Coupling Pyrolysis and Gasification Processes for Methane-Rich Syngas Production: Fundamental Studies on Pyrolysis Behavior and Kinetics of a Calcium-Rich High Volatile Bituminous Coal

Bin Tian[†], Yingyun Qiao[†,*], Junfeng Fan[§], Lei Bai[‡], Yuanyu Tian[†,§,*]

Table S1. Peak assignments of IR spectrum for the volatile species

Wavenumber (cm^{-1})	Assignments
3700–3500	H_2O
3100–3000	Light arenes
3016/1305	CH_4
3000–2700	C^{2+} aliphatics
2400–2240/780–560	CO_2
2175/2115	CO
1765	C=O bond containing species
1455/950	C_2H_4
1374/1359	SO_2
1300–1100	C–O bond containing species

Table S2. Calculated E and R^2 According to Different Model-Free Methods

α	KAS method		FWO method		Friedman method	
	E (kJ/mol)	R^2	E (kJ/mol)	R^2	E (kJ/mol)	R^2
0.10	212.4	0.9988	212.4	0.9989	224.5	0.9976
0.15	218.0	0.9948	218.2	0.9954	222.9	0.9955
0.20	215.9	0.9954	216.6	0.9960	219.9	0.9973
0.25	215.9	0.9958	216.9	0.9963	220.5	0.9980
0.30	217.4	0.9970	218.5	0.9974	224.1	0.9988
0.35	220.7	0.9971	221.8	0.9975	231.0	0.9986
0.40	224.0	0.9987	225.2	0.9989	239.2	0.9995
0.45	230.6	0.9980	231.7	0.9983	251.8	0.9991
0.50	248.6	0.9985	249.1	0.9987	276.8	0.9996
0.55	273.7	0.9995	273.3	0.9995	305.4	1.0000
0.60	306.1	0.9994	304.5	0.9994	335.8	1.0000
0.65	328.2	1.0000	326.1	1.0000	355.8	0.9997
0.70	355.9	0.9980	353.1	0.9982	379.7	0.9999
0.75	339.8	1.0000	338.5	1.0000	327.4	0.9976
0.80	291.5	0.9998	293.1	0.9998	265.8	0.9987
0.85	272.6	0.9991	275.6	0.9992	272.1	0.9987
0.90	300.1	1.0000	302.3	1.0000	360.7	0.9974

Table S3. Common Used Mechanism Function during Pyrolysis of Solid-State Materials

Mechanism	Mechanism description	f(α)	g(α)
R1	Shrinking core model (n=1)	1	α
R2	Shrinking core model (n=2)	$2\ (1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
R3	Shrinking core model (n=3)	$3\ (1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
D1	One-dimension diffusion	$1/2\alpha^{-1}$	α^{2}
D2	Two-dimension diffusion	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha) + \alpha$
D3	Three-dimension diffusion (spherical symmetry)	$3/2\ (1-\alpha)^{2/3}(1-(1-\alpha)^{1/3})^{-1}$	$[1-(1-\alpha)^{1/3}]^{2}$
D4	Three-dimension diffusion (cylindrical symmetry)	$3/2\ [(1-\alpha)^{-1/3}-1)]^{-1}$	$1-2/3\alpha-(1-\alpha)^{2/3}$
A1.5	Nucleation growth model (n=3/2)	$3/2\ (1-\alpha)[-\ln(1-\alpha)]^{1/3}$	$[-\ln(1-\alpha)]^{2/3}$
A2	Nucleation growth model (n=2)	$2\ (1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
A3	Nucleation growth model (n=3)	$3\ (1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
A4	Nucleation growth model (n=4)	$4\ (1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
A4/5	Nucleation growth model (n=4/5)	$4/5\ (1-\alpha)[-\ln(1-\alpha)]^{-1/4}$	$[-\ln(1-\alpha)]^{5/4}$
A5/6	Nucleation growth model (n=6/5)	$5/6\ (1-\alpha)[-\ln(1-\alpha)]^{-1/5}$	$[-\ln(1-\alpha)]^{6/5}$
F1	Reaction order model (n=1)	$1-\alpha$	$-\ln(1-\alpha)$
F1.5	Reaction order model (n=3/2)	$(1-\alpha)^{3/2}$	$2[(1-\alpha)^{-1/2}-1]$
F2	Reaction order model (n=2)	$(1-\alpha)^{2}$	$(1-\alpha)^{-1}-1$
P1.5	Power law (2/3)	$3/2\alpha^{1/3}$	$\alpha^{2/3}$
P2	Power law (1/2)	$2\alpha^{1/2}$	$\alpha^{1/2}$
P3	Power law (1/3)	$3\alpha^{2/3}$	$\alpha^{1/3}$