Electronic Supplementary Information (ESI)

From citrus waste to value: Optimizing sulfonated carbons for limonene upcycling into value-added products

Gabrielle M. Reis[1], Renan S. Nunes [1], Gabriela T. M. Xavier [1], Marina V. Kirillova[2], Alexander M. Kirillov[2], Dalmo Mandeli[1], Wagner A. Carvalho [1,*]

[1] *Center for Natural and Human Sciences, Federal University of ABC (UFABC), Santo André, Brazil*
[2] *MINDlab: Molecular Design & Innovation Laboratory, Centro de Química Estrutural, Institute of Molecular Sciences, Departmento de Engenharia Química, Instituto Superior Técnico, University of Lisbon, Lisbon, Portugal.*

The ESI includes additional tables and figures detailing the preparation and characterization of the carbon catalyst, as well as catalytic activity studies (Tables S1-S3, Figures S1-S6), and data from control experiments (Figures S7 and S8).

Table S1: ANOVA for Central composite experimental design.

| | Response analyzed | | | | | | | | |
| | y1 | | | y3 | | | y4 | | |
Source	Coded Equation	Sum of squares	p-value	Coded Equation	Sum of squares	p-value	Coded Equation	Sum of squares	p-value
Regression	5.13	3.38	0.0069	98.59	11887.6	<0.0001	21,56	799,74	0,0068
x1	0.415	1.38	0.0059	-17.39	2418.16	0.0002	-3.45	94.95	0.0651
x2	0.308	0.7607	0.0213	24.69	4878.63	<0.0001	5.44	237.02	0.0119
x1 x2	0.37	0.5476	0.0393	5.37	115.49	0.0761	-7.27		
x1²				23.71	3174.7	<0.0001	-7.37	298.69	0.0071
x2²	0.334	0.6889	0.0258	-21.48	2605.13	0.0001		306.64	0.0067
Residual		0.4768			116.07			112.13	
Lack of fit		0.1579	0.8903		114.86	0.0156		46.9	0.825
Pure error		0.3189			1.21			65.22	
R²		0.8763			0.9903			0.8770	
R²ajd		0.7526			0.9807			0.7951	
R²pred		0.6619			0.9317			0.6855	

| | Response analyzed | | | | | | | | |
| | y5 | | | y6 | | | y7 | | |
Source	Coded Equation	Sum of squares	p-value	Coded Equation	Sum of squares	p-value	Coded Equation	Sum of squares	p-value
Regression	6,29	56.67	0.0122	8.07	137.9	0.0565	14.6	136.62	0.0137
x1	-0,4565	1.67	0.3578	-1.92	29.48	0.0743	-3.57	101.77	0.0501
x2	0,6562	3.44	0.2023	2.54	51.79	0.0307	4.78	182.89	0.0157
x1 x2				-1.56	9.68	0.2538			
x1²	-2,27	29.12	0.0059	-1.8	18.36	0.136			
x2²	-2,57	37.39	0.0033	-2.68	40.59	0.046	.4.5	125.21	0.0343
Residual		4.03			29.12			127.53	
Lack of fit		6.06	0.8404		9.99	0.7991		100.51	0.4486
Pure error		66.76			19.13			27.03	
R²		0.8489			0.8256			0.7627	
R²ajd		0.7482			0.6513			0.661	
R²pred		0.5046			0.317			0.2964	

(x 1) mass of sulfuric acid for 1 g of glucose (g); (x 2) temperature (°C); (y 1) total acid groups (mmol g^{-1}), (y 2) sulfonic and carboxylic groups (mmol g^{-1}), (y 3) conversion of limonene (%); (y 4) α-terpinene yield (%); (y 5) p-cymene yield (%); (y 6) γ-terpinene yield (%); (y 7) terpinolene yield (%)
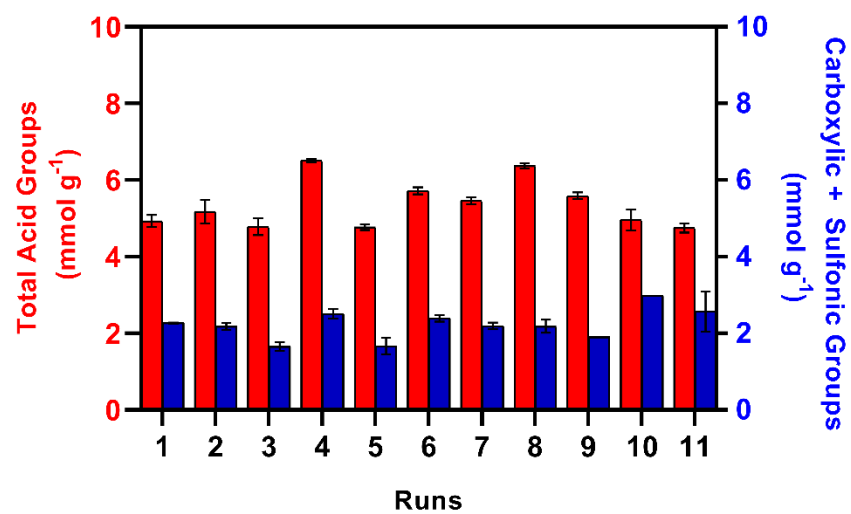
Figure S1: Amount of total groups and carboxylic + sulfonic groups present in the carbons of each trial of the experimental design.
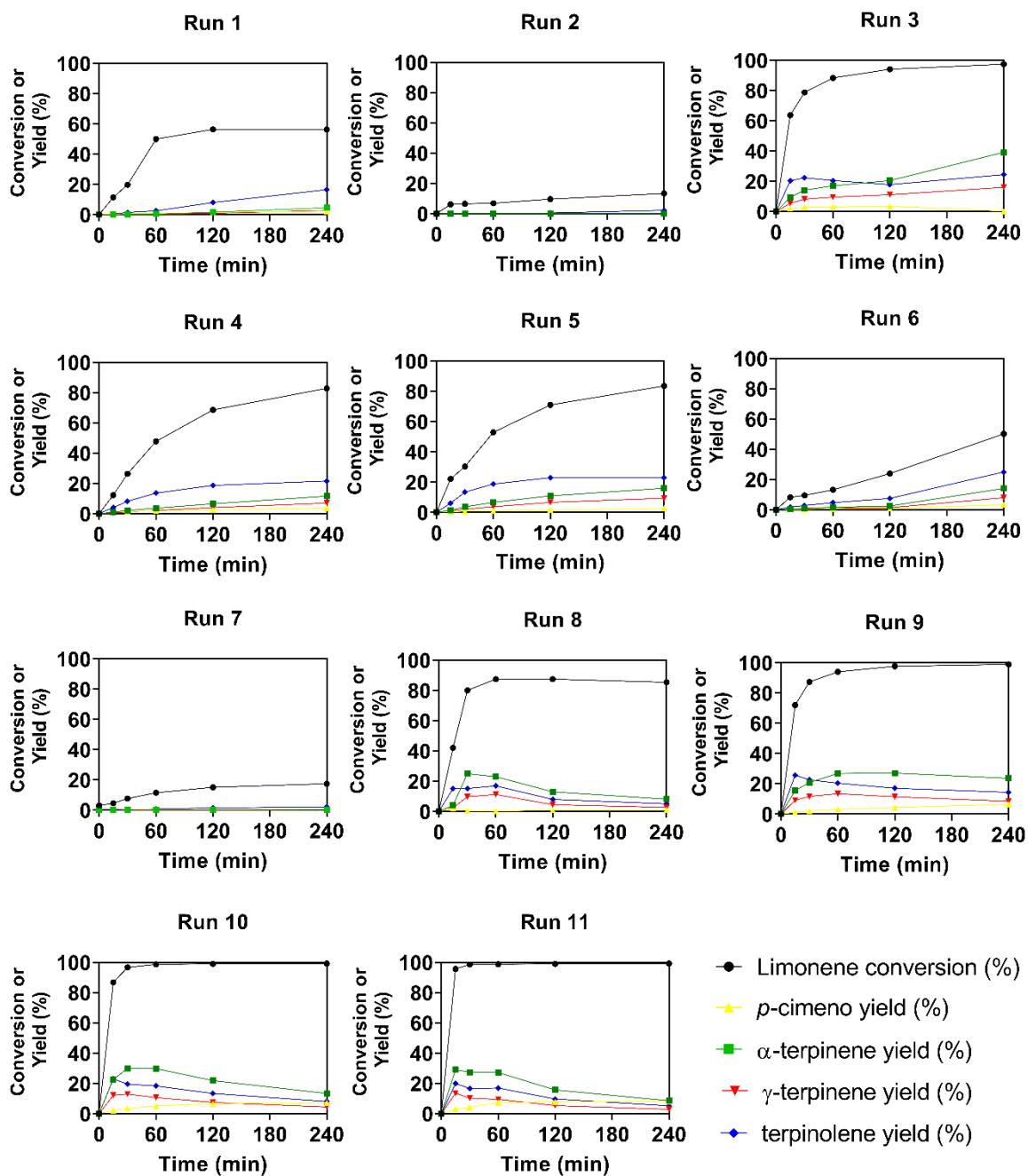
Figure S2: Catalytic outcomes of limonene isomerization. Figure illustrates the performance of each catalyst prepared through the Central Composite Experimental Design (referred to as Runs). The synthesis conditions for each catalyst are detailed in Table 1. The reactions were carried out in a two-neck round-bottom flask heated in an oil bath and fitted with a reflux condenser. The experimental setup involved the utilization of 30 mmol of limonene, a catalyst loading of 15% by weight, and a reaction temperature of 150 °C.
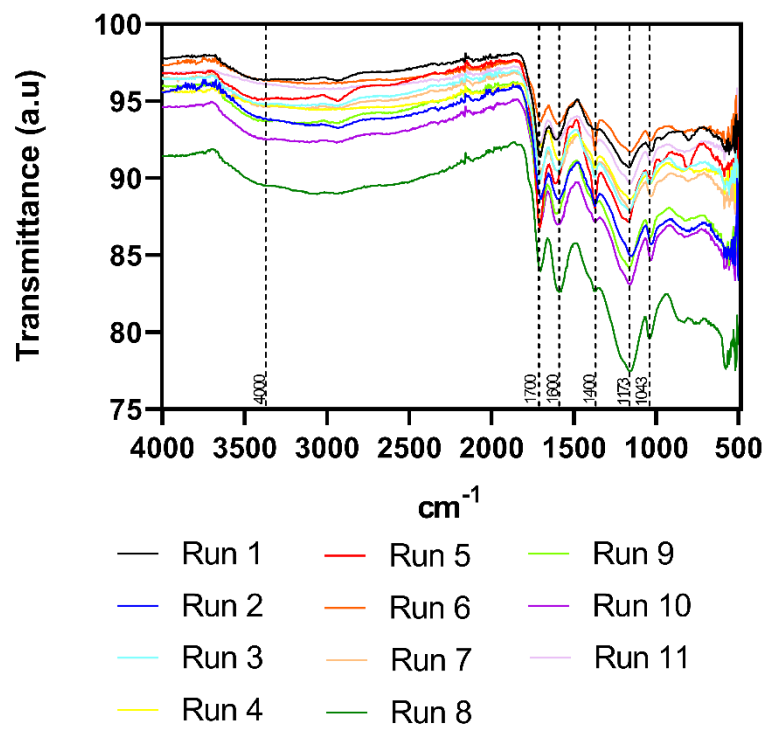
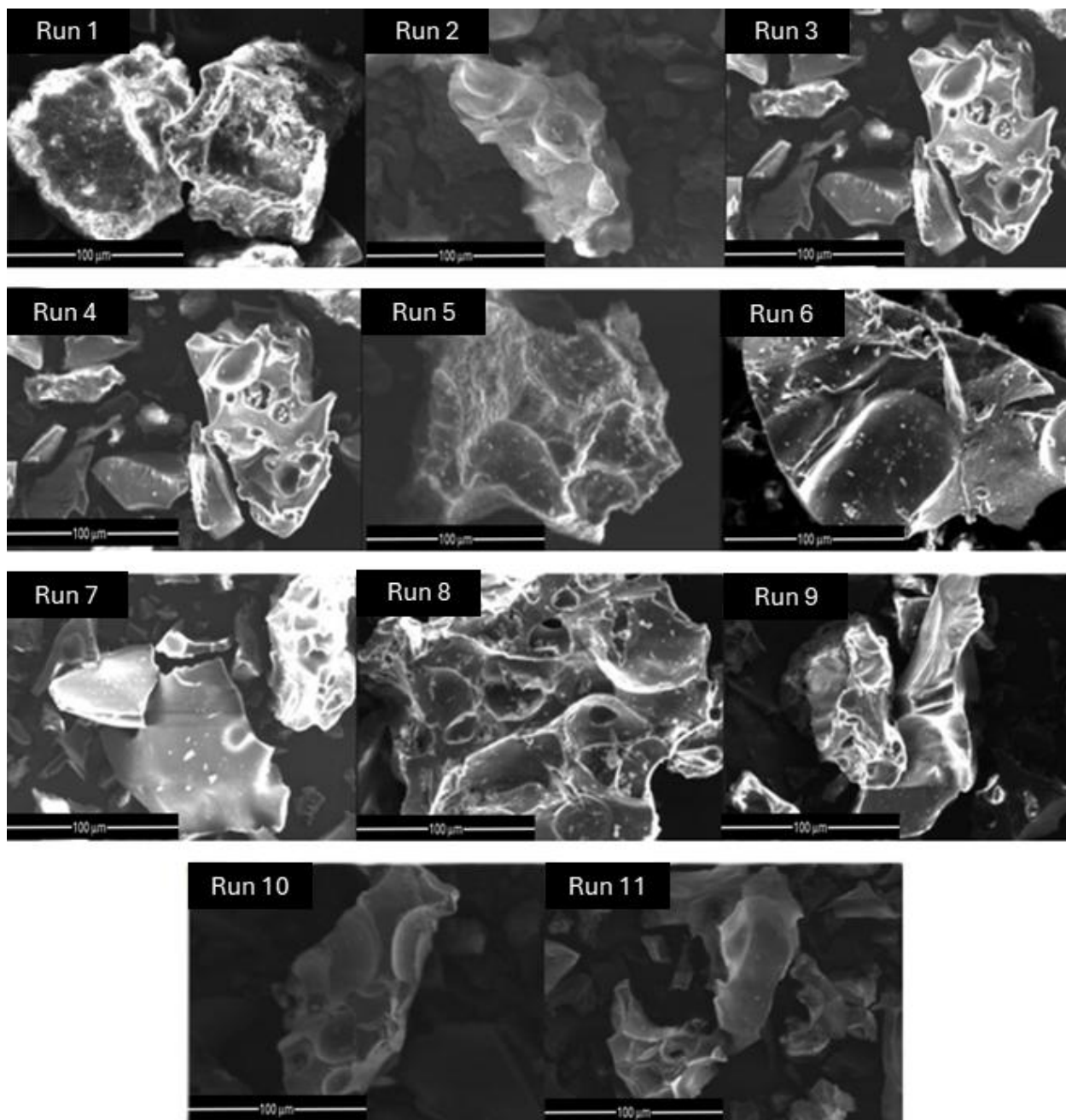Figure S3: FTIR results of the CCRD experiments, according to Table 1.

Figure S4: SEM micrographs of the sulfonated carbons in the experimental design (runs are those of Table 1).

Table S2: Elementary amount of sulfur in the elemental analysis and Energy dispersive X-ray (EDX) analysis present in the catalysts obtained through CCRD.

Run	(x 1) m sulfuric acid for 1 g of glucose (g)	(x 2) temperature (°C)	S_{EA} (%)	S_{EDS} (%)
1	0.9	97.6	0.4 ± 0.01	0.4 ± 0.1
2	2.6	97.6	1.6 ± 0.1	2.6± 0.5
3	0.9	182.4	3.2 ± 0.2	3.8 ± 0.7
4	2.6	182.4	3.1 ± 0.1	3.4 ± 0.1
5	0.5	140.0	0.3 ± 0.03	0.5 ± 0.1
6	3.0	140.0	1.5 ± 0.1	2.5 ± 0.8
7	1.7	80.0	1.0 ± 0.04	1.7 ± 0.5
8	1.7	200.0	12.07± 1.00	10.3± 1.7
9	1.7	140.0	0.9 ± 0.4	1.6 ± 0.3
10	1.7	140.0	1.2 ± 0.1	1.7 ± 0.4
11	1.7	140.0	1.3 ± 0.2	2.3 ± 0.3

S_{EA} (%)= Elementary amount of sulfur according to the elemental analysis.
S_{EDS} (%)= Elementary amount of sulfur according to the Energy dispersive X-ray (EDX) analysis.

Table S3: Texture characteristics of sulfonated carbons obtained through CCRD. Runs are those of Table 1.

Run	(x 1) m sulfuric acid for 1 g of glucose (g)	(x 2) temperature (°C)	BET Surface area ($m^2\,g^{-1}$)	Total Pore volume ($cm^3\,g^{-1}$)	Micropore Volume ($cm^3\,g^{-1}$)
1	0.9	97.6	15.1	0.04	0.006
2	2.6	97.6	1.3	0.001	-
3	0.9	182.4	109.9	0.1	0.05
4	2.6	182.4	32.9	0.03	0.02
5	0.5	140.0	47.4	0.1	0.02
6	3.0	140.0	2.7	0.003	0.001
7	1.7	80.0	2.4	0.004	0.001
8	1.7	200.0	133.2	0.1	0.06
9	1.7	140.0	74.1	0.06	0.03
10	1.7	140.0	51.4	0.06	0.02
11	1.7	140.0	86.9	0.07	0.04

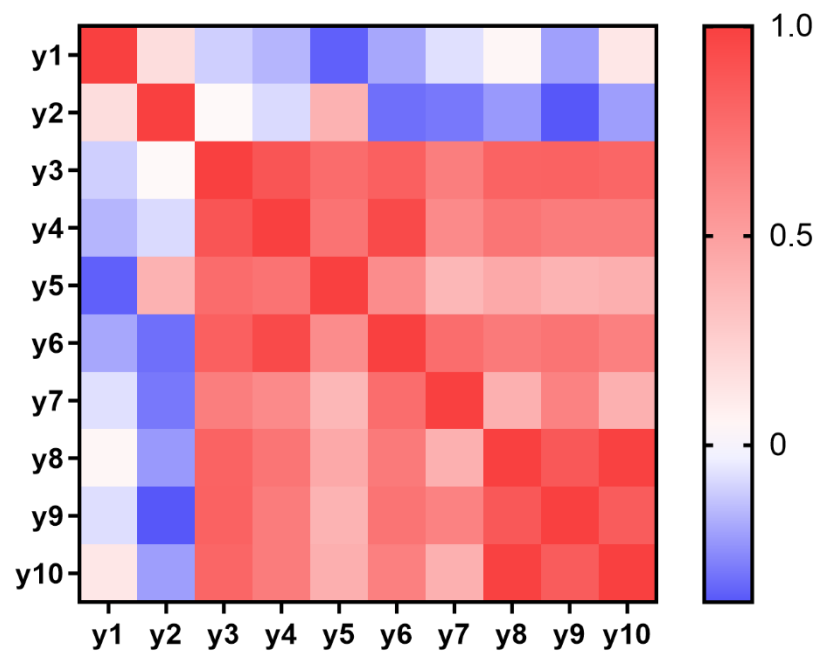Figure S5. Heat map of Pearson correlation coefficient matrix. (y1) total acid groups (mmol g^{-1}), (y2) sulfonic and carboxylic groups (mmol g^{-1}), (y3) conversion of limonene (%); (y4) α-terpinene yield (%); (y5) p-cymene yield; (y6) γ-terpinene yield; (y7) terpinolene yield (%); (y8) BET Surface area ($m^2 g^{-1}$); (y9) Total Pore volume ($cm^3 g^{-1}$);(y10) Micropore Volume($cm^3 g^{-1}$).
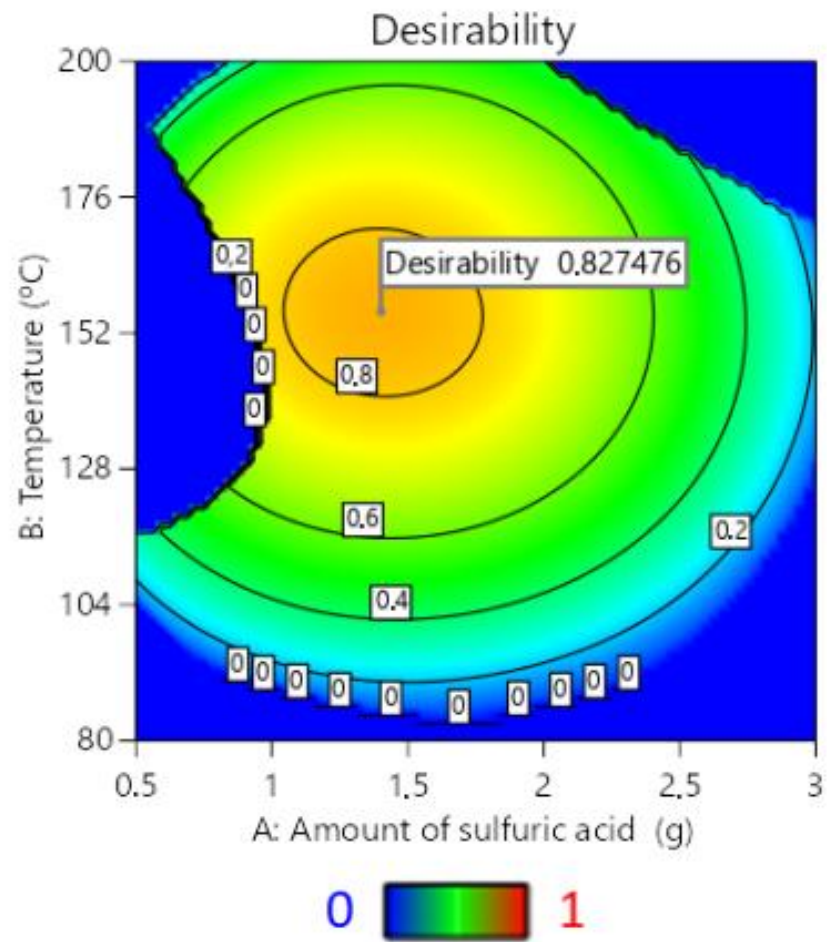
Figure S6. Results from the established optimization criteria. the overall desirability function emerges.

Control Experiments

Control experiments were conducted to assess the activity of free sulfuric acid as a catalyst (Figure S7). In the first experiment, 0.8 mmol of H_2SO_4 was added, resulting in 100% limonene conversion, but with reduced selectivity toward α-terpinene (yield 0.6%) and γ-terpinene (yield 0.2%). In the second experiment, using 0.1 mmol of H_2SO_4, limonene conversion was limited to 52.9% after 240 min. The yields of isomerization products were also significantly lower than those achieved with the sulfonated catalyst. As shown in Figure S8, the reaction medium transitioned from colorless to brown in both cases, indicating the formation of undesirable polymers.
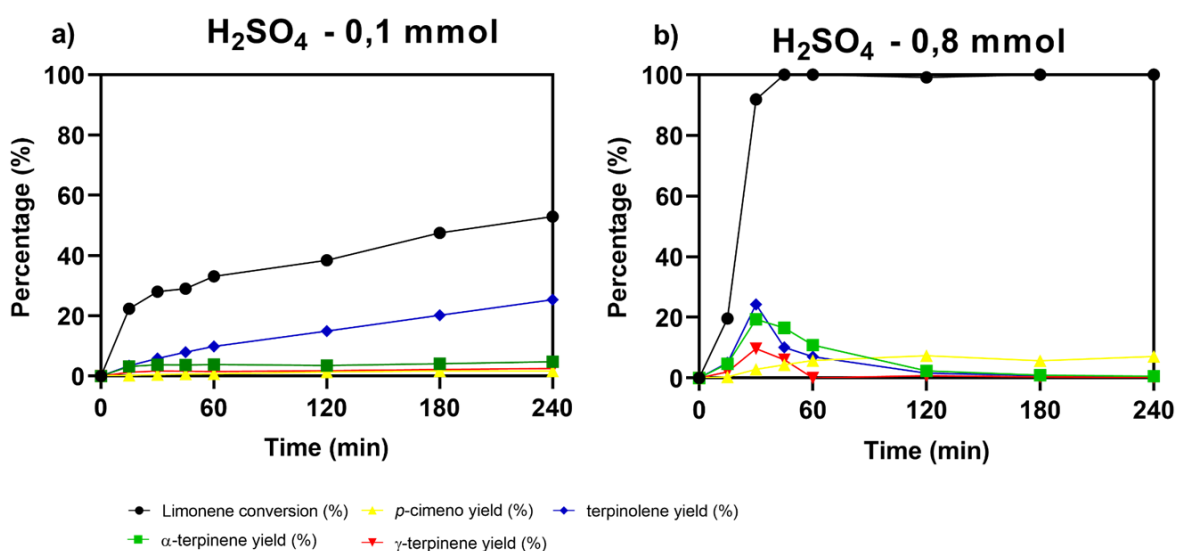

Figure S7. Catalytic results of limonene isomerization using 0.1 and 0.8 mmol of H_2SO_4. The experiment was performed with 30 mmol of limonene at 150 °C.
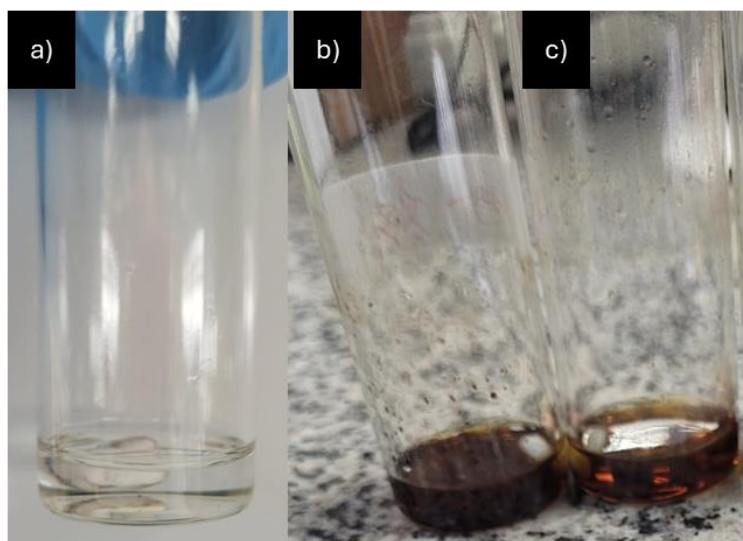
Figure S8. Color changes observed in the reaction with H_2SO_4 after 4 h of reaction: a) Pure limonene before the reaction. b) Reaction with 0.8 mmol of H_2SO_4. c) Reaction with 0.1 mmol of H_2SO_4.