

Research on the Characteristics and Kinetics of the Pyrolysis Process and Products Generation of Jimsar (China) Oil Shale Using TG-FTIR

Hao Lu, Luwei Pan *, Pingan Chen and Ting Liu

The State Key Laboratory of Refractories and Metallurgy, Wuhan University of Science and Technology, No.947 Heping Avenue, Qingshan District, Wuhan 430081, China; luhao1227@126.com (H.L.); chenpingan1203@163.com (P.C.); liuting666@wust.edu.cn (T.L.)

* Correspondence: panluwei@wust.edu.cn

Part A

Table S1. Differential and integral expressions for different reaction models [1-4].

Reaction model	Differential form $f(\alpha)$	Integral form $g(\alpha)$
<i>Chemical Reaction models</i>		
First order, F1	$1 - \alpha$	$-\ln(1 - \alpha)$
Second order, F2	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$
Third order, F3	$(1 - \alpha)^3$	$\left[(1 - \alpha)^{-2} - 1\right]/2$
<i>Diffusion models</i>		
1-D Diffusion, D1	$1/2\alpha$	α^2
2-D Diffusion, D2	$-1/\ln(1 - \alpha)$	$(1 - \alpha)\ln(1 - \alpha) + \alpha$
3-D Diffusion-Jander, D3	$3/2(1 - \alpha)^{2/3} \left[1 - (1 - \alpha)^{1/3}\right]^{-1}$	$\left[1 - (1 - \alpha)^{1/3}\right]^2$
3-D Diffusion-Ginstling, D4	$3/2 \left[(1 - \alpha)^{-1/3} - 1\right]^{-1}$	$1 - 2\alpha/3 - (1 - \alpha)^{2/3}$
<i>Nucleation and growth</i>		
Avrami-Erofeev, A2	$2(1 - \alpha) \left[-\ln(1 - \alpha)\right]^{1/2}$	$\left[-\ln(1 - \alpha)\right]^{1/2}$
Avrami-Erofeev, A3	$3(1 - \alpha) \left[-\ln(1 - \alpha)\right]^{2/3}$	$\left[-\ln(1 - \alpha)\right]^{1/3}$
Avrami-Erofeev, A4	$4(1 - \alpha) \left[-\ln(1 - \alpha)\right]^{3/4}$	$\left[-\ln(1 - \alpha)\right]^{1/4}$
<i>Phase interfacial reaction</i>		
Contraction Area, R2	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
Contraction Volume, R3	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
<i>Power law</i>		
Power Law, P2/3	$(2/3)\alpha^{-1/2}$	$\alpha^{3/2}$

Note: The reaction model in this study is also applicable to the generation model of pyrolysis products.

Table S2. Absorption bands of pyrolysis products [1, 5–7].

Functional Groups	Wavenumber (cm ⁻¹)
CH ₄	3018
CO	2240–2060
CO ₂	2400–2240, 780–560
SO ₂	1374
R ₂ -sym –CH ₂	2860
asym R ₂ –CH ₂	2930
asym R–CH ₃	2960
O–H stretching vibration	4000–3500
C–H stretching vibration	3100–3000 (adjacent to a double bond or aromatic ring), 3000–2850 (aliphatic compounds)
C=O stretching vibration	1850–1600 (carbonyl compounds: ketone, acid, aldehyde, ester, acylamide, acyl chloride, estolide, etc.)
C=C stretching vibration	1600–1420 (aromatic compounds)
S=O stretching vibration	1420–1300 (sulfur–oxygen compounds: sulfones, sulphoxides, etc.)
C–H stretching vibration	1500–1300, 840–1100 (saturated aliphatic hydrocarbons)
	750–600 (aromatic rings and unsaturated aliphatic hydrocarbons)

Table S3. Kinetic parameters of the functional groups represented at 2180 cm⁻¹ wavenumber for different reaction models and heating rates.

Generation models	Heating Rates (K/min)	573.15–873.15 (K)			873.15–1073.15 (K)		
		E_{α_G} (kJ/mol)	R ²	$\ln A_{\alpha_G}$ (s ⁻¹)	E_{α_G} (kJ/mol)	R ²	$\ln A_{\alpha_G}$ (s ⁻¹)
F1	20	81.725	0.873	12.165	371.650	0.997	45.902
	30	65.814	0.900	10.052	270.255	0.992	32.725
	40	185.377	0.880	28.963	323.309	0.999	38.420
F2	20	122.607	0.944	19.877	519.790	0.963	65.235
	30	93.380	0.827	15.615	377.554	0.944	46.734
	40	274.125	0.959	43.749	454.997	0.974	54.930
F3	20	173.850	0.961	29.348	703.183	0.913	89.025
	30	127.327	0.757	22.319	510.259	0.886	63.915
	40	385.561	0.987	62.125	618.231	0.929	75.247
D1	20	118.850	0.778	17.458	546.550	0.983	66.870
	30	102.920	0.944	15.585	402.310	0.993	48.079
	40	261.090	0.768	39.895	474.920	0.975	55.584
D2	20	134.080	0.815	19.656	605.020	0.993	73.814
	30	114.030	0.940	17.129	444.810	0.998	52.936
	40	293.850	0.807	44.685	526.601	0.988	61.378
D3	20	153.940	0.857	21.871	679.190	0.998	81.957
	30	127.970	0.929	18.398	498.610	0.998	58.423
	40	336.780	0.998	50.310	592.330	0.997	68.083
D4	20	140.595	0.831	19.372	629.410	0.995	75.482

A2	30	118.615	0.937	16.539	462.499	0.999	53.733
	40	307.924	0.823	45.521	548.207	0.992	62.574
	20	34.792	0.829	3.726	177.856	0.997	21.200
	30	27.232	0.862	2.803	127.055	0.991	14.626
	40	86.253	0.863	12.917	153.293	0.999	17.678
A3	20	19.147	0.761	0.604	113.258	0.997	12.760
	30	14.372	0.798	0.039	79.322	0.990	8.371
	40	53.211	0.842	7.340	96.621	0.999	10.553
A4	20	11.325	0.654	-1.187	80.959	0.997	8.431
	30	7.942	0.682	-1.611	55.455	0.989	5.123
	40	36.690	0.817	4.419	68.285	0.999	6.873
R2	20	66.019	0.811	8.430	313.382	0.996	37.552
	30	54.879	0.923	7.096	227.996	0.999	26.465
	40	151.403	0.818	22.540	271.636	0.993	31.194
R3	20	70.901	0.834	8.976	331.626	0.998	39.549
	30	58.312	0.917	7.406	241.233	0.998	27.809
	40	161.952	0.840	23.918	287.803	0.997	32.838
P2/3	20	86.104	0.765	12.115	405.928	0.982	49.443
	30	74.350	0.940	10.807	297.698	0.993	35.365
	40	192.600	0.762	29.304	352.010	0.975	41.092

Table S4. Kinetic parameters of the functional groups represented at 2358 cm⁻¹ wavenumber for different reaction models and heating rates.

Generation models	Heating Rates (K/min)	573.15–873.15 (K)			873.15–1073.15 (K)		
		E_{α_G} (kJ/mol)	R ²	$\ln A_{\alpha_G}$ (s ⁻¹)	E_{α_G} (kJ/mol)	R ²	$\ln A_{\alpha_G}$ (s ⁻¹)
F1	20	130.913	0.980	18.525	321.858	0.998	39.620
	30	122.398	0.995	17.572	295.070	0.999	35.780
	40	181.668	0.980	26.400	286.259	0.998	34.078
F2	20	189.403	0.988	28.196	451.313	0.966	56.648
	30	176.209	0.986	26.531	414.634	0.967	51.267
	40	253.771	0.924	37.793	402.076	0.964	48.766
F3	20	262.240	0.965	40.072	611.628	0.917	77.597
	30	243.080	0.951	37.499	562.735	0.919	70.304
	40	342.881	0.861	51.732	545.497	0.914	66.814
D1	20	192.370	0.922	26.899	473.930	0.982	57.772
	30	181.520	0.952	25.598	434.980	0.981	52.051
	40	272.930	0.993	38.915	423.020	0.984	49.563
D2	20	214.860	0.945	29.934	524.950	0.992	63.793
	30	202.400	0.971	28.392	482.050	0.991	57.458
	40	301.570	0.995	42.749	468.660	0.994	54.666
D3	20	243.750	0.968	33.176	589.710	0.999	70.779
	30	229.100	0.987	31.300	541.820	0.999	63.667
	40	337.770	0.991	46.931	526.590	0.999	60.477
D4	20	224.352	0.954	29.992	546.239	0.995	65.082
	30	211.174	0.977	28.339	501.702	0.995	58.493
	40	313.474	0.994	43.116	487.701	0.996	55.570
A2	20	58.835	0.975	7.115	152.979	0.998	17.982
	30	54.595	0.993	6.800	139.421	0.999	16.195
	40	84.094	0.977	11.571	134.824	0.998	15.447
A3	20	34.809	0.967	3.049	96.686	0.998	10.558

	30	31.994	0.991	2.944	87.538	0.998	9.449
	40	51.570	0.973	6.397	84.346	0.998	9.018
	20	22.796	0.957	0.857	68.540	0.998	6.733
A4	30	20.694	0.987	0.847	61.596	0.998	5.962
	40	35.307	0.969	3.675	59.107	0.998	5.683
	20	108.151	0.953	14.005	270.973	0.996	32.176
R2	30	101.381	0.977	13.319	248.095	0.996	28.947
	40	153.239	0.993	21.162	240.737	0.997	27.556
	20	115.255	0.964	14.799	286.903	0.998	33.889
R3	30	107.947	0.985	14.032	262.798	0.998	30.470
	40	162.147	0.990	22.184	254.987	0.999	28.979
	20	140.970	0.919	19.284	351.474	0.981	42.584
P2/3	30	132.839	0.949	18.397	322.182	0.980	38.361
	40	201.329	0.993	28.555	313.109	0.983	36.551

Table S5. Kinetic parameters of the functional groups represented at 1462 cm^{−1} wavenumber for different reaction models and heating rates.

Generation models	Heating Rates (K/min)	573.15–873.15 (K)		
		E_{α_G} (kJ/mol)	R ²	$\ln A_{\alpha_G}$ (s ^{−1})
F1	20	176.168	0.963	29.085
	30	146.243	0.881	23.828
	40	279.998	0.982	44.854
F2	20	253.215	0.978	42.953
	30	217.160	0.962	36.500
	40	400.341	0.999	64.823
F3	20	349.352	0.961	60.090
	30	306.188	0.991	52.219
	40	550.360	0.982	89.559
D1	20	256.080	0.910	41.686
	30	206.690	0.770	32.949
	40	403.070	0.920	63.505
D2	20	285.320	0.930	46.275
	30	232.890	0.810	36.964
	40	449.060	0.940	70.456
D3	20	323.110	0.950	51.541
	30	267.200	0.850	41.569
	40	508.290	0.970	78.758
D4	20	297.723	0.936	46.996
	30	244.135	0.824	37.462
	40	468.504	0.952	72.173
A2	20	82.170	0.957	12.692
	30	67.044	0.860	10.127
	40	133.708	0.980	21.115
A3	20	50.838	0.950	7.001
	30	40.645	0.834	5.319
	40	84.945	0.978	12.996
A4	20	35.171	0.941	4.027
	30	27.445	0.800	2.773
	40	60.564	0.976	8.824
R2	20	146.349	0.936	22.964

R3	30	119.089	0.817	18.206
	40	233.290	0.954	36.350
	20	155.639	0.946	24.255
	30	127.520	0.840	19.337
	40	247.855	0.965	38.387
P2/3	20	189.103	0.904	30.510
	30	151.981	0.760	23.989
	40	299.160	0.917	47.137

Table S6. Kinetic parameters of the functional groups represented at 2930 cm⁻¹ wavenumber for different reaction models and heating rates.

Generation models	Heating Rates (K/min)	573.15–873.15 (K)		
		E_{α_G} (kJ/mol)	R ²	$\ln A_{\alpha_G}$ (s ⁻¹)
F1	20	238.891	0.981	39.994
	30	215.671	0.993	36.347
	40	263.618	0.974	42.235
F2	20	342.060	0.998	58.274
	30	307.159	0.993	52.637
	40	378.577	0.999	61.371
F3	20	470.689	0.981	80.903
	30	421.001	0.966	72.749
	40	522.023	0.988	85.085
D1	20	344.400	0.920	56.916
	30	313.680	0.940	52.000
	40	378.330	0.900	59.571
D2	20	383.780	0.940	63.214
	30	348.930	0.960	57.594
	40	348.930	0.960	57.594
D3	20	434.530	0.970	70.677
	30	394.150	0.980	64.113
	40	478.500	0.960	74.040
D4	20	400.436	0.950	64.655
	30	363.779	0.971	58.728
	40	440.583	0.939	67.746
A2	20	113.529	0.978	18.316
	30	101.926	0.992	16.643
	40	125.519	0.971	19.774
A3	20	71.742	0.976	10.879
	30	64.011	0.991	9.857
	40	79.486	0.968	12.078
A4	20	50.848	0.973	7.046
	30	45.054	0.989	6.345
	40	56.469	0.964	8.114
R2	20	198.867	0.952	32.149
	30	180.044	0.973	29.252
	40	219.082	0.941	34.066
R3	20	211.346	0.963	33.979
	30	191.165	0.981	30.850
	40	232.962	0.953	35.996
P2/3	20	255.340	0.916	42.011

30	232.305	0.943	38.400
40	280.602	0.901	44.169

Table S7. Kinetic parameters of the functional groups represented at 2960 cm^{−1} wavenumber for different reaction models and heating rates.

Generation models	Heating Rates (K/min)	573.15–873.15 (K)		
		E_{α_G} (kJ/mol)	R ²	$\ln A_{\alpha_G}$ (s ^{−1})
F1	20	240.656	0.991	40.341
	30	200.090	0.995	33.676
	40	273.087	0.985	43.788
F2	20	342.639	0.995	58.432
	30	284.388	0.988	48.760
	40	390.117	0.999	63.258
F3	20	469.582	0.970	80.789
	30	389.200	0.956	67.363
	40	535.944	0.980	87.357
D1	20	348.910	0.940	57.747
	30	292.420	0.950	48.384
	40	393.690	0.920	62.077
D2	20	388.140	0.960	64.028
	30	325.010	0.970	53.536
	40	438.500	0.950	68.852
D3	20	438.510	0.980	71.429
	30	366.760	0.990	59.476
	40	496.170	0.970	76.914
D4	20	404.682	0.968	65.451
	30	338.725	0.978	54.479
	40	457.438	0.956	70.491
A2	20	114.425	0.990	18.498
	30	94.148	0.995	15.265
	40	130.263	0.983	20.572
A3	20	72.349	0.989	11.004
	30	58.834	0.994	8.908
	40	82.655	0.982	12.625
A4	20	51.310	0.988	7.144
	30	41.177	0.993	5.608
	40	58.851	0.979	8.538
R2	20	200.966	0.970	32.551
	30	167.215	0.979	27.040
	40	227.624	0.958	35.475
R3	20	213.353	0.978	34.364
	30	177.482	0.986	28.494
	40	241.805	0.968	37.457
P2/3	20	258.730	0.939	42.640
	30	216.367	0.953	35.673
	40	292.125	0.922	46.062

Table S8. Kinetic parameters of the functional groups represented at 3018 cm⁻¹ wavenumber for different reaction models and heating rates.

Generation models	Heating Rates (K/min)	573.15–873.15 (K)		
		E_{α_G} (kJ/mol)	R ²	$\ln A_{\alpha_G}$ (s ⁻¹)
F1	20	125.085	0.849	19.685
	30	110.585	0.830	17.421
	40	265.209	0.956	42.193
F2	20	187.597	0.945	30.942
	30	166.973	0.933	27.605
	40	383.265	0.996	61.703
F3	20	266.175	0.983	44.897
	30	237.902	0.976	40.212
	40	530.832	0.996	85.918
D1	20	176.350	0.730	27.256
	30	156.100	0.710	23.989
	40	378.050	0.870	59.104
D2	20	199.310	0.770	30.722
	30	176.720	0.750	27.042
	40	422.590	0.900	65.789
D3	20	229.460	0.820	34.625
	30	203.860	0.800	30.416
	40	480.310	0.930	73.796
D4	20	209.188	0.789	30.991
	30	185.616	0.770	27.140
	40	441.528	0.913	66.254
A2	20	56.426	0.818	7.754
	30	49.111	0.790	6.735
	40	126.262	0.951	19.748
A3	20	33.540	0.779	3.520
	30	28.619	0.738	2.901
	40	79.946	0.946	12.055
A4	20	22.097	0.726	1.246
	30	18.374	0.667	0.814
	40	56.789	0.940	8.096
R2	20	101.203	0.777	14.613
	30	89.080	0.753	12.764
	40	219.623	0.915	33.904
R3	20	108.613	0.802	15.573
	30	95.749	0.780	13.594
	40	233.815	0.930	35.869
P2/3	20	129.202	0.718	19.568
	30	113.986	0.695	17.180
	40	280.364	0.869	3.391

Part B

- Kinetic models-theoretical background

According to the theory of non-isothermal pyrolysis kinetics and the guidance of ICTAC[8], the basic equations for the study of the kinetics of heterogeneous solid-state thermal decomposition can be described as follows.

$$\frac{d\alpha}{dt} \frac{dT}{dt} = \frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (\text{B1})$$

where α is the conversion rate; R , the universal gas constant, $8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$; T , the temperature, K ; $\beta = dT/dt$, the heating rate, $\text{K}\cdot\text{min}^{-1}$; E , the activation energy, $\text{kJ}\cdot\text{mol}^{-1}$; A , the preexponential factor, $1/\text{s}$; $f(\alpha)$ is the reaction mechanism function related only to the conversion rate.

In Equation B1, the conversion rate α is calculated as follows by the following equation.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (\text{B2})$$

where m_0 , m_t , m_∞ are initial mass, current mass at time t , and final mass of sample, respectively.

Depending on the fundamental equations of kinetic mentioned above, researchers have classified kinetic analysis methods into two categories: “model-fitting kinetics” and “model-free kinetics” [9]. The model-fitting method compulsorily fits the kinetic parameters into the equation, leading to the ambiguity of the kinetic interpretation [10]. In contrast, based on the conversion rate method, the model-free function method can generate unique kinetic parameters without assuming a specific reaction model [11]. Currently, isoconversional methods are more frequently employed because they do not require hypothetical reaction models and are increasingly used in oil shale thermochemical conversion studies [8]. The different forms of isoconversional methods are primarily classified as differential (Friedman) and integral ((Flynn Wall Ozawa (FWO), Kissinger Akahira Sunnose (KAS) and Starink, etc.). The present work adopts four isoconversional methods for kinetic analysis based on ICTAC guidance, as shown below [8]. The subscripts α in the equations below all refer to the value related to the considered conversion rate, while i and j is introduced to denote various temperature programs. For distinguishing the product generation rate (α_G), the conversion rate (α) is replaced by α_p in the text of this study.

- Differential isoconversional method
- Friedman method

The Friedman method [12] is the most straight forward and the most common differential isoconversional method to evaluate the activation energy. The equation is as follows.

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left(\beta_i \frac{d\alpha}{dT}\right) = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_{\alpha,i}} \quad (\text{B3})$$

The method finds the activation energy by fitting the slope of the curve of

$\ln\left(\beta_i \frac{d\alpha}{dT}\right)$ against $\frac{1}{T_{\alpha,i}}$ for the same conversion rate at different heating rates.

- Integral iso-conversional methods

The integral isoconversional method originated from the application of the principle of isoconversional functions to the integration method (B4). However, the integral in equation B4 has no analytical solution for arbitrary temperature programs. Therefore, there are many integral isoconversional methods that take an approximation to the temperature integral and obtain the general form of the Equation B5 [8].

$$g(\alpha) = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (\text{B4})$$

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^B}\right) = \text{Const} - C \frac{E_\alpha}{RT_{\alpha,i}} \quad (\text{B5})$$

where B and C are the parameters determined by the type of the temperature integral approximation.

- Starink method

The method is a Starink method when B and C in Equation B5 are set to 1.92 and 1.0008, respectively. The method equation is shown in Equation B6 [13].

$$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right) = \text{Const} - 1.0008 \frac{E_\alpha}{RT_{\alpha,i}} \quad (\text{B6})$$

For a constant value of conversion rate, the plot $\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1.92}}\right)$ vs. $\frac{1}{T_{\alpha,i}}$, obtained from thermograms recorded at several heating rates, yield a straight line whose slope allows evaluation of the apparent activation energy.

- FWO

B=0 and C=1.052 in the FWO method and the equation is shown in B7 [14, 15].

$$\ln(\beta_i) = \text{Const} - 1.052 \frac{E_\alpha}{RT_{\alpha,i}} \quad (\text{B7})$$

Plots of $\ln(\beta_i)$ vs. $\frac{1}{T_{\alpha,i}}$, at fixed value of conversion help in evaluating the activation energy from the slope of a straight-line plot.

- Vyazovkin method

The Vyazovkin equation is an exact non-linear equation used to increase the accuracy of evaluating the activation energy by the isoconversional method[8]. The Vyazovkin method is based on the following equation for the determination of activation energy value (E_α) at any particular value of α which minimizes the following function[16],

$$\phi(E_\alpha) = \min \sum_i^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i}) \beta_j}{I(E_\alpha, T_{\alpha,j}) \beta_i} \quad (\text{B8})$$

$$I(E_\alpha, T_\alpha) = \int_0^{T_\alpha} \exp\left(-\frac{E_\alpha}{RT}\right) dT \quad (\text{B9})$$

Substituting experimental values of T and b into this equation and varying E_α to reach the minimum value of this function gives the value of the activation energy at a given conversion. The values of $I(E_\alpha, T_\alpha)$ are calculated with the help of an accurate Senum-Yang approximation [17]. The minimization procedure is repeated for each value of α to find the dependence of the activation energy on the extent of conversion.

- Evaluation of reaction mechanism

The reaction mechanism is a theoretical function that describes the nature of the reaction process. It is essential to calculate the activation energy, reaction model and pre-exponential factor to get a complete reaction kinetics. This work evaluates the reac-

tion mechanism of the Jimsar oil shale pyrolysis process based on the $Z(\alpha)$ master plot method, which are derived by combining the differential and integral forms of the reaction models [8].

$$Z(\alpha) = f(\alpha) \times g(\alpha) \quad (\text{B10})$$

$$Z(\alpha) = f(\alpha) \times g(\alpha) = \frac{d\alpha}{dT} e^{\frac{E}{RT}} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \quad (\text{B11})$$

In Equation **B10** and **B11**, the algebraic expressions of $f(\alpha)$ and $g(\alpha)$ for considered the theoretical reaction models are given in **Table A1**. The conversion rate of 0.5 is taken as the reference point of Equation **B11** to obtain Equation **B12**.

$$\frac{Z(\alpha)}{Z(0.5)} = \frac{f(\alpha) \times g(\alpha)}{f(0.5) \times g(0.5)} = \frac{\frac{\pi(x) T_\alpha \left(\frac{d\alpha}{dt}\right)_\alpha}{\beta}}{\frac{\pi(x) T_{0.5} \left(\frac{d\alpha}{dt}\right)_{0.5}}{\beta}} \quad (\text{B12})$$

$$\pi(x) = \frac{x^3 + 18x^2 + 86x + 96}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (\text{B13})$$

where $x = E/RT$. $\pi(x)$ is obtained from the fourth basic principle of Senum-Yang, given by the equation shown in **B13** [17]. In Equation **B12**, the point $\alpha = 0.5$ is considered as the reference point because at $\alpha = 0.5$ the standard master plots of each considered kinetic mechanism intersect each other corresponding to value of $\frac{Z(\alpha)}{Z(0.5)} = 1$ [18].

- Evaluation of preexponential factor

The paper seeks the preexponential factor of one of the kinetic triple factors by means of a compensating parameter approach. A significant compensation effect is observed when the model fitting method is applied to a single heating rate. Different pairs of Arrhenius parameters A_i and E_i were obtained by substituting the different Model $f(\alpha)$ in **Table A1** into the rate equation (**B1**) and fitting it to the experimental data. Although the parameters of the chosen model $f(\alpha)$ differed considerably, they all exhibited a strong correlation known as the compensation effect [8].

$$\ln A_i = a + bE_i \quad (\text{B14})$$

where a and b are constants (the compensation effect parameters). For each heating rate, β , using an integral or differential method, the pairs (A_i, E_i) , characteristic for each conversion function $f(\alpha)$, are determined using any form of equation (differential or integral). Using the relation of the apparent compensation effect, for each heating rate the compensation parameters are determined. Now using these compensation parameters the A_α obtained at using E_α values at each conversion value.

$$\ln A_\alpha = a + bE_\alpha \quad (\text{B15})$$

In the present work, the parameters E_α and $\ln A_\alpha$ obtained by the model-fitting procedure are only used here to evaluate the relationship that exists between E_α and $\ln A_\alpha$.

References

- [1] Baruah B, Tiwari P. Compositional and kinetic study of thermal degradation of kerogen using TG-FTIR, NMR, and microscopic study. *AIChE J.* 2022;68(1).
- [2] Khawam A, Flanagan DR. Solid-state kinetic models: Basics and mathematical fundamentals. *J. Phys. Chem. B* 2006;110(35):17315-28.
- [3] Qu BY, Li AM, Qu Y, Wang T, Zhang Y, Wang X, et al. Kinetic analysis of waste tire pyrolysis with metal oxide and zeolitic catalysts. *J. Anal. Appl. Pyrolysis* 2020;152.
- [4] Vyazovkin S, Chrissafis K, Di Lorenzo ML, Koga N, Pijolat M, Roduit B, et al. ICTAC Kinetics Committee recommendations for collecting experimental thermal analysis data for kinetic computations. *Thermochim. Acta* 2014;590:1-23.
- [5] Yan J, Jiang X, Han X, Liu J. A TG-FTIR investigation to the catalytic effect of mineral matrix in oil shale on the pyrolysis and combustion of kerogen. *Fuel* 2013;104:307-17.
- [6] Li S, Ma X, Liu G, Guo M. A TG-FTIR investigation to the co-pyrolysis of oil shale with coal. *J. Anal. Appl. Pyrolysis* 2016;120:540-8.
- [7] Wang Q, Wang YF, Zhang HX, Xu XC, Yang QK, Wang P. THE SIMULATION STUDY OF APPLICATION OF THE FG-DVC MODEL TO THE PYROLYSIS OF HUADIAN OIL SHALE OF CHINA AT DIFFERENT HEATING RATES. *Oil Shale* 2016;33(2):111-24.
- [8] Vyazovkin S, Burnham AK, Criado JM, Perez-Maqueda LA, Popescu C, Sbirrazzuoli N. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim. Acta* 2011;520(1-2):1-19.
- [9] Rodante F, Vecchio S, Tomassetti M. Kinetic analysis of thermal decomposition for penicillin sodium salts: model-fitting and model-free methods. *Journal of pharmaceutical and biomedical analysis* 2002;29(6):1031-43.
- [10] Vyazovkin S, Wight CA. Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data. *Thermochim. Acta* 1999;340-341(1):53-68.
- [11] Vyazovkin S. Computational aspects of kinetic analysis. Part C. The ICTAC Kinetics Project - The light at the end of the tunnel? *Thermochim. Acta* 2000;355:155-63.
- [12] Friedman HL. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *Journal of Polymer Science Part C: Polymer Symposia* 1964;6(1):183-95.
- [13] Starink MJ. The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of iso-conversion methods. 2003;404(1-2):163-76.
- [14] Flynn J, Wall L. General Treatment of the Thermogravimetry of Polymers. *Journal of Research of the National Bureau of Standards Section A: Physics and Chemistry* 1966;70A.
- [15] Ozawa T. A New Method of Analyzing Thermogravimetric Data. *Bulletin of The Chemical Society of Japan - BULL CHEM SOC JPN* 1965;38:1881-6.
- [16] Vyazovkin S, Dollimore D. Linear and Nonlinear Procedures in Isoconversional Computations of the Activation Energy of Nonisothermal Reactions in Solids. *Journal of Chemical Information and Computer Sciences* 1996;36(1):42-5.
- [17] Vyazovkin S. ADVANCED ISOCONVERSIONAL METHOD Non-linear isoconversional method. 1997;49(3):1493-9.
- [18] Gotor F, Criado J, Malek J, Koga N. Kinetic Analysis of Solid-State Reactions: The Universality of Master Plots for Analyzing Isothermal and Nonisothermal Experiments. *The Journal of Physical Chemistry A* 2000;104.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.