Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Use of a Lewis acid, a Brønsted acid, and their binary mixtures for the liquefaction of lignocellulose by Supercritical Ethanol Processing

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Table S1. Identified compounds in bio-oils from the supercritical ethanol liquefaction of teak wood without and with $MgClO_4$ catalysts at 300 °C for 30 min

Retention Time (min)	Compounds	Area (%)			
		without catalyst	$Mg(ClO_4)_2$ (2 mmol)	$Mg(ClO_4)_2$ (5 mmol)	$Mg(ClO_4)_2$ (10 mmol)
4.28	Hydroxy-acetic acid ethyl ester	11.51	-	4.28	3.45
5.26	2-Hydroxypropanoic acid ethyl ester	3.50	26.21	17.51	24.43
5.84	2-Hydroxy-2-methylpropanoic acid ethyl ester	-	-	0.18	-
5.97	2-Cyclopenten-1-one	-	-	0.18	-
7.11	2-Furanmethanol	2.63	-	-	-
9.23	2-Methyl-2-cyclopenten-1-one	-	-	0.54	-
9.39	1,1-Dimethoxyethane	3.67	-	-	6.09
9.40	2-Hydroxybutanoic acid methyl ester	-	5.32	-	-
9.51	2-Hydroxybutanoic acid ethyl ester	-	-	4.22	-
9.81	Butyrolactone	-	-	0.25	-
9.97	Ethoxyacetic acid ethyl ester	-	-	1.79	3.90
12.16	Dihydro-5-methyl-2(3H)-furanone	-	-	1.04	2.51
12.69	5-Methyl-2-furancarboxaldehyde	-	-	0.87	-
14.75	2,3-Dimethyl-2-cyclopenten-1-one	-	-	0.93	-
15.59	3-Hexenoic acid ethyl ester	-	-	0.73	2.51
16.94	3-Methyl-1,2-cyclopentanedione	1.97	2.79	-	-
18.12	2-Hexenoic acid ethyl ester	-	-	0.74	3.42
18.73	2-Furancarboxylic acid ethyl ester	-	-	1.34	-
19.53	4-Oxo-pentanoic acid ethyl ester (Ethyl levulinate)	1.42	4.36	7.56	13.43
20.45	Butanoic acid anhydride	-	6.71	2.38	-
20.99	2-Methoxypenol	7.24	5.07	2.49	-
21.22	4-Methylphenol	-		0.62	-
23.18	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	2.74	2.37	0.49	-
25.41	2-Ethoxyphenol	-	-	0.48	-
27.83	Butanedioic acid diethyl ester	2.20	2.47	2.55	2.12
28.11	2-Methoxy-4-methylphenol	2.13	2.14	1.43	-
29.65	Diethyl methylsuccinate	-	-	1.24	-
33.89	4-Ethyl-2-methoxyphenol	4.88	0.95	1.64	-
34.57	Pentanedioic acid diethyl ester	1.96	-	1.29	-
38.75	2,6-Dimethoxyphenol	7.92	2.92	-	-
39.59	2-Methoxy-4-propylphenol	5.30	-	-	-
44.67	2-Methoxy-4-(1-propenyl)phenol	6.80	-	-	-
80.89	(E)-9-Octadecenoic acid	-	-	0.37	-
87.04	Diisooctyl adipate	-	1.79	-	-
93.58	Hexadecanoic acid ethyl ester	0.63	-	0.36	-
93.60	Octadecanoic acid ethyl ester	-	-	1.30	2.41
94.02	Squalene	-	5.23	-	-
95.04	1-Nonadecene	-	-	0.56	-
96.56	2,4,6-Trimethyl-tetracosanoic acid methyl ester	-	-	2.99	2.85
98.45	Cyclotetracosane	-	-	1.25	-
100.54	Docosanoic acid ethyl ester	0.93	-	-	-

Table S2. Identified compounds in bio-oils from the supercritical ethanol liquefaction of teak wood without and with $HClO_4$ catalysts at 300 °C for 30 min.

Retention Time (min)	Compounds	Area (%)			
		without catalyst	$HClO_4$ (2 mmol)	$HClO_4$ (5 mmol)	$HClO_4$ (10 mmol)
4.28	Hydroxyacetic acid ethyl ester	11.51	9.70	8.57	-
5.26	2-Hydroxypropanoic acid ethyl ester	3.50	-	5.24	1.47
5.89	Furfural	-	-	0.80	-
7.11	2-Furanmethanol	2.63	3.10	-	-
9.36	2-Hydroxybutanoic acid ethyl ester	-	1.08	-	0.41
9.39	1,1-Dimethoxyethane	3.67	-	1.37	-
12.09	Dihydro-5-methyl-2(3H)-furanone	-	-	-	1.35
12.64	5-Methyl-2-furancarboxaldehyde	-	-	1.16	-
16.94	3-Methyl-1,2-cyclopentanedione	1.97	-	-	-
17.06	2-Hydroxy-3-methyl-2-cyclopenten-1-one	-	3.56	2.34	-
18.71	2-Furancarboxylic acid ethyl ester	-	-	0.98	1.23
19.53	4-Oxo-pentanoic acid ethyl ester (Ethyl levulinate)	1.42	3.43	14.24	29.45
20.45	2-Furaldehyde diethyl acetal	-	-	3.54	1.68
20.99	2-Methoxypenol	7.24	5.49	3.16	1.88
23.18	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	2.74	2.41	1.31	-
27.83	Butanedioic acid diethyl ester	2.20	2.83	1.79	1.61
28.11	2-Methoxy-4-methylphenol	2.13	2.59	1.22	0.82
32.98	3-Methoxy-1,2-benzenediol	-	-	2.39	-
33.89	4-Ethyl-2-methoxyphenol	4.88	2.84	-	-
34.57	Pentanedioic acid diethyl ester	1.96	1.44	-	-
38.75	2,6-Dimethoxyphenol	7.92	5.99	2.61	1.20
39.59	2-Methoxy-4-propylphenol	5.30	-	-	-
44.67	2-Methoxy-4-(1-propenyl)phenol	6.80	-	-	-
44.71	3-Hydroxy-4-methoxybenzoic acid	-	-	1.26	-
44.73	4-Hydroxy-3-methoxy-benzoic acid	-	2.87	-	-
50.92	4-Hydroxy-3-methoxy-benzeneacetic acid methyl ester	-	-	-	0.90
52.87	4-Hydroxy-3-methoxy-benzoic acid ethyl ester	-	-	1.09	0.94
56.07	Ethyl homovanillate	-	-	1.35	0.92
61.55	Ethyl 3-(4-hydroxy-3-methoxyphenyl)propionate	-	-	0.87	0.47
62.89	Desaspidinol	-	2.85	-	-
62.93	1-(2,4,6-Trihydroxyphenyl)-2-pentanone	-	-	5.75	1.20
90.52	Octadecanoic acid ethyl ester	-	1.49	0.46	0.52
93.58	Hexadecanoic acid ethyl ester	0.63	-	-	-
93.59	Pentadecanoic acid ethyl ester	-	-	1.06	-
96.53	2,4,6-Trimethyl-tetracosanoic acid methyl ester	-	2.56	1.27	1.25
100.57	Docosanoic acid ethyl ester	0.93	1.99	-	0.89

Table S3. Identified compounds in bio-oils from the supercritical ethanol liquefaction of teak wood without and with $Mg(ClO_4)_2/HClO_4$ catalysts at 300 °C for 30 min.

Retention Time (min)	Compounds	Area (%)			
		without catalyst	$Mg(ClO_4)_2/HClO_4$ (2mmol/10mmol)	$Mg(ClO_4)_2/HClO_4$ (5mmol/5mmol)	$Mg(ClO_4)_2/HClO_4$ (10mmol/2mmol)
4.28	Hydroxyacetic acid ethyl ester	11.51	-	-.	2.93
5.26	2-Hydroxypropanoic acid ethyl ester	3.50	3.53	12.45	15.25
7.11	2-Furanmethanol	2.63	-	-	-
9.39	1,1-Dimethoxyethane	3.67	-	-	-
9.41	2-Hydroxybutanoic acid methyl ester	-	-		5.12
9.42	3-Pentanol	-	-	4.57	-
9.93	Ethoxyacetic acid ethyl ester	-	-	2.16	2.56
10.70	2,5-Hexanedione	-	0.95	-	-
12.21	Dihydro-5-methyl-2(3H)-furanone	-	7.22	2.32	4.02
14.75	2,3-Dimethyl-2-cyclopenten-1-one	-		1.77	-
15.12	Phenol	-	2.07	0.71	-
15.60	3-Hexenoic acid ethyl ester	-	-	1.36	2.28
16.94	3-Methyl-1,2-cyclopentanedione	1.97	-	-	-
18.12	2-Hexenoic acid ethyl ester	-	-	1.55	3.17
18.73	2-Furancarboxylic acid ethyl ester	-	1.28	1.59	2.19
19.53	4-Oxo-pentanoic acid ethyl ester (Ethyl levulinate)	1.42	49.10	12.74	13.59
20.99	2-Methoxypenol	7.24	2.57	2.33	-
22.92	2,2,5,5-Tetramethyl-3-cyclopenten-1-one	-	-	1.30	-
23.18	3-Ethyl-2-hydroxy-2-cyclopenten-1-one	2.74	-	-	-
27.83	Butanedioic acid diethyl ester	2.20	2.44	1.71	2.16
28.11	2-Methoxy-4-methylphenol	2.13	-	-	-
29.61	Diethyl methylsuccinate	-	-	1.84	2.69
33.89	4-Ethyl-2-methoxyphenol	4.88	-	-	-
34.57	Pentanedioic acid diethyl ester	1.96	-	1.49	1.93
38.75	2,6-Dimethoxyphenol	7.92	-	-	-
39.59	2-Methoxy-4-propylphenol	5.30	-	-	-
44.67	2-Methoxy-4-(1-propenyl)phenol	6.80	-	-	-
90.52	Heptadecanoic acid ethyl ester	-	0.49	0.65	-
93.58	Hexadecanoic acid ethyl ester	0.63	-	-	0.82
93.59	Octadecanoic acid ethyl ester	-	-	2.68	-
93.59	Pentadecanoic acid ethyl ester	-	1.72	-	2.78
95.02	9-Hexacosene	-	-	0.68	-
95.03	1,2-Diethyl-cyclohexadecane	-	0.47	-	-
96.53	[S-(R,S)]-2,10-Dimethylpentacosanoic acid methyl ester	-	-	4.82	-
96.54	2,4,6-Trimethyltetracosanoic acid methyl ester	-	3.82	-	-
98.10	Cyclotetracosane	-	0.45	-	-
98.42	Cyclooctacosane	-	1.01	-	-
98.43	1-Nonadecene	-	-	1.48	-
100.55	Docosanoic acid ethyl ester	0.93	-	-	3.93
100.56	2,9-Dimethyltetracosanoic acid methyl ester	-	-	3.92	-

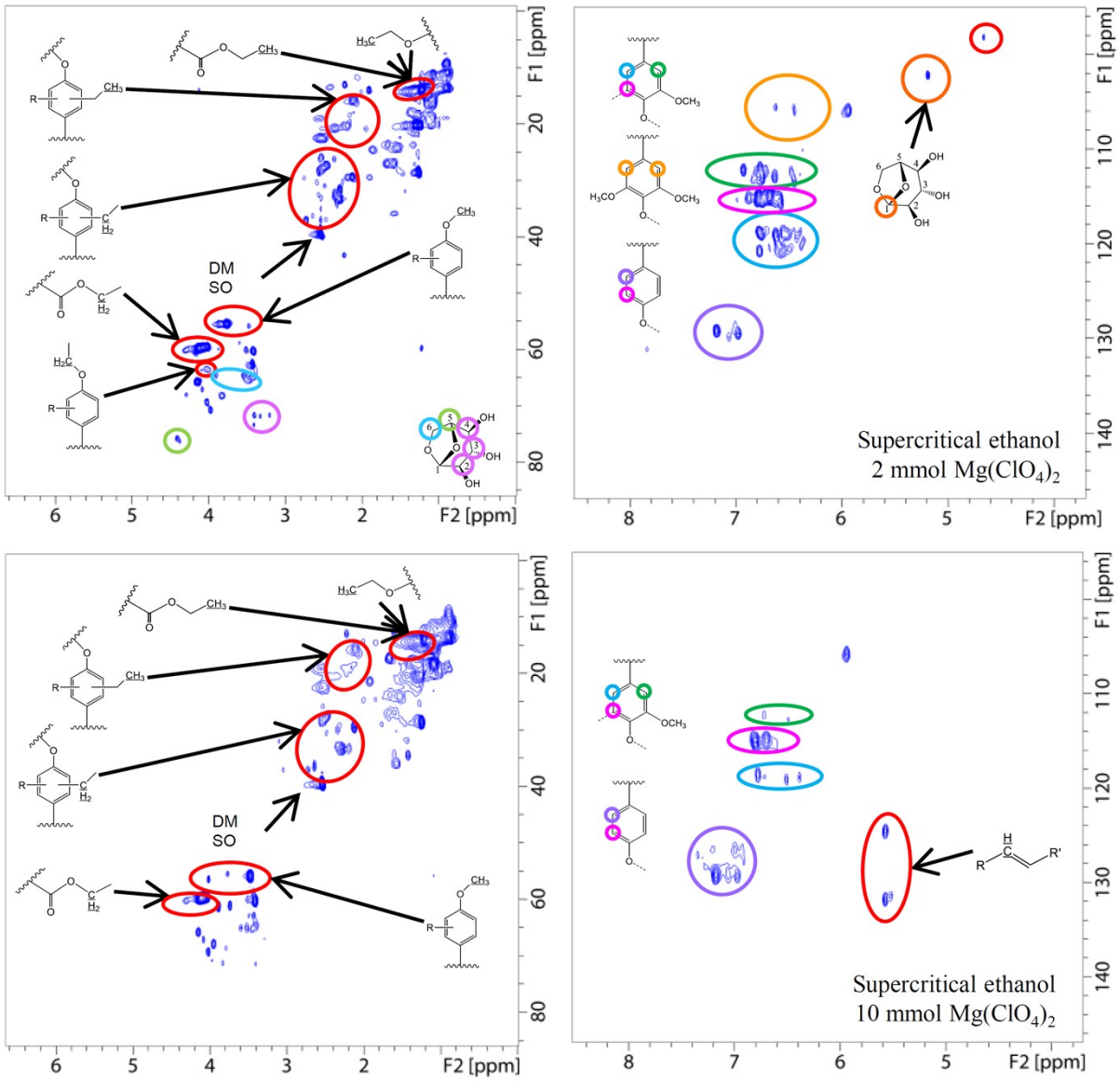

Figure S1. HSQC spectra of the bio-oils from the supercritical ethanol liquefaction of teak wood at 300 ºC for 30 min using catalyst by 2 and 10 mmol $Mg(ClO_4)_2$.

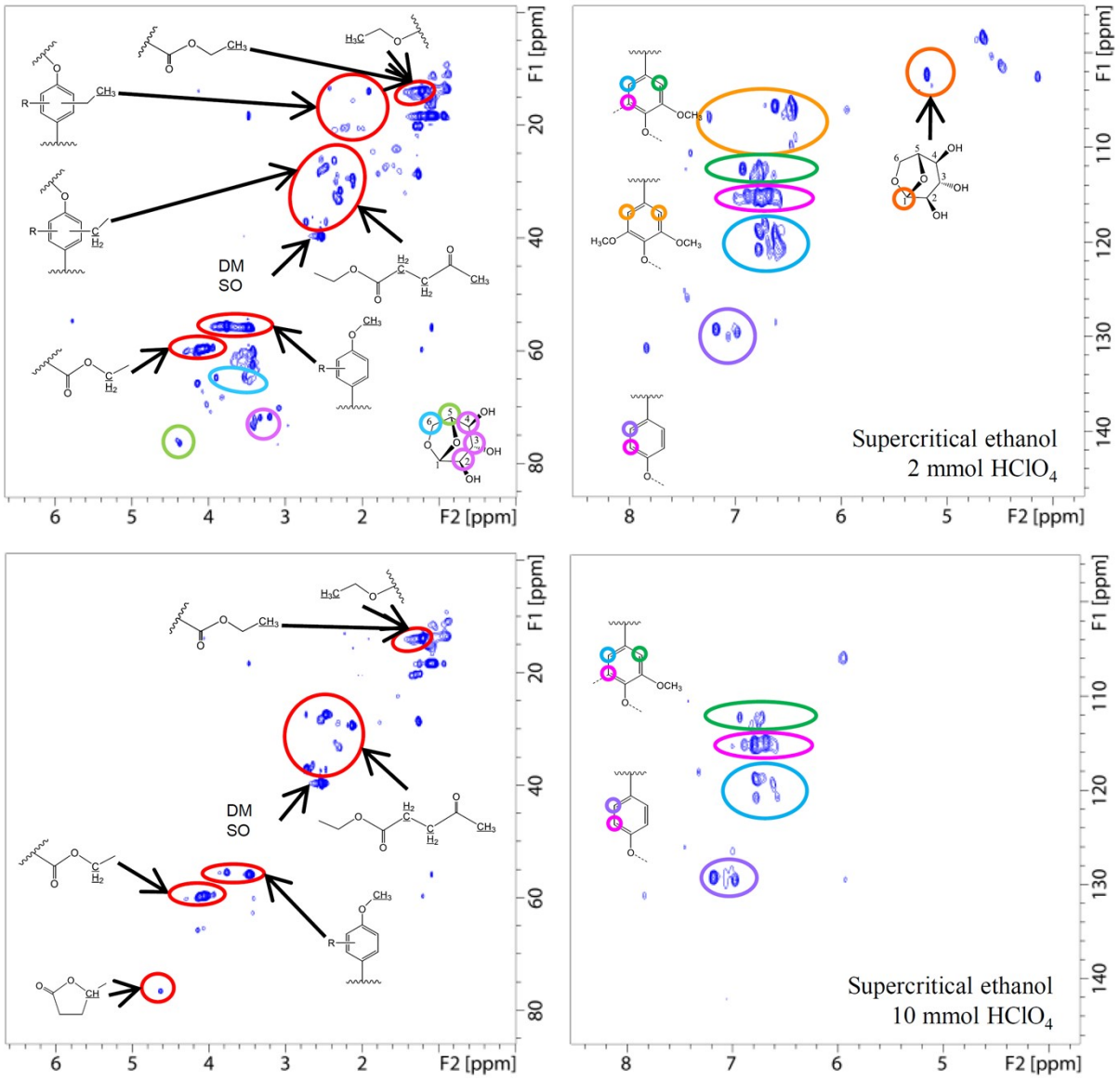

Figure S2. HSQC spectra of the bio-oils from the supercritical ethanol liquefaction of teak wood at 300 ºC for 30 min using catalyst by 2 and 10 mmol $HClO_4$.

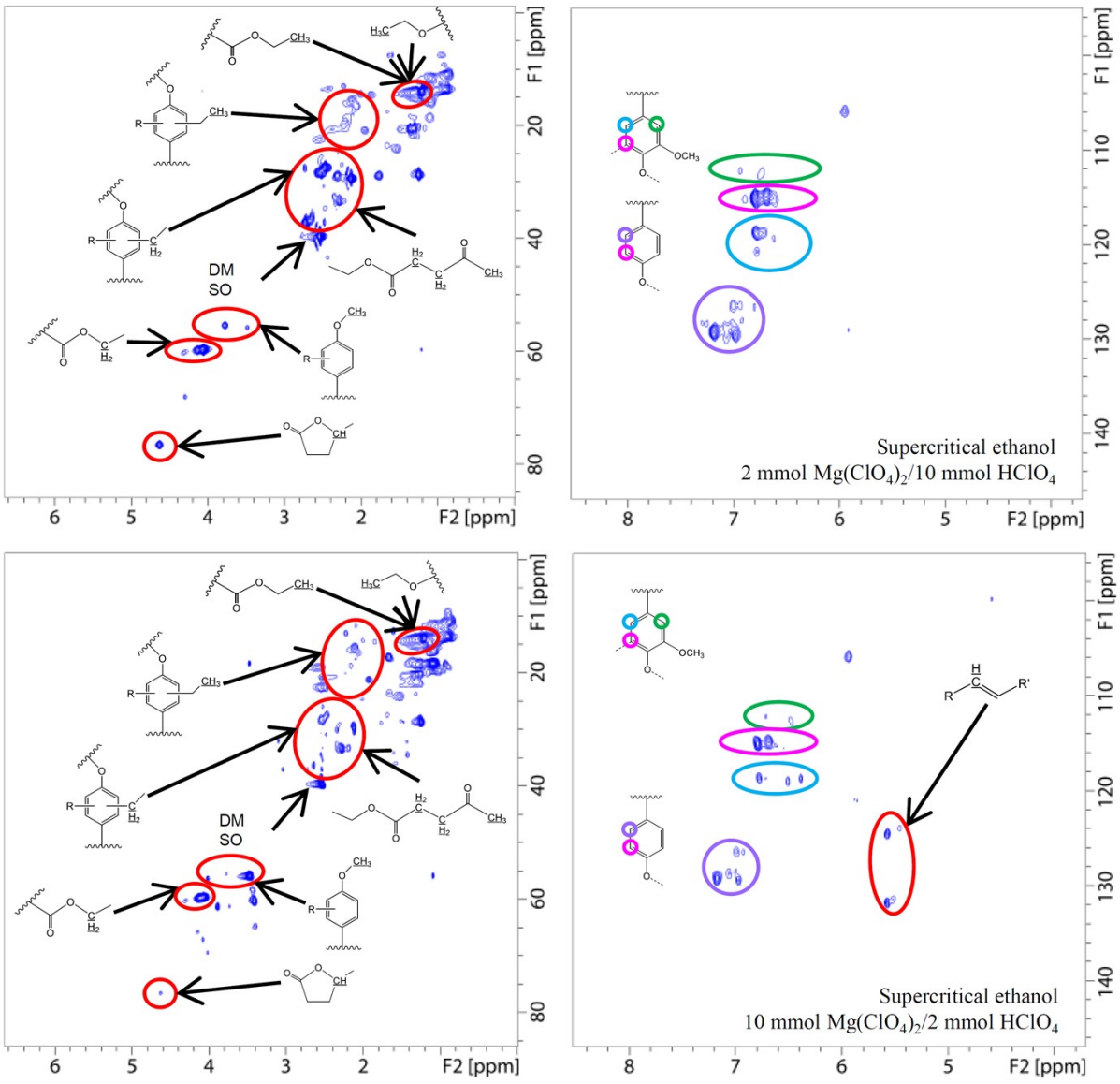

Figure S3. HSQC spectra of the bio-oils from the supercritical ethanol liquefaction of teak wood at 300 ºC for 30 min using catalyst by 2 mmol/10 mmol and 10 mmol/2 mmol $Mg(ClO_4)_2/HClO_4$.

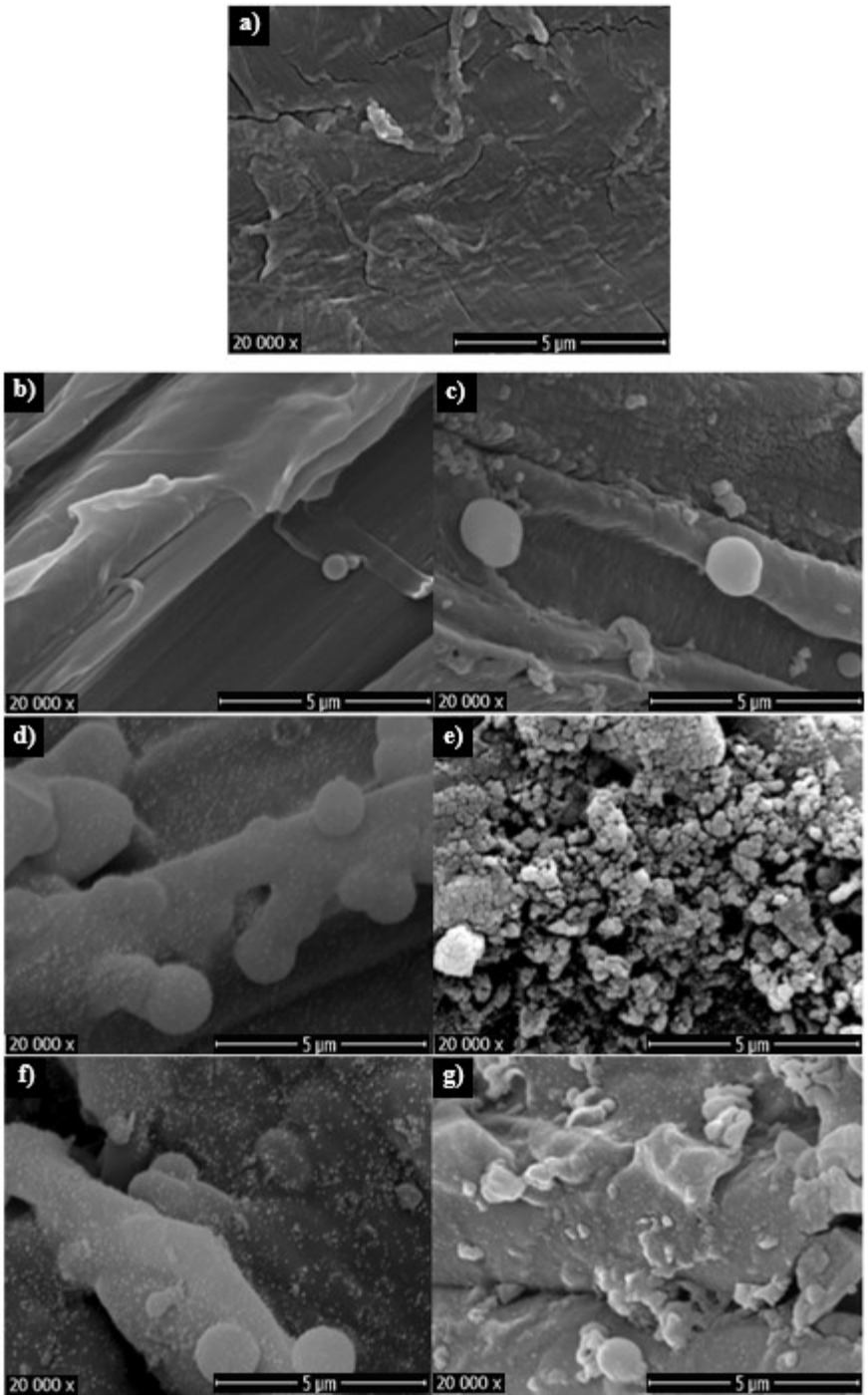

Figure S4. SEM images of teak wood and solid residues from the supercritical ethanol liquefaction of teak wood without and with catalysts at 300 ºC for 30 min. a) Teak wood b) Solid residue from the non-catalytic hydrothermal liquefaction of teak wood c) Solid residue from the catalytic run with 10 mmol of $Mg(ClO_4)_2$, d) Solid residue from the catalytic run with 10 mmol of $HClO_4$ e) Solid residue from the catalytic run with $Mg(ClO_4)_2$/ $HClO_4$ (10 mmol:2 mmol), f) Solid residue from the catalytic run with $Mg(ClO_4)_2$/ $HClO_4$ (2 mmol:10 mmol) g) 5 mmol $Mg(ClO_4)_2$/5 mmol $HClO_4$