Investigation of Mediterranean biomass pyrolysis by thermogravimetric analysis: Thermal behaviour and sensitivity of kinetic parameters

Nourelhouda Boukaous[1,2], Lokmane Abdelouahed[1], Mustapha Chikhi[2], Chetna Mohabeer[1], Abdeslam Hassen Meniai[2] *, Bechara Taouk[1]

1: Normandie Univ, INSA Rouen Normandie, UNIROUEN, Laboratoire de Sécurité des Procédés Chimiques LSPC-EA 4704, 76000 Rouen, France

2: Faculté de génie des procédés, Université Salah Boubnider Constantine 3, Constantine, Algérie

* meniai@yahoo.fr

Supplementary Materials

This part shows the different tables and graphs that are related to the different results discussed in the text.

Proximate analysis protocol:

Details of the method can be found in reference 26. The method can be summarized as follows:

FC% = 100 - %Ash - VM%

TG of pyrolysis of biomass sample gives the humidity and VM percent

TG of char combustion (by using air) gives the Ash percent

The author of the article recommends the use of 10 and 20 mg of biomass sample, and 40 ml/min flow for both nitrogen and air.

Mineral analysis:

The detailed mineral analysis of different biomasses can be shown in Table S.1.

Table S.1 ICP AES analysis for the five biomasses.

	Mass (mg/kg of raw material)				
	CM	OK	APH	WS	DK
Ag	0.85	0.07	1.87	0.20	0.52
Al	467.17	107.34	8.75	268.23	33.46
Ba	49.11	0.93	0.27	26.31	0.56
Be	< 0.00003	< 0.00003	< 0.00003	< 0.00003	< 0.00003
Bi	17.96	18.81	20.96	20.41	14.26
Ca	5735.66	522.90	1299.19	4067.55	287.49
Cd	0.50	0.07	< 0.00002	0.02	< 0.00002
Co	< 0.0004	< 0.0003	< 0.0004	< 0.0004	< 0.0003
Cr	2.39	1.38	2.17	4.55	1.34
Cu	4.63	3.01	6.34	5.95	4.98
Fe	195.45	34.35	31.70	141.04	54.15
Ga	< 0.0002	0.05	< 0.0002	< 0.0002	< 0.0002
In	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
K	1260.81	2600.47	1164.71	> 15000	3000.77
Mg	580.63	579.67	207.49	1000.73	652.85
Mn	39.44	6.52	3.07	23.03	11.57
Mo	1.62	0.02	< 0.003	0.76	0.19
Na	217.37	112.50	5841.61	11177.19	54.78
Ni	< 0.00004	< 0.00004	0.38	< 0.00004	< 0.00004
Pb	1.64	0.33	0.05	1.00	0.31

Rb	0.89	6.10	0.65	6.34	1.61
Sr	30.26	1.26	17.55	27.44	1.10
Tl	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001
Zn	38.11	11.12	4.74	17.69	10.44

Thermal characteristics

All thermal characteristics of the different thermogravimetric experiments at different heating rates can be found in Table S.2.

Table S.2 Characteristics of the thermogravimetric experiment at different heating rates:

Biomass materials	B(°C min^{-1})	T_i(°C)	T_{max}(°C)	T_f (°C)	$R_{max/}$(min^{-1})
Ciste de Monteplier CM	2	200	334.88	361	0.25
	5	206	350.03	375	0.44
	10	210	359.95	395	0.98
	20	215	376.09	405	2.6
	30	224	383.69	430	2.3
	40	229	390.34	436	3.9
Olive Kernels OK	2	200	304.42	350	0.29
	5	209	318.18	375	0.51
	10	215	330.52	400	1.26
	20	221	343.81	425	2.88
	30	236	350.46	435	3.72
	40	240	356.16	441	4.46
Aleppo Pine husks APH	2	185	318.01	349	0.25
	5	198	333.37	375	0.64
	10	200	344.21	395	0.73
	20	205	358.06	405	2.83
	30	215	364.7	419	3.36
	40	219	371.35	440	4.75
Straw wheat WS	2	160	293.49	335	0.27
	5	165	310.58	365	0.71
	10	171	322.92	375	1.42
	20	370	334.32	365	2.44
	30	180	340.02	385	3.34
	40	185	345.71	395	5.45
Date Kernels DK	2	165	276.4	410	0.28
	5	171	285.9	447	0.48
	10	174	296.34	463	1.58
	20	190	306.78	474	3.41

	30	198	313.43	489	4.47
	40	210	318.1	495	7.14

As discussed in the text, Figure S.1 and S.2 show the linearization of different samples according to KAS method and Coast Redferem.

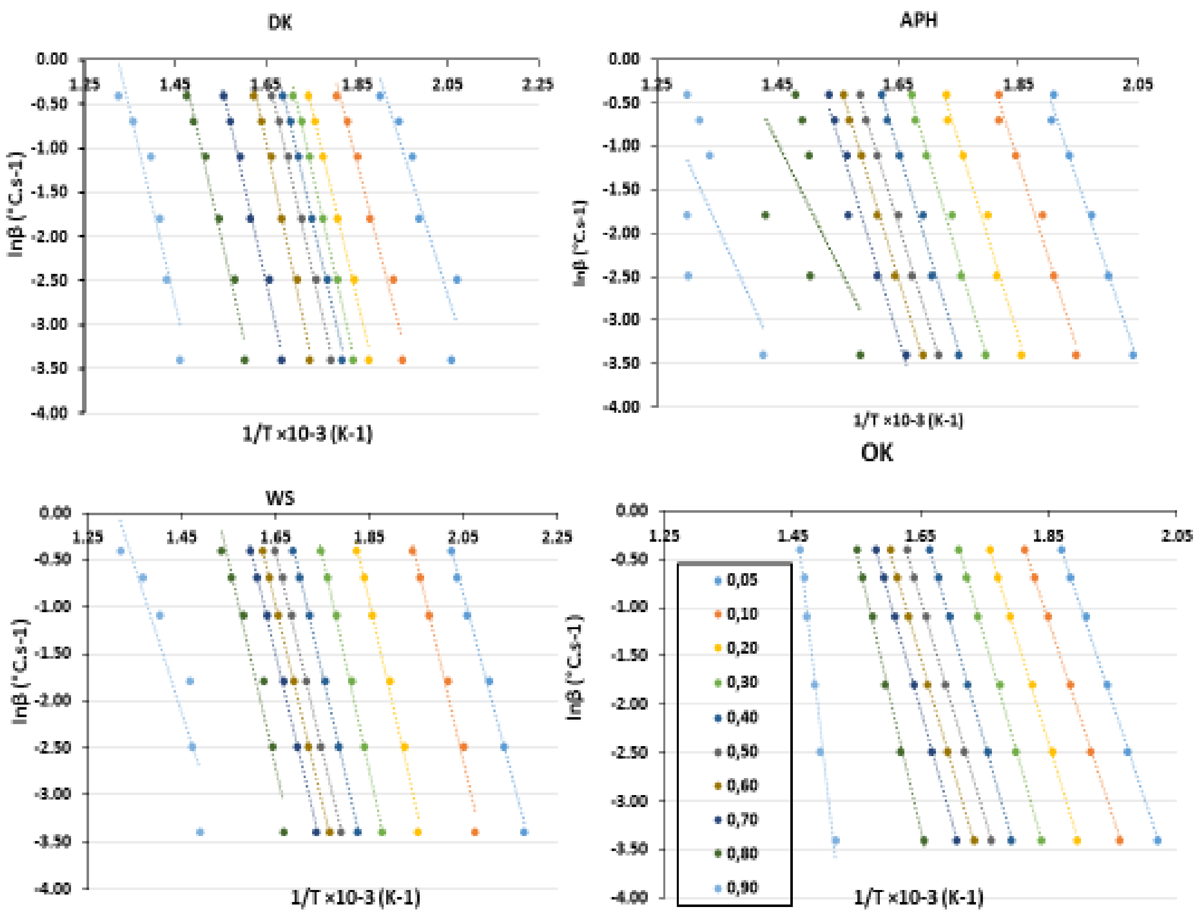

Figure S.1 KAS plots of OK, APH, WS and DK

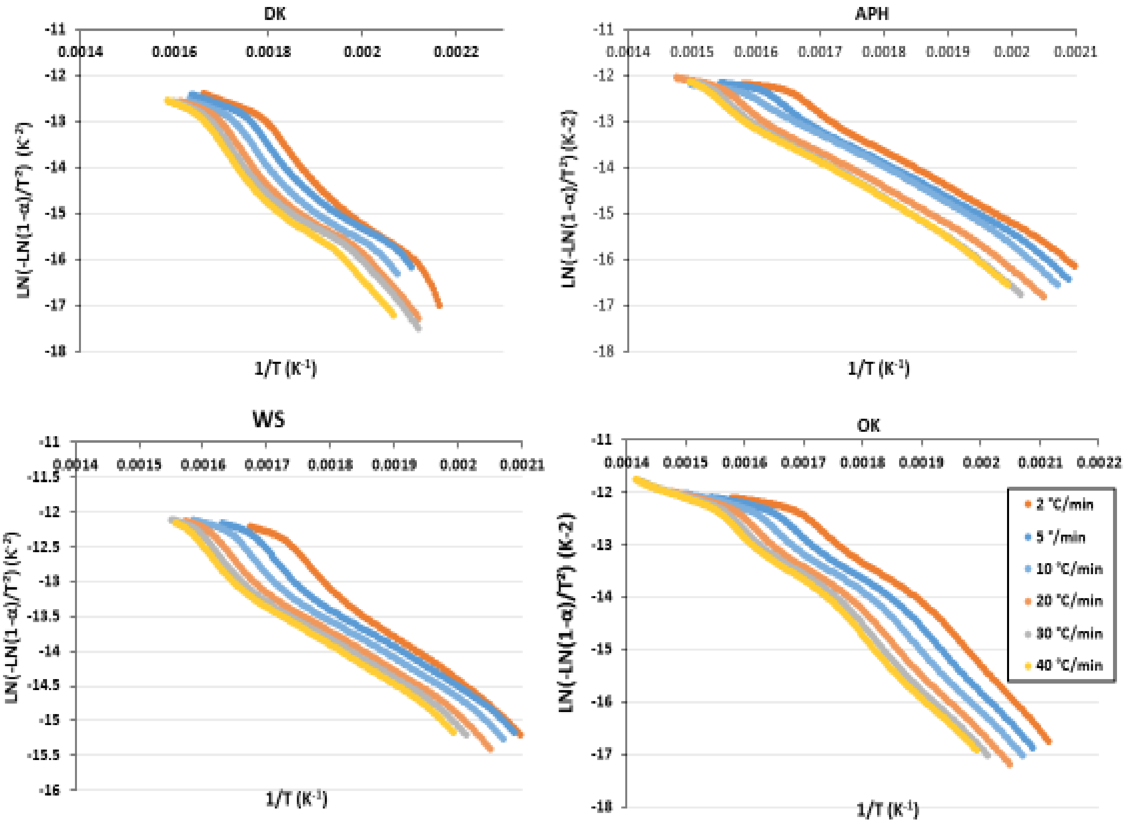

Figure S.2 Coast redferem plots of DK, APH, WS and OK

Kinetic parameters:

Table S.3 The activation energy and pre-exponential factor of CM, OK, APH, WS and DK according to KAS method.

	CM			OK			APH			WS			DK		
α/-	E_a(kJ mol^{-1})	A(s^{-1})	R^2	E_a(kJ mol^{-1})	A(s^{-1})	R^2	E_a(kJ mol^{-1})	A(s^{-1})	R^2	E_a(kJ mol^{-1})	A(s^{-1})	R^2	E_a(kJ mol^{-1})	A(s^{-1})	R^2
0.05	193.03	1.31E+22	0.960	1.75E+02	2.39E+20	0.999	183.7	3.23E+21	0.987	164.2	4.17E+20	0.995	142.67	4.04E+17	0.876
0.1	187.28	8.19E+20	0.971	1.77E+02	1.21E+20	1.000	190.02	1.98E+21	0.978	187.64	1.98E+22	0.986	173.25	5.33E+19	0.973
0.15	183.93	1.67E+20	0.984	1.81E+02	1.59E+20	0.999	197.02	2.95E+21	0.981	191.9	1.15E+22	0.988	181.92	1.37E+20	0.989
0.2	189.38	2.61E+20	0.987	1.89E+02	5.01E+20	0.999	199.45	2.04E+21	0.985	194.19	6.16E+21	0.991	191.44	5.84E+20	0.995
0.25	190.88	1.85E+20	0.989	1.97E+02	1.35E+21	0.999	202.92	1.99E+21	0.986	200.11	8.45E+21	0.991	193.02	5.46E+20	0.997
0.3	194.31	1.93E+20	0.991	2.02E+02	2.48E+21	0.999	205.42	1.78E+21	0.987	201.16	4.64E+21	0.998	198	1.11E+21	0.996
0.35	196.31	1.57E+20	0.991	2.02E+02	1.37E+21	1.000	203.64	7.05E+20	0.984	196.76	9.08E+20	0.996	200.82	1.49E+21	0.996
0.4	196.98	9.82E+19	0.990	2.05E+02	1.45E+21	1.000	201.86	2.97E+20	0.988	190.21	1.33E+20	0.999	197.72	6.13E+20	0.996
0.45	200.95	1.24E+20	0.993	1.98E+02	2.29E+20	1.000	202.6	2.21E+20	0.995	191.22	1.05E+20	0.999	198.63	5.55E+20	0.997
0.5	199.68	6.01E+19	0.995	1.98E+02	1.66E+20	1.000	200.35	9.63E+19	0.997	187.85	3.67E+19	0.999	198.74	4.28E+20	0.995
0.55	197.2	2.46E+19	0.996	1.98E+02	1.08E+20	1.000	200.64	7.21E+19	0.998	185.63	1.75E+19	0.998	206.48	1.37E+21	0.995
0.6	198.81	1.61E+19	0.997	2.01E+02	1.17E+20	1.000	202.15	5.01E+19	0.997	187.46	1.37E+19	0.999	215.24	2.94E+21	0.991
0.65	195	5.78E+18	0.999	2.02E+02	9.97E+19	1.000	205.29	6.68E+19	0.993	186.4	8.59E+18	0.999	211.96	7.48E+20	0.989
0.7	194.59	4.02E+18	0.990	2.10E+02	3.60E+20	1.000	203.14	3.04E+19	0.951	187.65	8.34E+18	0.998	201.95	4.83E+19	0.991
0.75	193.99	1.89E+18	0.997	2.21E+02	1.26E+21	1.000	160.92	5.62E+15	0.681	200.09	4.29E+19	0.991	191.54	2.21E+18	0.996
0.8	187.2	4.92E+17	0.988	2.56E+02	6.31E+23	0.997	122.82	3.23E+12	0.383	190.31	4.24E+18	0.955	198.89	4.77E+18	0.982
0.85	177.14	2.26E+16	0.933	3.41E+02	7.59E+29	0.997	135.97	1.05E+13	0.427	163.8	7.26E+15	0.886	211.91	1.09E+19	0.967
0.9	154.34	8.49E+13	0.919	4.95E+02	1.39E+40	0.976	135.14	2.21E+12	0.428	137.33	1.23E+13	0.846	193.91	9.52E+16	0.908
0.95	134.05	4.47E+11	0.869	7.14E+02	1.34E+53	0.981	120.7	3.85E+10	0.465	101.22	5.57E+9	0.823	121.98	1.20E+11	0.811

Activation energy and pre-exponential factor according to Coats and Redfern method are shown in Table S.4. The variation in the value of E_a with the different heating rates can be explained by the experimental error, on one hand, and by the limitations of heat transfer, which tended to increase with high heating rates, on the other hand. The error on E_a and A according to Coats Redfern method reported in Table S.5 has been calculated with respect to the different heating rates.

Table S.4: Detailed kinetic parameters according to Coats–Redfern method.

	β(°C min^{-1})	E_a(kJ mol^{-1})	A(s^{-1})	R^2
CM	2	73.92	1.94E+03	0.979
	5	70.95	4.26E+03	0.982
	10	73.21	8.10E+03	0.979
	20	76.64	1.57E+04	0.988
	30	69.95	1.98E+04	0.988
	40	75.67	2.64E+04	0.990
OK	2	75.87	2.71E+03	0.971
	5	73.33	5.71E+03	0.977
	10	71.83	9.76E+03	0.977
	20	76.15	1.81E+04	0.983
	30	73.04	2.27E+04	0.978
	40	74.27	2.69E+04	0.981
WS	2	59.87	5.61E+01	0.981
	5	53.82	1.17E+02	0.987
	10	53.34	2.15E+02	0.986
	20	54.01	4.04E+02	0.989
	30	53.94	5.62E+02	0.986
	40	53.86	6.96E+02	0.988
APH	2	67.42	5.02E+02	0.996
	5	64.19	1.11E+03	0.996
	10	60.67	1.97E+03	0.988
	20	67.52	4.10E+03	0.996
	30	68.12	5.82E+03	0.995
	40	66.84	7.15E+03	0.996
DK	2	76.04	7.73E+02	0.926
	5	72.03	1.70E+03	0.941
	10	75.84	3.33E+03	0.951
	20	77.39	6.31E+03	0.969
	30	77.26	8.77E+03	0.976
	40	82.08	1.15E+04	0.974