

## Supplementary information

### Effect of carbon-based materials and CeO<sub>2</sub> on Ni catalysts for Kraft lignin liquefaction in supercritical water

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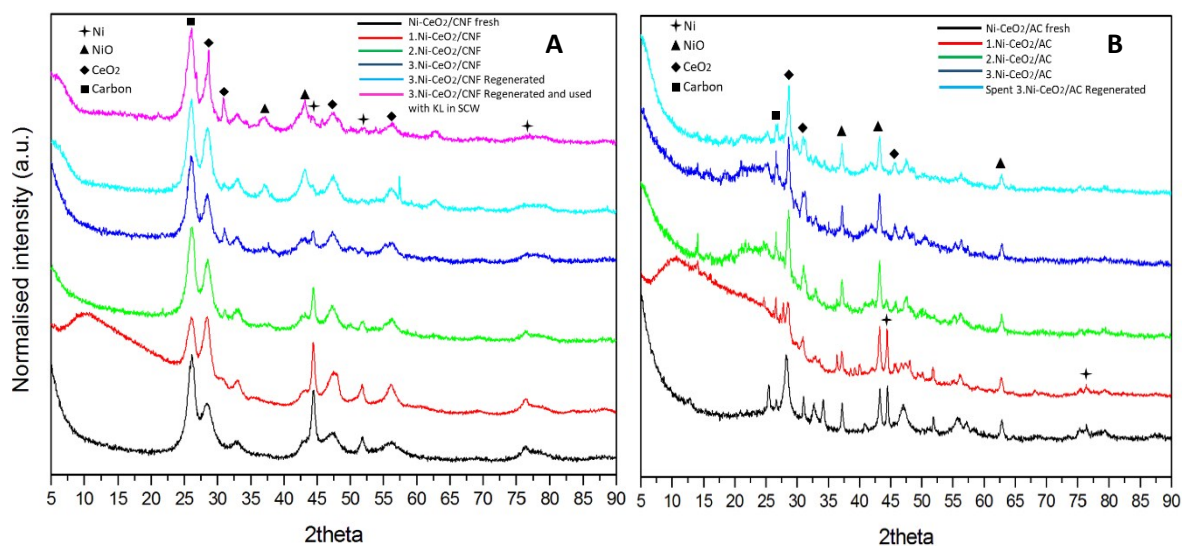
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#### 1. Reusability test of the Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC catalysts

A significant amount of solid products was obtained when Ni-CeO<sub>2</sub>/AC was used (0.60 g per g of catalyst at 0 min and 0.53 g g<sub>cat</sub><sup>-1</sup> at 15 min). On the other hand, the amount of solids produced when Ni-CeO<sub>2</sub>/CNF was used was 0.20 g g<sub>cat</sub><sup>-1</sup> at 0 min and 0.17 g g<sub>cat</sub><sup>-1</sup> at 15 min. In order to study the reusability of the Ni-CeO<sub>2</sub>/carbon based catalysts, the spent Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC catalysts recovered from the initial runs (at 400 °C, 230 bar and 0 min reaction time) were reused twice under the same conditions without regeneration between uses. After the Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC catalysts had been used three times, the carbon deposited on the catalysts was removed. This regeneration was done by placing the spent catalysts in a furnace and heating it in air at 10 °C min<sup>-1</sup> up to 350 °C, temperature at which it was kept for 15 min. 350 °C is not a high enough temperature to affect the carbon supports. The regenerated catalysts were characterised via XRD, XRF and BET, using the same instruments and methods already described in this work.

Fig. S1 shows the diffractograms of the fresh, spent and regenerated Ni-CeO<sub>2</sub>/carbon based catalysts. After the catalysts were used three times, Ni and CeO<sub>2</sub> metal loading remained close to the amounts observed in the fresh catalysts when CNF was used as support (Table S1). The textural properties of the fresh, spent and regenerated catalysts can be seen in Table S2. The textural properties had a significant change after both catalysts were used three times. However, the textural properties of the regenerated Ni-CeO<sub>2</sub>/CNF had values close to those of fresh Ni-CeO<sub>2</sub>/CNF.

Fig. S2 shows the yield of products obtained after the reusability test. It shows that the DCM-soluble fraction was the predominant product when Ni-CeO<sub>2</sub>/CNF was reused. However, the yield of bio-oil (DCM-soluble fraction) was reduced (with values around 40 wt. %) and the yield of solids gradually increased. In comparison with Ni-CeO<sub>2</sub>/AC, the yield of bio-oil increased and solids were reduced. After the regeneration of the catalysts, Ni-CeO<sub>2</sub>/CNF was reused with KL in SCW at 400 °C, 230 bar and 0 min reaction time. A bio-oil yield of 50 wt.% was observed, close to the one obtained when this catalyst was used for the first time (55 wt.%), which shows that Ni-CeO<sub>2</sub>/CNF is a promising catalyst for KL liquefaction in SCW.



**Fig. S1.** X-ray diffractograms of the fresh, reused and regenerated Ni-CeO<sub>2</sub>/CNF (A) and Ni-CeO<sub>2</sub>/AC (B) catalysts. Catalysts used for the first time (1), reused once (2) and twice (3).

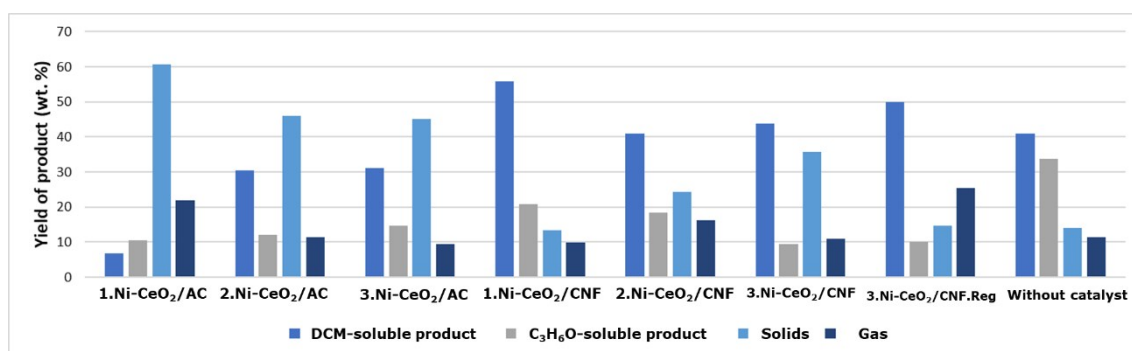
**Table S1.** Concentration of Ni and CeO<sub>2</sub> in the fresh carbon-based catalysts and after activity tests, reusability and regeneration. Catalysts used for the first time (1), reused once (2) and twice (3).

Catalyst	Ni (wt. %)	CeO <sub>2</sub> (wt. %)
<i>Fresh catalyst</i>		
Ni-CeO <sub>2</sub> /AC	12	16
Ni-CeO <sub>2</sub> /CNF	11	15
<i>Spent catalysts after KL/SCW</i>		
1.Ni-CeO <sub>2</sub> /AC	5	8
2.Ni-CeO <sub>2</sub> /AC	2	5
3.Ni-CeO <sub>2</sub> /AC	1	3
Regenerated 3.Ni-CeO <sub>2</sub> /AC	7	13
1.Ni-CeO <sub>2</sub> /CNF	10	14
2.Ni-CeO <sub>2</sub> /CNF	3	6
3.Ni-CeO <sub>2</sub> /CNF	2	4
Regenerated 3.Ni-CeO <sub>2</sub> /CNF	8	11

**Table S2.** Textural properties (specific surface area, pore volume and average pore diameter) of the fresh Ni-CeO<sub>2</sub> carbon-based catalysts and after activity tests, reusability and regeneration. 1, 2 and 3 means that the catalyst was used for the first time, reused once and twice, respectively.

Catalyst	$A_{BET}$ (m <sup>2</sup> ·g <sup>-1</sup> )	$V_{Pore}$ (cm <sup>3</sup> ·g <sup>-1</sup> )	$D_{pore}$ (nm)
<i>Fresh catalyst</i>			
Ni-CeO <sub>2</sub> /AC	1184	0.61	3
Ni-CeO <sub>2</sub> /CNF	76	0.33	17
<i>Spent catalyst after tests in KL/SCW</i>			
1.Ni-CeO <sub>2</sub> /AC	27	0.15	29
2.Ni-CeO <sub>2</sub> /AC	371	0.31	4
3.Ni-CeO <sub>2</sub> /AC	783	0.65	5
Regenerated 3.Ni-CeO <sub>2</sub> /AC	815	0.18	3
1.Ni-CeO <sub>2</sub> /CNF	55	0.30	24
2.Ni-CeO <sub>2</sub> /CNF	60	0.22	23
3.Ni-CeO <sub>2</sub> /CNF	25	0.13	32
Regenerated 3.Ni-CeO <sub>2</sub> /CNF	79	0.32	17

**Fig. S2** Yield (wt. %) of products obtained after the reusability test with Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC. Catalysts used for the first time (1), reused once (2) and twice (3). 3.Ni-CeO<sub>2</sub>/CNF.Reg: yield of products obtained when the regenerated catalyst was used.



## 2. Carbon balance of the products obtained with Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC catalysts

The carbon balance was determined by separately measuring the amount of carbon present in the organic phases (DCM-soluble and C<sub>3</sub>H<sub>6</sub>O-soluble), aqueous phase, solid and gas products from KL reactions in SCW at both 0 and 15 min reaction time in the presence of Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC catalysts.

The carbon contents in the DCM-soluble and C<sub>3</sub>H<sub>6</sub>O-soluble were obtained by using an Elementar varioMICRO CUBE elemental analyser. The amount of carbon deposited on the spent carbon-based catalysts was determined by thermogravimetric analysis (TGA – Perkin Elmer Pyris 1). The sample was heated at 20 °C min<sup>-1</sup> from 30 °C to 105 °C with isothermal of 20 min at 105 °C, then from 105 °C to 950 °C at 10 °C min<sup>-1</sup> and isothermal of 20 min at 950 °C based on the lower combustion temperatures of carbon deposits (from 350 °C to 400 °C) than AC (500 °C) and CNF (600 °C). The carbon originated in KL was also calculated by difference ( $\text{solid}_{\text{spent catalyst and char}} - \text{solid}_{\text{fresh catalysts}}$ ) and the results were similar to those obtained from TGA. After the total mass of solid deposits on the catalysts was obtained, the spent catalysts had their carbon composition quantified by using Elementar varioMICRO CUBE elemental analyser. The amount of carbon in the aqueous phase recovered from the reactor was determined by using a TOC INNOVOX analyzer (GE analytical instruments). The carbon-containing gases (CO, CO<sub>2</sub> and CH<sub>4</sub>) were analysed using a Perkin Elmer Clarus 500 GC equipped with a TCD and with a capillary Carboxen 1010 Plot (30 m × 0.53 mm) column.

Table S3 shows the amount of carbon in each product obtained after reaction with Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC at 0 min and 15 min. The total amount of carbon from the products obtained with Ni-CeO<sub>2</sub>/CNF at 15 min was less than 80 mol %. This smaller amount of carbon detected may be related to the presence of other higher hydrocarbon gases (*e.g.*, from C<sub>2</sub>H<sub>6</sub> to C<sub>4</sub>H<sub>10</sub>), which can be formed from lignin gasification with carbon-based catalysts in supercritical water (Osada *et al.*, 2006).

**Table S3** Carbon products reaction with Ni-CeO<sub>2</sub>/AC, at 0

Catalyst	Carbon balance (mol %)					
	DCM-soluble	C <sub>3</sub> H <sub>6</sub> O-soluble	Solids	Gas	Aqueous	Total
Ni-CeO <sub>2</sub> /AC 0 min	1.9	10.9	73.8	7.6	2.8	97.0
Ni-CeO <sub>2</sub> /AC 15 min	3.5	6.8	66.1	12.5	4.1	92.9
Ni-CeO <sub>2</sub> /CNF 0 min	50.2	22.4	19.1	1.6	1.9	95.1
Ni-CeO <sub>2</sub> /CNF 15 min	20.6	20.0	21.6	12.4	3.5	78.2

balance from the obtained after Ni-CeO<sub>2</sub>/CNF and min and 15 min.

### 3. Sulphur balance of the products obtained with Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC catalysts

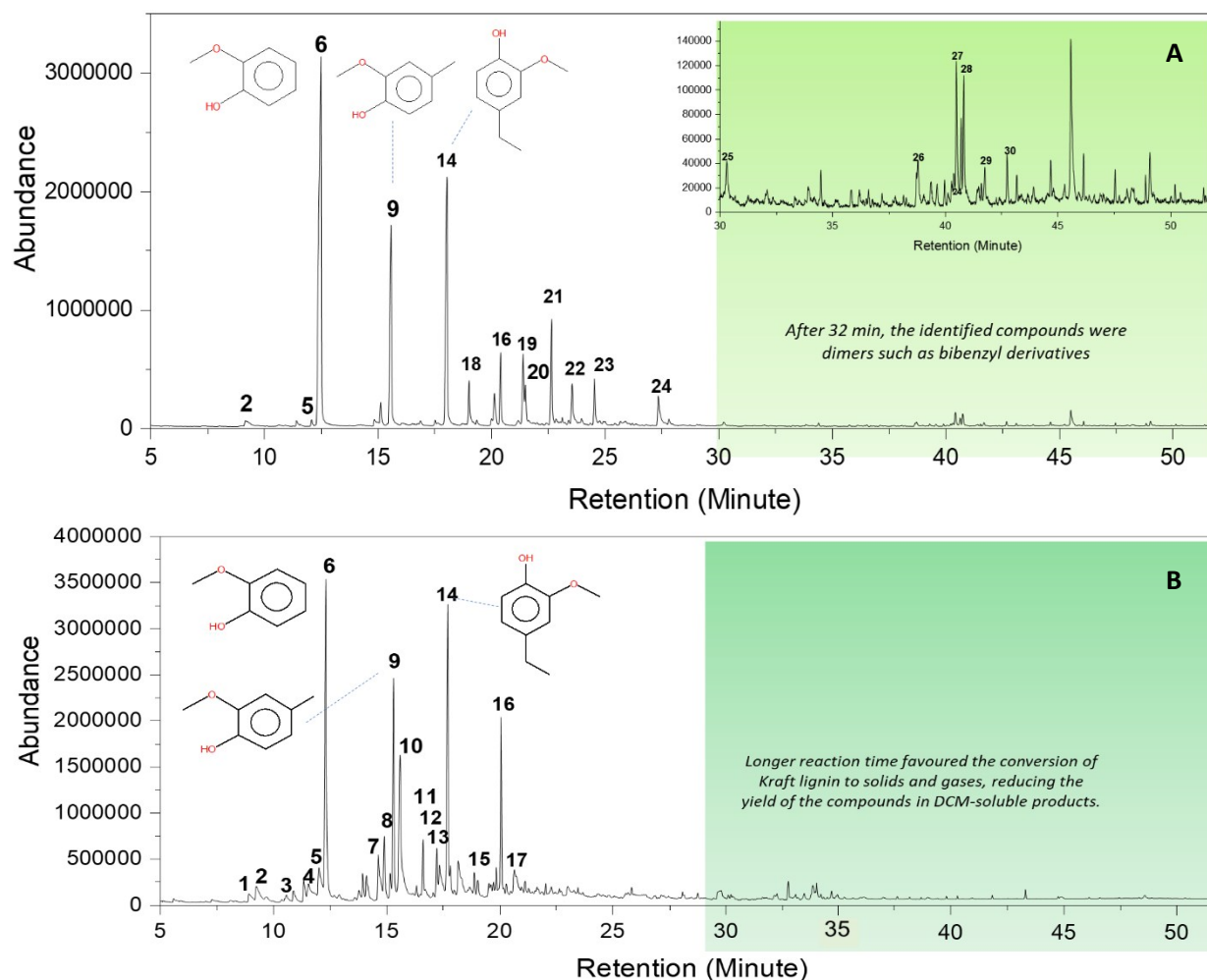
The amount of sulphur in the DCM-soluble and C<sub>3</sub>H<sub>6</sub>O-soluble products was quantified by an Elemental varioMICRO CUBE elemental analyser. The amount of sulphur in the spent Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC was determined by using a benchtop energy dispersive X-Ray Fluorescence (XRF) Epsilon 3XLE and the data were treated by using the Omnia software. The amount of sulphur in the gas products was calculated by difference as gas products analysed were only H<sub>2</sub>, CO, CH<sub>4</sub> and CO<sub>2</sub>. Table S4 shows the sulphur balance. It can be observed that most of the sulphur in Kraft lignin went to the gas products. Despite not being analysed by GC-TCD, the presence of H<sub>2</sub>S in the gas products was confirmed using a BW GasAlert Hydrogen Sulphide Extreme gas detector. The highest concentration (< 36 ppm) was detected when the reaction was conducted without catalyst.

**Table S4** Sulphur balance from the products obtained after reaction with Ni-CeO<sub>2</sub>/CNF and Ni-CeO<sub>2</sub>/AC, at 0 min and 15 min. Gas was obtained by difference.

Catalyst	Sulphur balance (mol %)				
	DCM-soluble	C <sub>3</sub> H <sub>6</sub> O-soluble	Solids	Gas	Aqueous
Ni-CeO <sub>2</sub> /AC 0 min	1.4	7.7	14.9	75.0	1.0
Ni-CeO <sub>2</sub> /AC 15 min	2.6	2.1	16.4	76.8	2.1
Ni-CeO <sub>2</sub> /CNF 0 min	23.2	4.7	2.4	68.1	1.7
Ni-CeO <sub>2</sub> /CNF 15 min	10.5	3.9	2.8	80.7	2.1

#### 4. GC-MS chromatograms of the identified compounds in the DCM-soluble products obtained from KL without and with Ni-CeO<sub>2</sub>/AC and Ni-CeO<sub>2</sub>/CNF at 0 min and 15 min

Fig. S3 to S5 show the GC-MS chromatograms of the identified compounds in the DCM-soluble products obtained from KL without and with catalysts at 0 min and 15 min.



**Fig. S3** GC-MS chromatograms of the identified compounds in the DCM-soluble products obtained from KL and without catalyst at 0 min (A) and 15 min (B). 1: 2-Cyclopenten-1-one, 3-methyl-; 2: Phenol; 3: 2-Cyclopenten-1-one, 2,3-dimethyl-; 4: Phenol, 2-methyl-; 5: Phenol, 4-methyl-; 6: Guaiacol; 7: Phenol, 4-ethyl-; 8: Benzene, 1,2-dimethoxy-; 9: Phenol, 2-methoxy-4-methyl-; 10: 1,2-Benzenediol; 11: Benzene, 1-methoxy-2-(methoxymethyl)-; 12: O-Methoxy- $\alpha$ -methylbenzyl alcohol; 13: 1,2-Benzenediol, 3-methyl-; 14: Phenol, 4-ethyl-2-methoxy-; 15: Benzene, 4-ethyl-1,2-dimethoxy-; 16: Phenol, 2-methoxy-4-propyl-; 17: 4-Ethylcatechol; 18: 2-Methoxy-4-vinylphenol; 19: Vanillin; 20: Phenol, 2-methoxy-4-(1-propenyl)-, (E)-; 21: Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-; 22: 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl)-; 23: Benzeneacetic acid, 4-hydroxy-3-methoxy-; 24: 2-Naphthalenol, 3-methoxy-; 25-30: dimers.

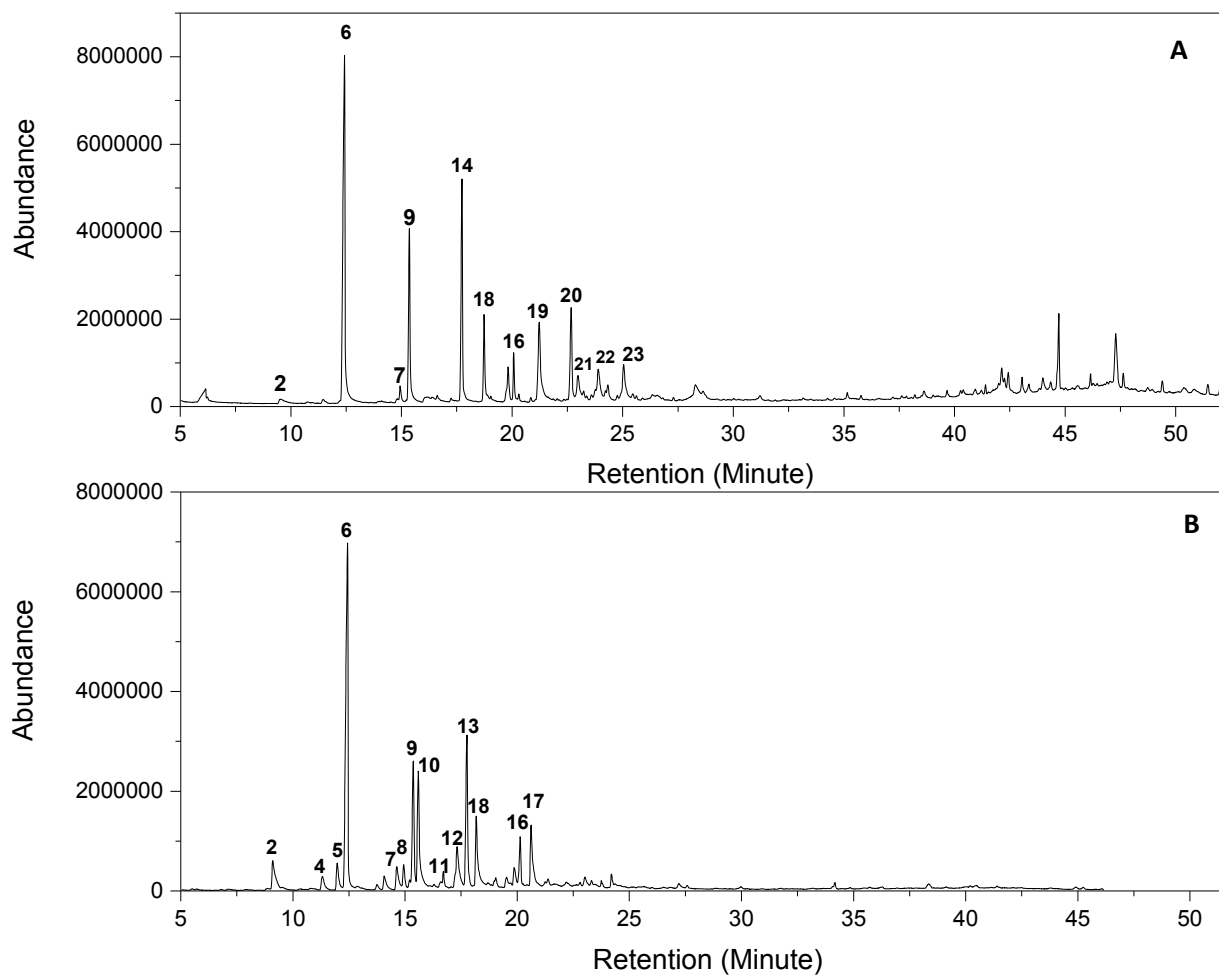


Fig. S4 GC-MS chromatograms of the identified compounds in the DCM-soluble products obtained from KL and with Ni-CeO<sub>2</sub>/CNF at 0 min (A) and 15 min (B).

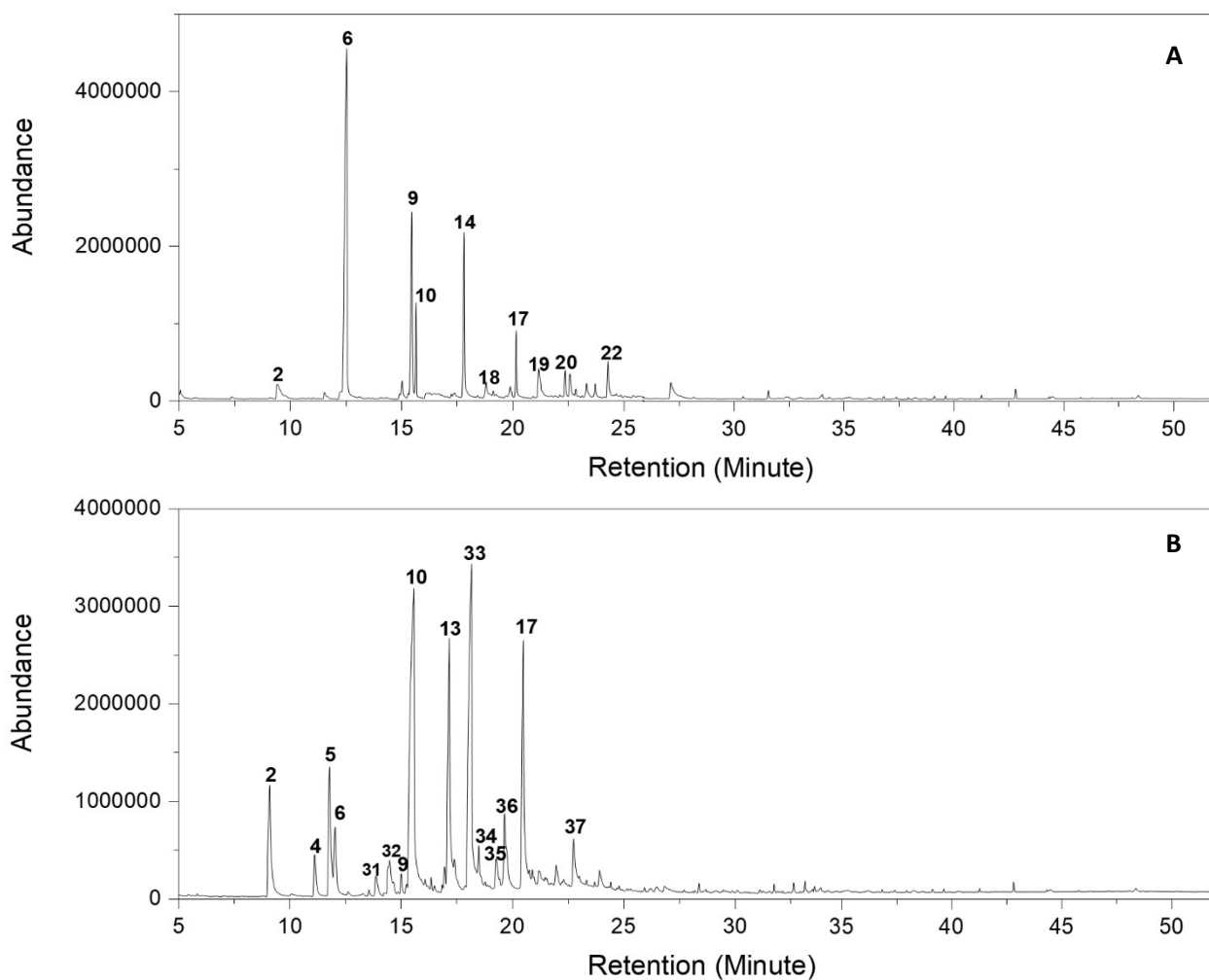


Fig. 55 GC-MS chromatograms of the identified compounds in the DCM-soluble products obtained from KL and with Ni-CeO<sub>2</sub>/AC at 0 min (A) and 15 min (B). **31**: Phenol, 2,4-dimethyl-; **32**: Phenol, 2,3-dimethyl-; **33**: 1,2-Benzenediol, 3-methyl-; **34**: 1,2-Benzenediol, 4-methyl-; **35**: 1,4-Benzenediol, 2,6-dimethyl-; **36**: 1,3-Benzenediol, 4-ethyl-; **37**: 2,5-Dimethylhydroquinone.

## Reference

M. Osada, O. Sato, K Arai, M. Shirai, *Energy Fuels*, 2006 **6**, 2337–43.