

MULTIVARIATE ANALYSIS APPLIED TO THE MICROWAVE-DRIVEN CYANIDE POLYMERIZATION: A STATISTICAL VIEW OF A COMPLEX SYSTEM

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SUPPLEMENTARY INFORMATION

Table S1. Reaction conditions for the production of NH₄CN polymers from equimolar solutions of NaCN and NH₄Cl (1 M) assisted by microwave radiation (MWR), series at 170 °C (green), 190 °C (yellow) and 205 °C (red) , or using conventional thermal heating, series 80 °C (blue). The series at 80 °C was taken as reference from [Ruiz-Bermejo et al. 2019]. All the conversion values, α (%), are represented in the **Figure 1** of the main text (green lines). Note that the syntheses were carried out by triplicate.

Experiment	T (°C)	t (min)	α (%)	Experiment	T (°C)	t (min)	α (%)	Experiment	T (°C)	t (min)	α (%)	Experiment	T (°C)	t (min)	α (%)
1	170	5	13	22	190	4	21	43	205	2	24	67	80	1440	35
2	170	5	17	23	190	4	22	44	205	2	23	68	80	1440	35
3	170	5	14	24	190	4	21	45	205	2	22	69	80	1440	34
121	170	9	12	88	190	5	17	97	205	5	16	70	80	2880	38
122	170	9	15	89	190	5	18	98	205	5	21	71	80	2880	41
123	170	9	15	90	190	5	18	99	205	5	20	72	80	2880	37
4	170	18	18	118	190	9	18	46	205	9	18	73	80	4320	37
5	170	18	19	119	190	9	17	47	205	9	20	74	80	4320	38
6	170	18	17	120	190	9	17	48	205	9	19	75	80	4320	40
7	170	36	16	25	190	18	15	49	205	18	12	76	80	5400	41
8	170	36	10	26	190	18	14	50	205	18	12	77	80	5400	39
9	170	36	7	27	190	18	14	51	205	18	13	78	80	5400	39
10	170	52	14	28	190	36	12	52	205	36	15	79	80	7200	39
11	170	52	14	29	190	36	13	53	205	36	16	80	80	7200	41
12	170	52	17	30	190	36	12	54	205	36	17	81	80	7200	40
94	170	58	20	31	190	52	16	55	205	52	16	82	80	8640	38
95	170	58	21	32	190	52	16	56	205	52	16	83	80	8640	39
96	170	58	19	33	190	52	15	57	205	52	17	84	80	8640	38
13	170	67	34	124	190	58	17	91	205	58	13	85	80	10080	40
14	170	67	39	125	190	58	17	92	205	58	11	86	80	10080	44
15	170	67	38	126	190	58	14	93	205	58	11	87	80	10080	38
106	170	72	16	34	190	67	12	58	205	67	36				
107	170	72	19	35	190	67	12	59	205	67	32				
108	170	72	17	36	190	67	12	60	205	67	36				
16	170	90	14	115	190	72	15	100	205	72	16				
17	170	90	19	116	190	72	14	101	205	72	15				
18	170	90	18	117	190	72	14	102	205	72	17				
109	170	105	13	37	190	90	10	61	205	90	13				
110	170	105	13	38	190	90	10	62	205	90	13				
111	170	105	12	39	190	90	9	63	205	90	13				
19	170	120	17	112	190	105	17	103	205	105	11				
20	170	120	18	113	190	105	15	104	205	105	14				
21	170	120	17	114	190	105	17	105	205	105	10				
				40	190	120	15	64	205	120	14				
				41	190	120	14	65	205	120	11				
				42	190	120	14	66	205	120	11				

Table S2. Elemental analysis data and the EOR (%) values for NH₄CN polymers synthesized using the indicated conditions of temperature and reaction time from equimolar solutions of NaCN and NH₄Cl (1 M) assisted by microwave radiation (MWR), series at 170 °C (green), 190 °C (yellow) and 205 °C (red) , or using conventional thermal heating, series 80 °C (blue).

Experiment	T (°C)	t (min)	% C	% H	% N	% O	C/N molar	C/O molar	C/H molar	N/O molar	EOR (%)
1	170	5	38.64	3.68	37.45	20.24	1.20	2.55	0.88	2.11	90.23
2	170	5	38.32	3.63	38.74	19.31	1.15	2.65	0.88	2.29	83.10
3	170	5	37.90	3.71	38.31	20.09	1.15	2.52	0.85	2.18	80.95
4	170	18	40.81	3.58	39.89	15.73	1.19	3.46	0.95	2.90	75.86
5	170	18	40.52	3.43	39.69	16.36	1.19	3.30	0.98	2.77	83.83
6	170	18	39.64	3.44	38.39	18.53	1.20	2.85	0.96	2.37	85.75
7	170	36	38.95	3.58	37.10	20.38	1.22	2.55	0.91	2.08	85.95
8	170	36	38.22	3.58	35.74	22.47	1.25	2.27	0.89	1.82	87.92
9	170	36	37.90	3.61	35.83	22.66	1.23	2.23	0.87	1.81	88.80
10	170	52	37.97	3.57	35.92	22.55	1.23	2.25	0.89	1.82	91.31
11	170	52	35.95	3.44	34.20	26.42	1.23	1.81	0.87	1.48	90.89
12	170	52	37.29	3.38	35.01	24.32	1.24	2.04	0.92	1.64	91.26
13	170	67	41.08	3.45	39.37	16.11	1.22	3.40	0.99	2.79	80.18
14	170	67	41.86	3.36	40.20	14.59	1.21	3.83	1.04	3.15	83.19
15	170	67	41.21	3.71	39.50	15.58	1.22	3.53	0.92	2.90	84.49
16	170	90	38.77	3.49	36.16	21.58	1.25	2.40	0.93	1.92	88.63
17	170	90	39.44	3.41	36.82	20.34	1.25	2.59	0.96	2.07	87.87
18	170	90	38.93	3.42	36.40	21.26	1.25	2.44	0.95	1.96	89.34
19	170	120	36.60	3.34	33.71	26.36	1.27	1.85	0.91	1.46	87.62
20	170	120	38.20	3.36	35.19	23.26	1.27	2.19	0.95	1.73	89.19
21	170	120	38.85	3.39	35.98	21.79	1.26	2.38	0.96	1.89	88.69
22	190	4	39.16	3.40	37.68	19.76	1.21	2.64	0.96	2.18	77.79
23	190	4	40.72	3.63	39.00	16.66	1.22	3.26	0.94	2.68	81.42
24	190	4	41.35	3.53	39.36	15.77	1.23	3.50	0.98	2.85	80.29
25	190	18	38.76	3.27	36.90	21.09	1.23	2.45	0.99	2.00	84.28
26	190	18	37.42	3.24	35.39	23.95	1.23	2.08	0.96	1.69	85.16
27	190	18	37.54	3.35	34.82	24.31	1.26	2.06	0.94	1.64	86.79
28	190	36	33.52	2.78	27.88	35.82	1.40	1.25	1.00	0.89	88.11
29	190	36	35.37	3.32	33.00	28.32	1.25	1.67	0.89	1.33	88.67
30	190	36	37.10	3.52	34.20	25.18	1.27	1.96	0.88	1.55	87.12
31	190	52	38.88	3.60	36.42	21.11	1.25	2.46	0.90	1.97	87.15
32	190	52	39.13	3.43	35.74	21.70	1.28	2.40	0.95	1.88	88.78
33	190	52	38.59	3.45	34.31	23.65	1.31	2.18	0.93	1.66	86.25
34	190	67	40.62	3.48	37.45	18.46	1.27	2.93	0.97	2.32	86.01
35	190	67	41.50	3.48	38.50	16.53	1.26	3.35	0.99	2.66	85.78
36	190	67	40.87	3.56	37.49	18.10	1.27	3.01	0.96	2.37	83.62
37	190	90	38.77	3.42	35.39	22.43	1.28	2.30	0.95	1.80	85.95
38	190	90	38.08	3.37	34.30	24.25	1.30	2.09	0.94	1.62	87.92
39	190	90	39.53	3.29	35.15	22.03	1.31	2.39	1.00	1.82	88.80
40	190	120	39.89	3.32	34.73	22.06	1.34	2.41	1.00	1.80	88.63
41	190	120	38.91	3.42	34.97	22.70	1.30	2.29	0.95	1.76	87.82
42	190	120	39.47	3.40	35.53	21.60	1.30	2.44	0.97	1.88	89.29
43	205	2	41.62	3.58	38.96	15.86	1.25	3.50	0.97	2.81	82.64
44	205	2	41.34	3.52	38.73	16.42	1.25	3.36	0.98	2.70	80.16
45	205	2	40.47	3.66	38.13	17.75	1.24	3.04	0.92	2.45	80.73
46	205	9	39.31	3.38	36.07	21.23	1.27	2.47	0.97	1.94	84.82
47	205	9	38.74	3.50	35.44	22.33	1.28	2.31	0.92	1.81	86.29
48	205	9	38.79	3.49	35.75	21.96	1.27	2.36	0.93	1.86	87.85
49	205	18	40.67	3.63	38.25	17.46	1.24	3.11	0.93	2.50	88.64
50	205	18	39.13	3.57	35.24	22.07	1.30	2.36	0.91	1.82	87.29
51	205	18	39.93	3.58	36.26	20.24	1.28	2.63	0.93	2.05	86.23
52	205	36	38.39	3.81	35.47	22.33	1.26	2.29	0.84	1.82	86.48
53	205	36	40.11	3.61	36.66	19.63	1.28	2.73	0.93	2.13	88.46
54	205	36	40.98	3.72	37.58	17.73	1.27	3.08	0.92	2.42	87.91
55	205	52	41.03	3.69	36.86	18.43	1.30	2.97	0.93	2.29	89.04
56	205	52	41.00	3.67	37.16	18.18	1.29	3.01	0.93	2.34	88.36
57	205	52	40.98	3.67	37.01	18.34	1.29	2.98	0.93	2.31	88.41
58	205	67	41.37	3.49	37.02	18.12	1.30	3.04	0.99	2.34	86.82
59	205	67	41.94	3.42	37.38	17.25	1.31	3.24	1.02	2.48	85.26
60	205	67	41.64	3.49	37.13	17.74	1.31	3.13	0.99	2.39	88.32
61	205	90	38.12	3.57	33.58	24.74	1.32	2.05	0.89	1.55	90.42
62	205	90	40.34	3.51	35.88	20.27	1.31	2.65	0.96	2.02	89.62
63	205	90	40.19	3.61	35.92	19.92	1.31	2.69	0.93	2.06	90.23
64	205	120	40.21	3.60	34.80	21.40	1.35	2.51	0.93	1.86	90.74
65	205	120	39.04	3.51	34.32	23.13	1.33	2.25	0.93	1.70	89.53
66	205	120	36.69	3.47	32.31	27.53	1.32	1.78	0.88	1.34	84.78
67	80	1440	39.07	3.54	38.98	18.42	1.17	3.06	0.92	2.62	90.08108
68	80	1440	38.76	3.44	38.73	19.08	1.17	3.04	0.94	2.60	87.73953
69	80	1440	38.56	3.73	38.31	19.40	1.17	3.02	0.86	2.57	89.45956
70	80	2880	38.05	3.62	37.46	20.87	1.19	2.98	0.88	2.52	89.57363
71	80	2880	38.91	3.77	38.54	18.79	1.18	3.05	0.86	2.59	88.1912
72	80	2880	38.09	3.75	37.56	20.61	1.18	2.99	0.85	2.52	87.57391
73	80	4320	38.32	3.53	37.47	20.69	1.19	3.00	0.90	2.52	85.68319
74	80	4320	38.05	3.76	36.99	21.21	1.20	2.98	0.84	2.48	89.50949
75	80	4320	38.88	3.55	38.10	19.48	1.19	3.05	0.91	2.56	90.51412
76	80	5400	39.22	3.53	38.00	19.26	1.20	3.07	0.93	2.55	91.18264
77	80	5400	38.80	3.42	37.87	19.92	1.20	3.04	0.95	2.54	87.2176
78	80	5400	39.58	3.56	38.24	18.63	1.21	3.10	0.93	2.57	88.95688
79	80	7200	39.75	3.63	38.22	18.41	1.21	3.12	0.91	2.57	89.92806
80	80	7200	40.24	3.84	38.70	17.23	1.21	3.15	0.87	2.60	90.28931
81	80	7200	39.88	3.43	38.42	18.28	1.21	3.13	0.97	2.58	89.70192
82	80	8640	41.61	3.62	40.70	14.08	1.19	3.26	0.96	2.73	87.34969
83	80	8640	41.07	3.90	39.59	15.45	1.21	3.22	0.88	2.66	89.05151
84	80	8640	41.90	4.01	40.54	13.57	1.21	3.28	0.87	2.72	89.42187
85	80	10080	41.47	3.64	40.26	14.65	1.20	3.25	0.95	2.70	89.95808
86	80	10080	41.67	4.04	40.41	13.89	1.20	3.27	0.86	2.72	90.04966
87	80	10080	41.03	3.73	39.70	15.55	1.21	3.22	0.92	2.67	85.52521

Table S3. CATPCA correlation matrix and eigenvalues (Figure 4). High positive values between two variables indicate that they are directly proportional. High negative values indicate that they are inversely proportional.

Correlations Original Variables												
	T (°C)	t (min)	α (%)	Carbon	Hydrogen	Nitrogen	Oxygen	C/N molar	C/O molar	C/H molar	N/O molar	EOR (%)
T (°C)	1.000	-0.066	0.015	0.303	0.211	-0.180	-0.022	0.617	0.074	0.130	-0.016	0.052
t (min)	-0.066	1.000	-0.186	-0.048	-0.300	-0.424	0.294	0.561	-0.289	0.107	-0.324	0.503
α (%)	0.015	-0.186	1.000	0.564	0.093	0.588	-0.659	-0.244	0.669	0.438	0.675	-0.456
Carbon	0.303	-0.048	0.564	1.000	0.426	0.731	-0.864	0.007	0.880	0.521	0.844	-0.319
Hydrogen	0.211	-0.300	0.093	0.426	1.000	0.424	-0.399	-0.213	0.446	-0.475	0.414	-0.103
Nitrogen	-0.180	-0.424	0.588	0.731	0.424	1.000	-0.927	-0.599	0.896	0.339	0.929	-0.567
Oxygen	-0.022	0.294	-0.659	-0.864	-0.399	-0.927	1.000	0.395	-0.945	-0.478	-0.960	0.522
C/N molar	0.617	0.561	-0.244	0.007	-0.213	-0.599	0.395	1.000	-0.335	0.183	-0.444	0.526
C/O molar	0.074	-0.289	0.669	0.880	0.446	0.896	-0.945	-0.335	1.000	0.436	0.964	-0.520
C/H molar	0.130	0.107	0.438	0.521	-0.475	0.339	-0.478	0.183	0.436	1.000	0.437	-0.263
N/O molar	-0.016	-0.324	0.675	0.844	0.414	0.929	-0.960	-0.444	0.964	0.437	1.000	-0.565
EOR (%)	0.052	0.503	-0.456	-0.319	-0.103	-0.567	0.522	0.526	-0.520	-0.263	-0.565	1.000
Dimension	1	2	3	4	5	6	7	8	9	10	11	12
Eigenvalue	6.110	2.146	1.565	1.007	0.476	0.386	0.103	0.065	0.047	0.039	0.033	0.024

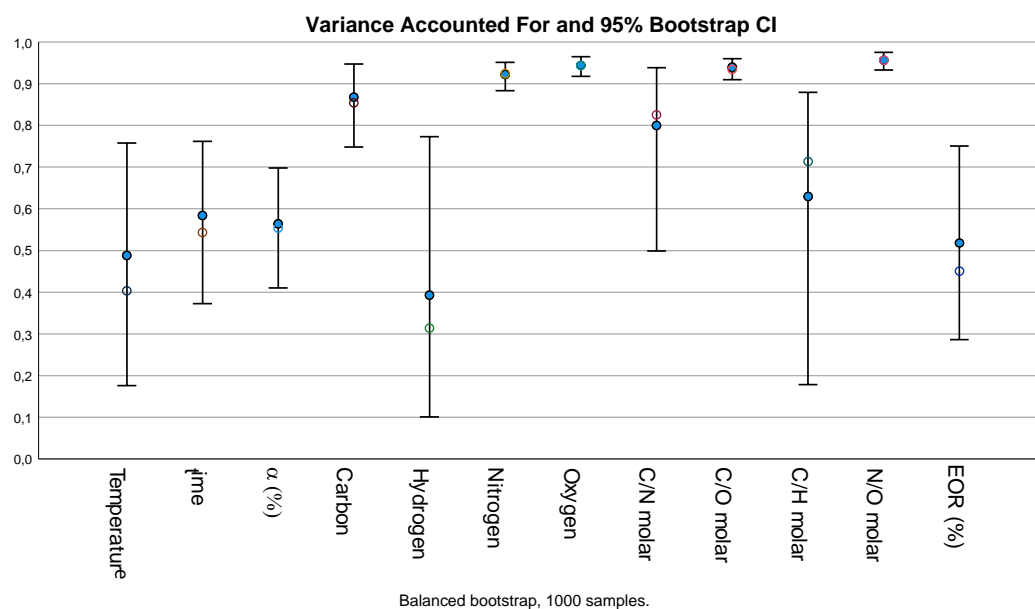


Figure S1. Variance accounted for by each question. Estimates and bootstrap 95% confidence intervals (CI) of variance on two categorical variables (temperature and time) and each spectroscopy characteristic. Temperature, hydrogen and molar C/H variations were significantly higher than the rest, while nitrogen, oxygen, molar C/O and N/O were the lowest.

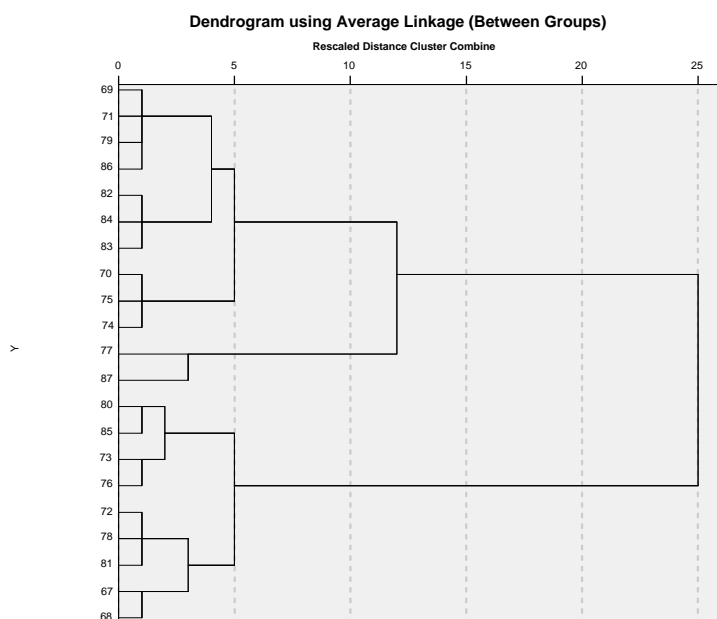


Figure S2. Hierarchical dendrogram based in principal component analysis of FT-IR sectors normalized (Series 80 °C). To clarify PCA results (3.1.2.), coefficient scores obtained by PCA analyses were arranged in a hierarchical dendrogram. The numeration of the experiments correspond with the Table S1.

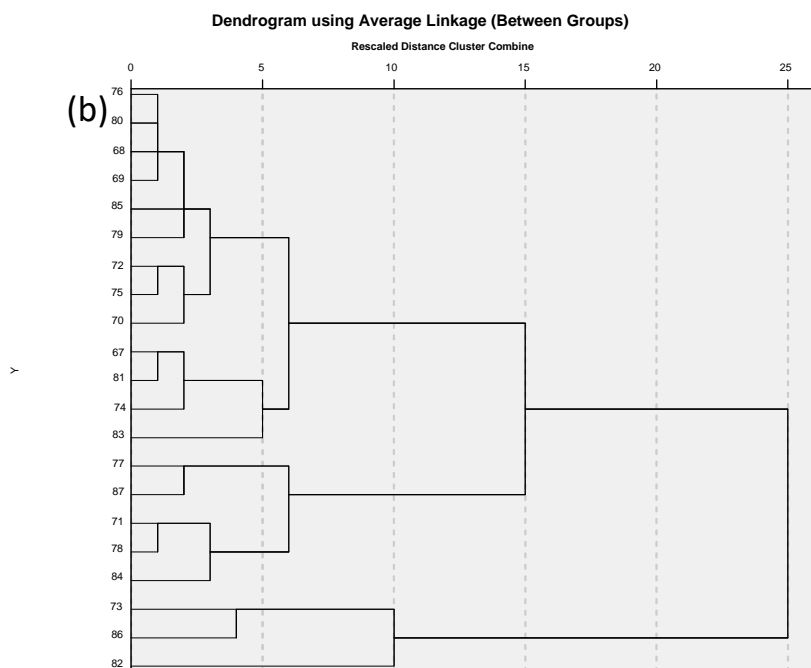
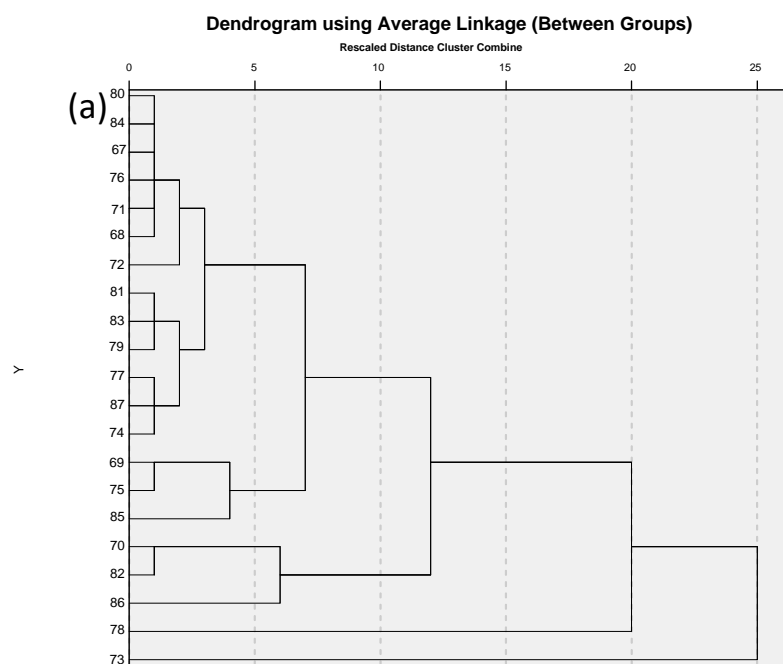


Figure S3. Hierarchical dendrogram based in principal component analysis of 2nd derivate FT-IR spectra (4000-450 cm^{-1}) (Series 80 °C). To clarify PCA results (3.1.2.), coefficient scores obtained by PCA analyses were arranged in a hierarchical dendrogram. (a) considering 13 smooth points. (b) considering 20 smooth points. The numeration of the experiments correspond with the Table S1.

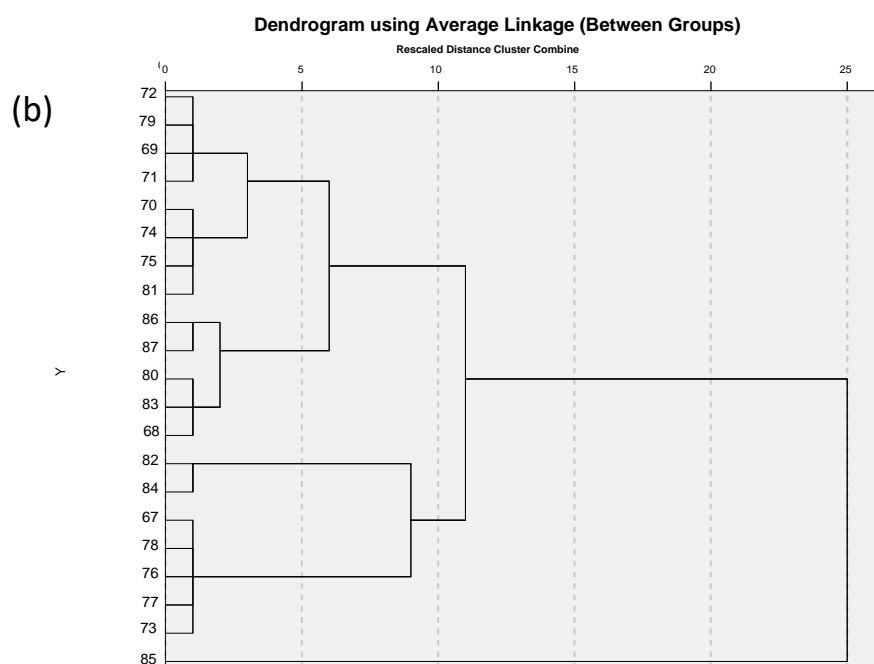
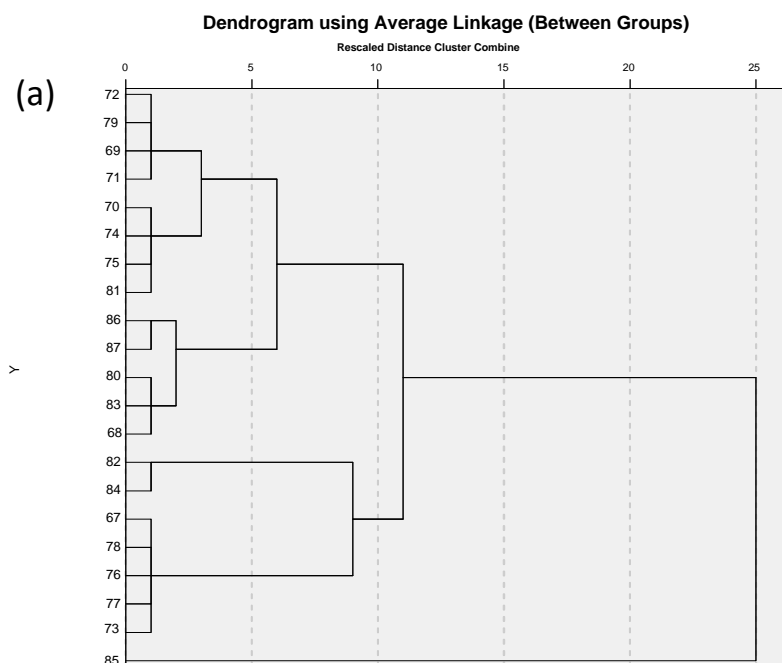


Figure S4. Hierarchical dendrogram based in principal component analysis of 2nd derivate FT-IR spectral region from 2300 to 2100 cm^{-1} (Series 80 $^{\circ}\text{C}$). To clarify PCA results (3.1.2.), coefficient scores obtained by PCA analyses were arranged in a hierarchical dendrogram. **(a)** considering 13 smooth points. **(b)** considering 20 smooth points. The numeration of the experiments correspond with the Table S1.

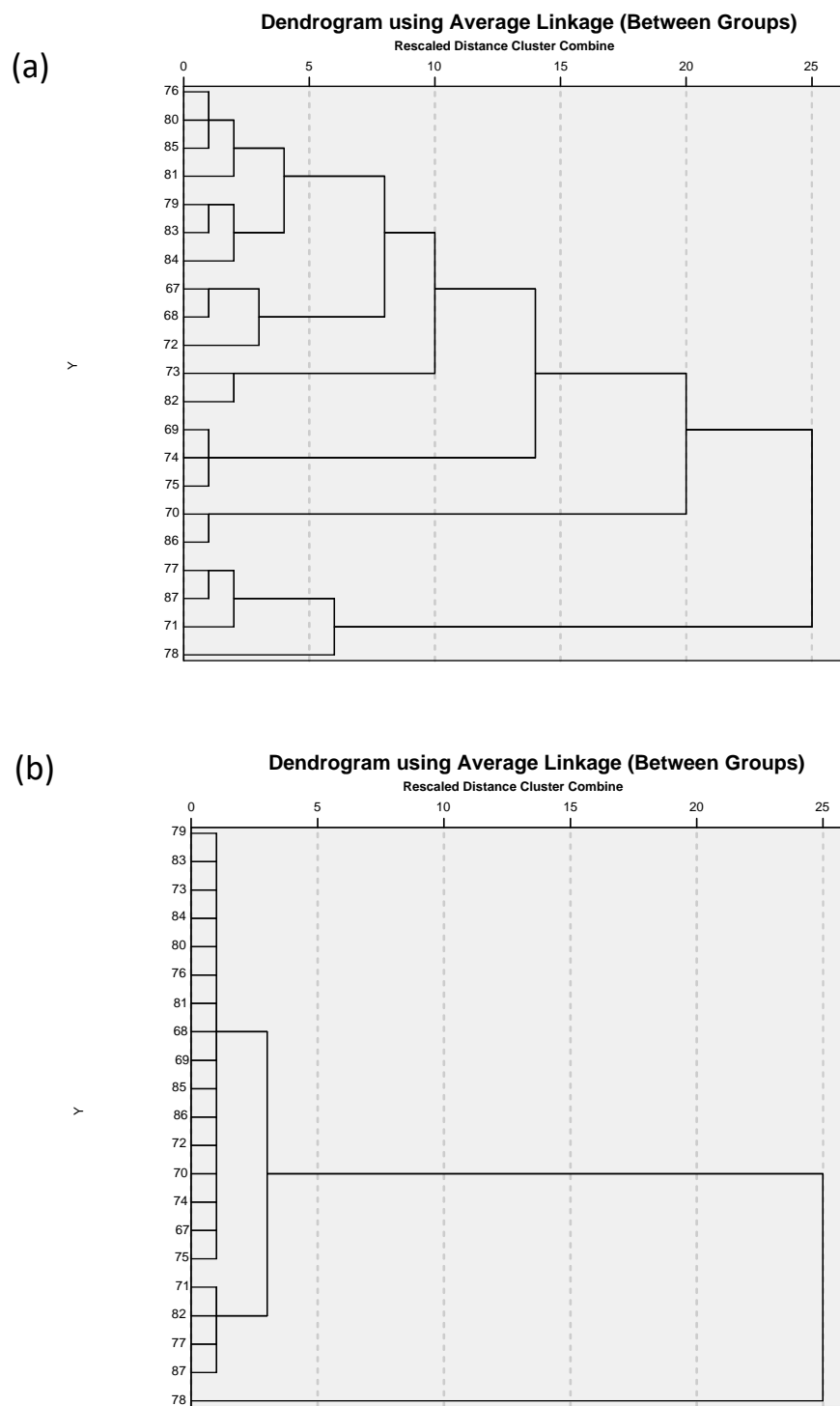


Figure S5. Hierarchical dendrogram based in principal component analysis of 2nd derivate FT-IR spectral región from 1820 to 950 cm^{-1} (Series 80 $^{\circ}\text{C}$). To clarify PCA results (3.1.2.), coefficient scores obtained by PCA analyses were arranged in a hierarchical dendrogram. **(a)** considering 13 smooth points. **(b)** considering 20 smooth points. The numeration of the experiments correspond with the Table S1.

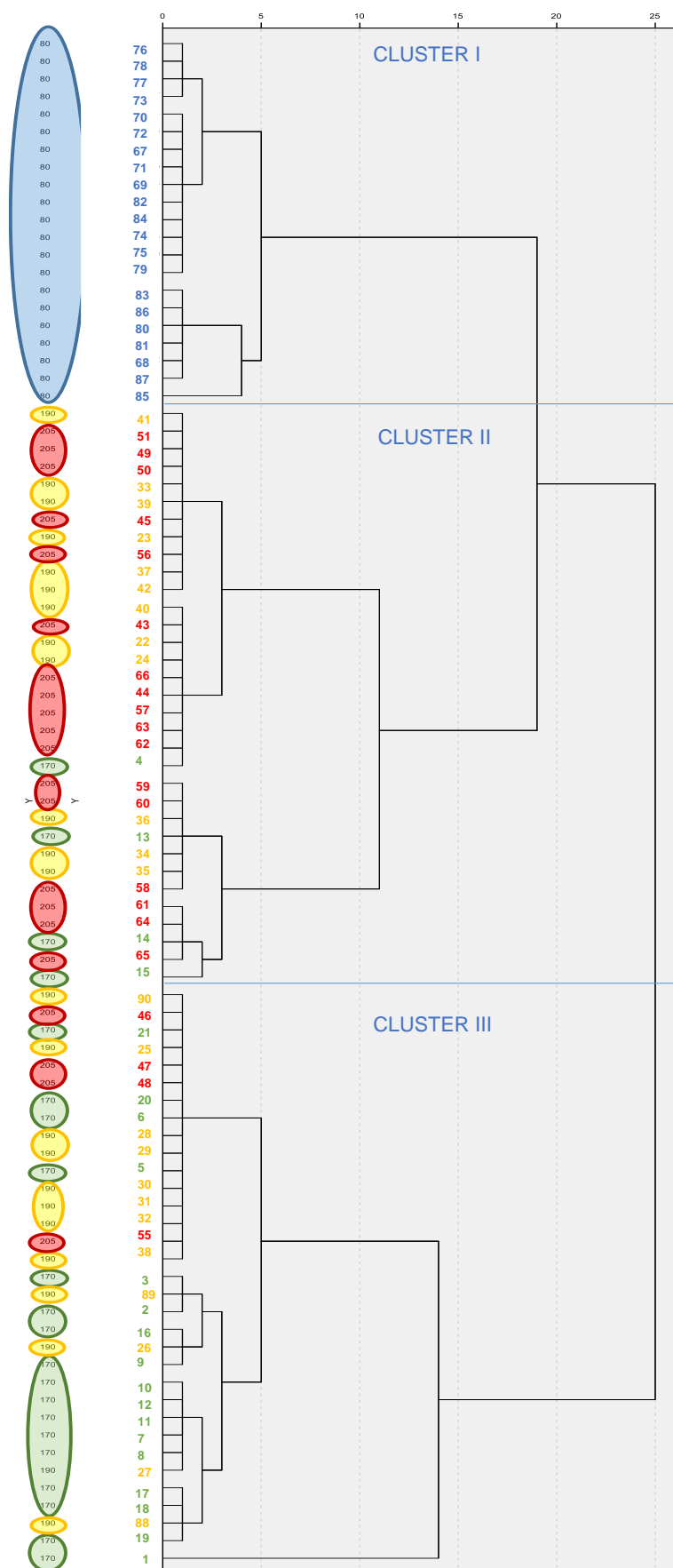


Figure S6. Hierarchical dendrogram based in principal component analysis of the 2nd derivate of the FTIR spectral region from 2300 to 2100 cm^{-1} . To clarify PCA results (3.1.2. and Figure 6e), coefficient scores obtained by PCA analyses were arranged in a hierarchical dendrogram. Similar to Figure 6e, a homogeneous cluster can be observed composed by 80°C series (cluster I). Rest of the experiments are distributed in two clusters, one of them presents most of the 205 °C experiments (cluster II), similarity to Figure 6e. Colored ellipses are used to indicate the experimental series: green represented samples from the 170 °C series, yellow 190 °C series, red 205 °C series and blue 80 °C series. The numeration of the experiments correspond with the Table S1. The samples in boxes are samples synthesized using equivalent reactions time based on the specifications of the microwave manufacture.

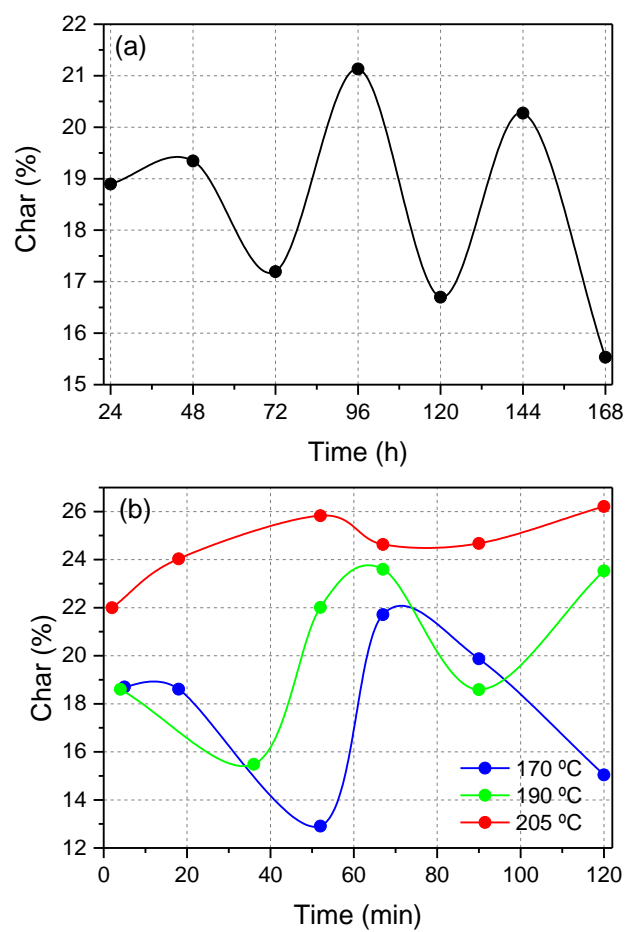
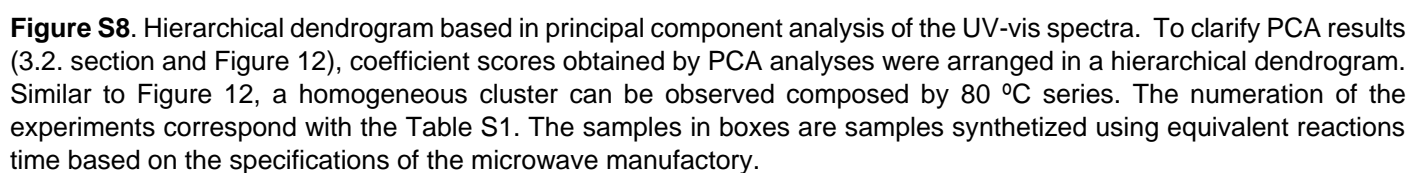


Figure S7. Evolution of the char (%) after heating of the samples at 1000 °C as function of the reaction time. (a) 80 °C series; (b) MWR series.



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