Supplementary material

For Sustainable Energy & Fuels

Management of waste crustacean shells for the construction of a carbon-negative circulation model

Xiaogang Sun [ab, 1], Zhen Du [a, 1], Yimeng Wang [b], Yuepeng Guan [b,*], Baoning Zhu [a, *],Yaqin Huang [a,*]

[a.] Beijing Laboratory of Biomedical Materials, Beijing Key Laboratory of Electrochemical Process and Technology for Materials, Beijing Engineering Center for Environmental Pollution Control and Resource Utilization, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China.

[b.] Beijing Key Laboratory of Clothing Materials R&D and Assessment, Beijing Engineering Research Center of Textile Nano Fiber, Beijing Institute of Fashion Technology, Beijing, 100029, People's Republic of China.

[1] These authors contributed equally to this work and should be considered co-first author.

[*] Corresponding author

E-mail:

huangyq@mail.buct.edu.cn (Yaqin Huang)

bnzhu@mail.buct.edu.cn (Baoning Zhu);

20210007@bift.edu.cn (Yuepeng Guan);

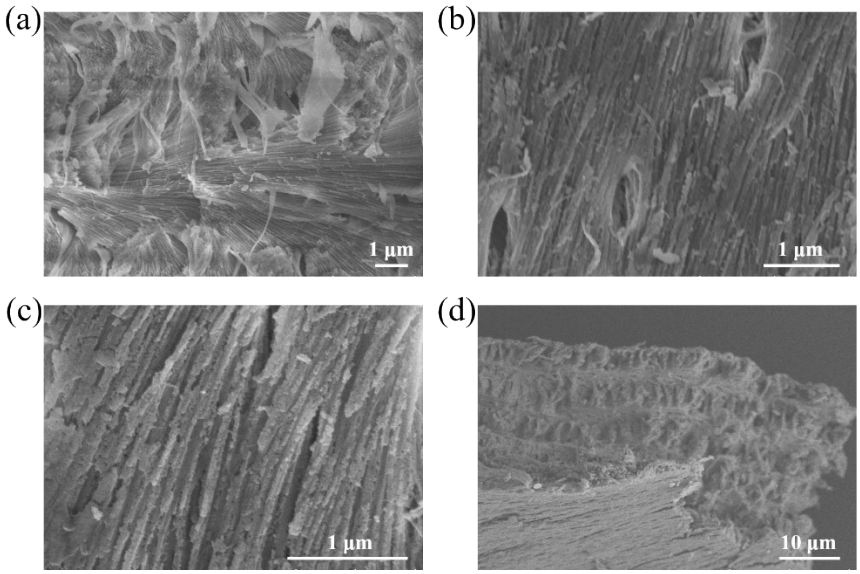


Figure S1. SEM images of WCS.

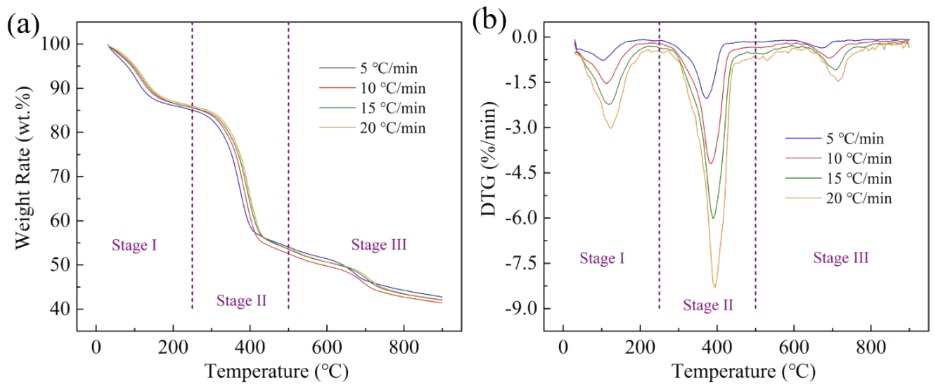


Figure S2. (a) TG and (b) DTG curves of WCS pyrolysis process at four different heating rates.

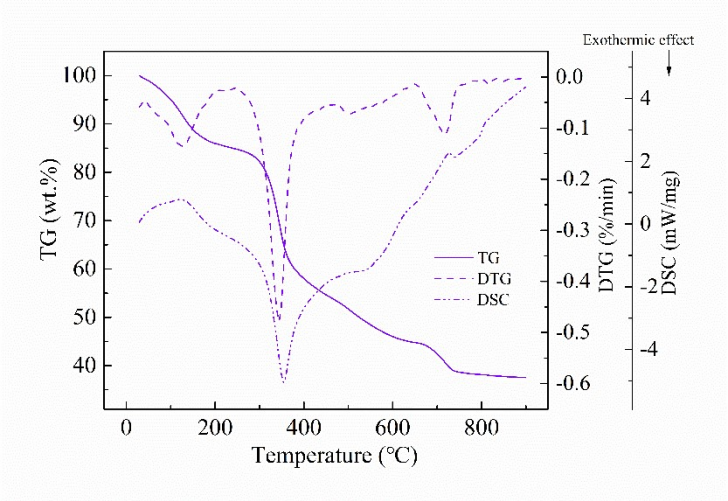


Figure S3. TG, DTG, and DSC curves of WCS pyrolysis process under air atmosphere at the heating rate of 10 ℃/min.

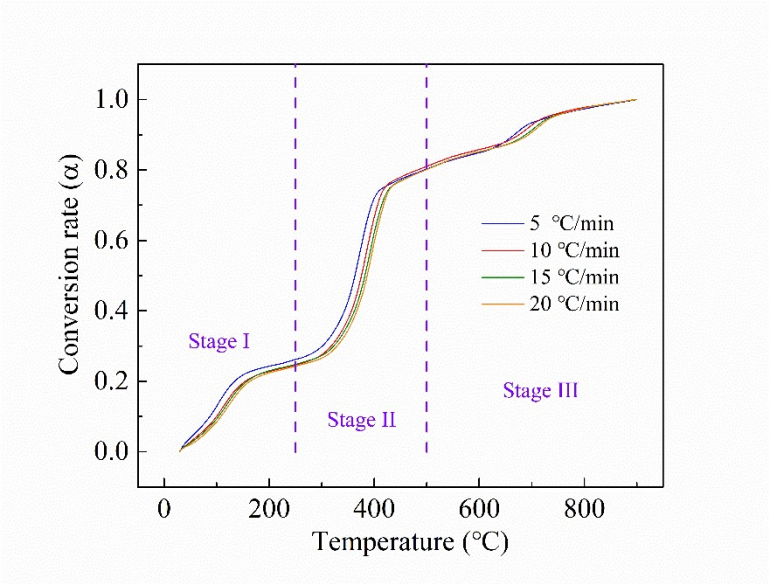


Figure S4. Changes of conversion rates to temperature at different heating rates.

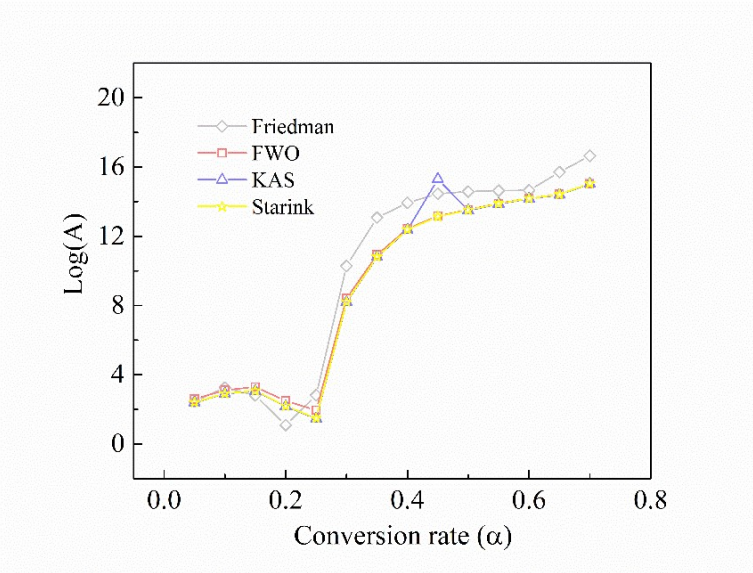


Figure S5. Comparison of experimental master plots of [$f(\alpha)g(\alpha)/f(0.5)g(0.5)$] against α of WCS pyrolysis process with theoretical master curves of [$f(\alpha)g(\alpha)$] against α.

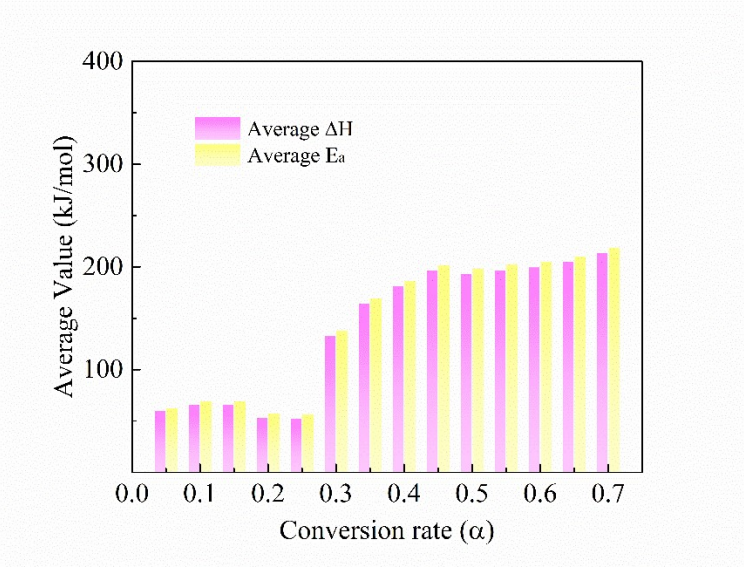
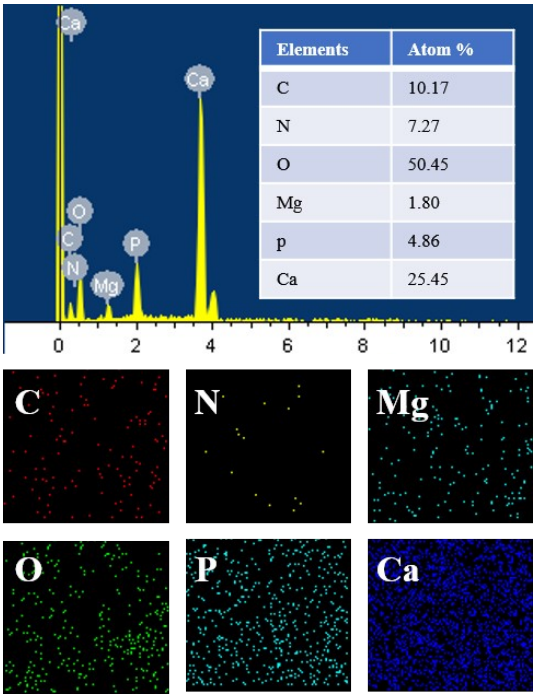


Figure S6. Changes of average values of ΔH and E_a of WCS pyrolysis process at different conversion rates.



Elements	Atom %
C	10.17
N	7.27
O	50.45
Mg	1.80
p	4.86
Ca	25.45

Figure S7. EDS analysis and elements mapping of WCS-750 (corresponding to Fig. 4a).

Table S1

Peaks and corresponding compounds in chromatograms of volatile products of WCS pyrolyzed at 125, 410 and 730 ℃.

Peak number #	Reaction time (min)	Compound	Molecular formula	CAS#	Peak area (%)
125 ℃					
1	1.37	Water	H_2O	7732-18-5	88.74
410 ℃					
1	1.30	L-alanylglycine	$C_5H_{10}N_2O_3$	687-69-4	14.11
2	1.39	D-alanine	$C_3H_7NO_2$	338-69-2	9.87
3	2.25	Oxaluric acid	$C_3H_4N_2O_4$	585-05-7	3.68
4	2.98	(S)-amphetamine	$C_9H_{13}N$	51-64-9	0.57
5	4.04	Acetamide	C_2H_5NO	60-35-5	8.07
6	4.76	2,4-dihydroxypyridine	$C_5H_5NO_2$	626-03-9	0.84
7	5.74	2-ethyl-4,5-dimethyloxazole	$C_7H_{11}NO$	53833-30-0	1.41
8	6.36	2,6,8-trihydroxypurine	$C_5H_4N_4O_3$	69-93-2	0.46
9	7.31	N-acetylglycine	$C_4H_7NO_3$	543-24-8	0.85
10	7.91	1-(methylsulfonyl)piperazine	$C_5H_{12}N_2O_2S$	55276-43-2	3.00
11	8.42	Acetic acid	$C_{12}H_{20}O_2$	3465-88-1	0.90
12	8.79	N-(hydroxymethyl)nicotinamide	$C_7H_8N_2O_2$	3569-99-1	0.46
13	9.16	Paromomycin	$C_{23}H_{45}N_5O_{14}$	7542-37-2	0.63
14	9.42	3-formyl-1-methyl-2(1H)-pyridone	$C_7H_7NO_2$	79138-28-6	2.50
15	9.67	3-ethoxyaniline	$C_8H_{11}NO$	621-33-0	5.96
16	10.31	N-(furan-3-yl)acetamide	$C_6H_7NO_2$	59445-85-1	2.49
17	11.22	2',3',5'-triacetyl -azacytidine	$C_{14}H_{18}N_4O_8$	10302-78-0	9.06
18	11.55	(2-oxo-1H-pyridin-3-yl) acetate	$C_7H_7NO_3$	61296-14-8	1.45
19	12.30	Kahweol	$C_{20}H_{26}O_3$	6894-43-5	0.43
20	12.59	5-(3'-hydroxy-n-hexyl)pyrrolidin-2-one	$C_{10}H_{19}NO_2$	120782-01-6	0.85
21	13.42	Piperidin-2-ylmethanamine	$C_6H_{14}N_2$	22990-77-8	5.43
22	13.57	N-(piperidin-4-ylmethyl)acetamide	$C_8H_{16}N_2O$	71207-33-5	1.86
23	14.38	DL-pipecolinic Acid	$C_6H_{11}NO_2$	535-75-1	4.97
24	14.62	Methyl cholate	$C_{25}H_{42}O_5$	1448-36-8	0.36
25	14.73	2-hydroxycyclopentadecanone	$C_{15}H_{28}O_2$	4727-18-8	0.6
26	15.17	Aldehydo-muramic acid	$C_9H_{17}NO_7$	1114-41-6	3.73
27	15.45	(1R,2R)-(-)-1,2-diaminocyclohexane	$C_6H_{14}N_2$	20439-47-8	2.28
28	15.86	N-(2,4-dihydroxyphenyl)acetamide	$C_8H_9NO_3$	71516-07-9	0.79
29	16.31	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-2-methyl-, (S)- (9CI)	$C_8H_{12}N_2O_2$	38074-80-5	0.54
30	17.17	7-methyl-(Z)-8-tetradecen-1-ol acetate	$C_{17}H_{32}O_2$	959269-58-0	0.51
31	18.48	Palmitic acid	$C_{16}H_{32}O_2$	57-10-3	0.89
32	20.14	Oleic acid	$C_{18}H_{34}O_2$	112-80-1	0.87
730 ℃					
1	1.29	Sarcosine	$C_3H_7NO_2$	107-97-1	4.04

2	1.38	Urea	CH_4N_2O	57-13-6	18.36

Continued Table S1

Peak number #	Reaction time (min)	Compound	Molecular formula	CAS#	Peak area (%)
3	1.5	2-cyanoacetamide	$C_3H_4N_2O$	107-91-5	7.14
4	1.74	Butyraldehyde	C_4H_8O	123-72-8	3.36
5	1.95	N,N-dimethyl-2-(1H-1,2,4-triazol-5-yl)acetamide	$C_4H_6N_4O$	875239-17-1	6.18
6	2.18	Acetic acid	$C_2H_4O_2$	64-19-7	2.32
7	2.56	1-methyl-1H-pyrrole-2(5H)-one	C_5H_7NO	13950-21-5	1.48
8	2.73	Pyridine	C_5H_5N	110-86-1	2.22
9	2.89	Toluene	C_7H_8	108-88-3	8.23
10	3.18	Oct-3-yn-1-ol	$C_8H_{14}O$	14916-80-4	0.74
11	3.49	2-methylpyridine	C_6H_7N	109-06-8	3.01
12	3.78	(E)-1,7-dodecadiene	$C_{12}H_{22}$	106051-46-1	0.79
13	3.89	Metamizole	$C_{13}H_{17}N_3O_4S$	50567-35-6	3.15
14	4.01	(2-aminoethyl)phosphonic acid	$C_2H_8NO_3P$	2041-14-7	3.19
15	4.47	Styrene	C_8H_8	100-42-5	1.39
16	5.15	2,4-lutidine	C_7H_9N	108-47-4	1.89
17	5.73	3-aminobenzenethiol	C_6H_7NS	22948-02-3	1.18
18	6.03	prop-2-enylbenzene	C_9H_{10}	300-57-2	0.75
19	6.6	Phenyl carbamate	$C_7H_7NO_2$	622-46-8	0.55
20	6.83	1H-indene	C_9H_8	95-13-6	0.48
21	7.52	2-acetylpyrrole	C_6H_7NO	1072-83-9	0.74
22	7.9	p-cresol	C_7H_8O	106-44-5	1.04
23	8.43	<15N>phenylacetonitrile	C_8H_7N	144987-02-0	1.01
24	9.21	2-ethylphenol	$C_8H_{10}O$	90-00-6	0.52
25	9.89	3-phenylpropionitrile	C_9H_9N	645-59-0	0.79
26	10.47	6-methylpurine	$C_6H_6N_4$	2004-03-7	0.53
27	10.93	1H-indole	C_8H_7N	120-72-9	0.8
28	11.16	3,4-dihydro-1H-pyridin-2-one	C_5H_7NO	57147-25-8	0.98
29	12.11	Skatole	C_9H_9N	83-34-1	0.44
30	13.37	DL-pipecolinic acid	$C_6H_{11}NO_2$	535-75-1	1.63
31	14.3	Piperidin-2-ylmethanamine	$C_6H_{14}N_2$	22990-77-8	1.67
32	15.14	Framycetin	$C_{23}H_{46}N_6O_{13}$	119-04-0	0.33
33	15.41	2-hexyldecyl acetate	$C_{18}H_{36}O_2$	82409-75-4	0.49

Table S2

Activation energies of feedstock pyrolysis process obtained from four iso-conversional methods.

α	Friedman		FWO		KAS		Starink	
	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2	E_a (kJ/mol)	R^2
0.05	62.91	0.9711	64.38	0.9894	62.10	0.9874	62.27	0.9875
0.1	72.03	0.9833	70.48	0.9716	68.01	0.9666	68.20	0.9668
0.15	66.87	0.9535	72.55	0.9714	69.82	0.9663	70.02	0.9665
0.2	47.22	0.6407	63.24	0.9138	59.55	0.8945	59.78	0.8954
0.25	67.04	0.848	57.01	0.7706	51.42	0.7045	51.72	0.7076
0.3	156.33	0.9866	133.77	0.9672	130.98	0.9624	131.26	0.9626
0.35	190.50	0.9909	164.26	0.9853	162.64	0.9835	162.92	0.9836
0.4	200.90	0.9957	182.74	0.9907	181.82	0.9896	182.09	0.9897
0.45	207.44	0.9984	191.63	0.9945	217.76	0.9800	191.26	0.9940
0.5	208.94	0.9964	196.09	0.9958	195.54	0.9954	195.81	0.9954
0.55	209.57	0.9945	200.61	0.9963	200.17	0.9959	200.45	0.9960
0.6	209.80	0.9954	204.17	0.9961	203.80	0.9958	204.08	0.9958
0.65	222.73	0.9826	206.97	0.9961	206.62	0.9957	206.90	0.9957
0.7	234.24	0.9938	214.55	0.9948	214.44	0.9942	214.71	0.9942

Table S3

Pre-exponential factors of feedstock pyrolysis process obtained from four iso-conversional methods.

α	Friedman	FWO	KAS	Starink
	A (s^{-1})	A (s^{-1})	A (s^{-1})	A (s^{-1})
0.05	2.89×10^{2}	3.88×10^{2}	2.46×10^{2}	2.55×10^{2}
0.1	1.76×10^{3}	1.30×10^{3}	7.95×10^{2}	8.26×10^{2}
0.15	6.34×10^{2}	1.95×10^{3}	1.14×10^{3}	1.18×10^{3}
0.2	1.23×10^{1}	3.09×10^{2}	1.48×10^{2}	1.55×10^{2}
0.25	6.57×10^{2}	8.92×10^{1}	2.89×10^{1}	3.07×10^{1}
0.3	1.89×10^{10}	2.61×10^{8}	1.54×10^{8}	1.62×10^{8}
0.35	1.19×10^{13}	8.47×10^{10}	6.25×10^{10}	6.58×10^{10}
0.4	8.43×10^{13}	2.77×10^{10}	2.33×10^{12}	2.45×10^{12}
0.45	2.88×10^{14}	1.48×10^{13}	2.00×10^{15}	1.38×10^{13}
0.5	3.82×10^{14}	3.42×10^{13}	3.08×10^{13}	3.24×10^{13}
0.55	4.29×10^{14}	7.98×10^{13}	7.35×10^{13}	7.74×10^{13}
0.6	4.48×10^{14}	1.56×10^{14}	1.45×10^{14}	1.53×10^{14}
0.65	5.06×10^{15}	2.64×10^{14}	2.47×10^{14}	2.60×10^{14}
0.7	4.37×10^{16}	1.09×10^{15}	1.07×10^{15}	1.13×10^{15}

Table S4

Algebraic expressions of $f(\alpha)$ and $g(\alpha)$ for the most common solid-state reaction mechanisms.

Reaction mechanism	Symbol	$f(\alpha)$	$g(\alpha)$
Reaction order			
Zero-order	F0	1	α
First-order (instantaneous nucleation and unidimensional growth)	F1	$(1-\alpha)$	$-\ln(1-\alpha)$
Second-order	F2	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third-order	F3	$(1-\alpha)^3$	$[(1-\alpha)^{-2}-1]/2$
Nucleation			
Johnson-Mehl-Avrami equation (random nucleation and growth of nuclei)	A_m	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	$[-\ln(1-\alpha)]^{1/m}$
Diffusion			
One-dimensional diffusion	D1	$1/(2\alpha)$	α^2
Two-dimensional diffusion (bidimensional particle shape) (Valensi)	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$
Three-dimensional diffusion (tridimensional particle shape) (Jander)	D3	$(3/2)(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
Three-dimensional diffusion (tridimensional particle shape) (Ginstling-Brounshtein)	D4	$(3/2)[(1-\alpha)^{-1/3}-1]^{-1}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
Contracting geometry			
Contracting cylinder	R2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Contracting sphere	R3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

Table S5

Thermodynamic parameters of feedstock pyrolysis process at the heating rate of 10 ℃/min.

	Friedman			FWO			KAS			Starink		
α	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/(mol K))	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/(mol K))	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/(mol K))	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (J/(mol K))
0.05	60.07	197.32	-208.69	61.55	197.19	-206.24	59.26	197.39	-210.02	59.44	197.37	-209.73
0.1	68.93	196.58	-194.09	67.38	196.69	-196.62	64.91	196.89	-200.68	65.10	196.87	-200.36
0.15	63.56	196.98	-202.85	69.26	196.54	-193.52	66.53	196.75	-198.00	66.73	196.73	-197.67
0.2	43.66	198.88	-236.02	59.68	197.29	-209.24	55.99	197.62	-215.35	56.22	197.60	-214.96
0.25	62.61	196.97	-204.30	52.58	197.85	-220.89	46.98	198.42	-230.26	47.28	198.39	-229.76
0.3	151.41	192.34	-62.23	128.85	193.19	-97.83	126.06	193.31	-102.26	126.34	193.29	-101.80
0.35	185.39	191.26	-8.92	159.15	192.07	-50.05	157.54	192.12	-52.59	157.81	192.11	-52.16
0.4	195.66	190.97	7.14	177.50	191.49	-21.27	176.58	191.51	-22.71	176.85	191.51	-22.28
0.45	202.11	190.79	17.21	186.31	191.23	-7.48	212.44	190.53	33.31	185.93	191.24	-8.07
0.5	203.55	190.75	19.46	190.70	191.10	-0.61	190.14	191.12	-1.48	190.42	191.11	-1.05
0.55	204.12	190.74	20.34	195.16	190.98	6.36	194.72	190.99	5.67	194.99	190.98	6.10
0.6	204.29	190.73	20.61	198.66	190.88	11.83	198.29	190.89	11.25	198.57	190.88	11.68
0.65	217.15	190.40	40.67	201.40	190.80	16.11	201.04	190.81	15.55	201.32	190.81	15.99
0.7	228.59	190.13	58.49	208.91	190.61	27.82	208.79	190.61	27.64	209.07	190.60	28.07

Table S6

Average values of activation energies and enthalpy changes of WCS pyrolysis process at different conversion rates.

Conversion rate (α)	Average E_α (kJ/mol)	Average ΔH (kJ/mol)
0.05	62.92	60.08
0.1	69.68	66.58
0.15	69.81	66.52
0.2	57.45	53.89
0.25	56.80	52.36
0.3	138.08	133.17
0.35	170.08	164.97
0.4	186.89	181.65
0.45	202.02	196.70
0.5	199.10	193.70
0.55	202.70	197.25
0.6	205.46	199.95
0.65	210.80	205.23
0.7	219.49	213.84