	Bentonite	OFW	122		21
PP	Al-MCM-41	OFW	104		21
PP	NZ	OFW	116		21
PP	HZSM-5	OFW	122	Catalyst to PP ratio: 5/1	22
PP	Ga-HZSM-5	OFW	110	Catalyst to PP ratio: 5/1	22
PS	$Ni_xCu_{1-x}O$	Coats-Redfern, Friedman, OFW, KAS.	121	E averaged from Coats-Redfern	23
PS	spent FCC	KAS	45		12
PS	Fe–K/Al_2O_3	Kissinger	138		24
Mixed	FCC	Friedman	83, 247	1^{st} and 2^{nd} decomposition step	25
Mixed	Fe-ZSM-5	Friedman	83, 212	1^{st} and 2^{nd} decomposition step	25

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