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


**Supplementary Material**

# Platform chemicals from hardwood black liquor via hydrothermal liquefaction: Influence of process conditions on product yields and quality

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Table S1. List of products from thermal desorption of hardwood black liquor from 100 °C to 500 °C at 10 °C $min^{-1}$.

| Retention time (min) | Compound name | Area % |
|---|---|---|
| 13.079 | Guaiacol, 4-ethyl- | 1.6 |
| 13.804 | 2-Methoxy-4-vinylphenol | 1.22 |
| 14.493 | Phenol, 2,6-dimethoxy- | 10.86 |
| 14.681 | 2-methoxy-4-ethyl-6-methylphenol | 0.75 |
| 14.795 | Phenol, 2-methoxy-4-propyl- | 0.51 |
| 15.997 | 3,5-Dimethoxy-4-hydroxytoluene | 1.06 |
| 16.337 | Cyclododecane | 0.68 |
| 16.587 | Acetovanillone | 1.68 |
| 16.702 | Nonadecane | 0.71 |
| 17.091 | 4-Ethyl-2,6-dimethoxyphenol | 1.24 |
| 17.595 | Phenol, 4-ethenyl-2,6-dimethoxy- | 0.91 |
| 17.685 | 4(10)-Thujen-3-ol, (1S,3R,5S)-(+)- | 0.55 |
| 19.619 | Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)- | 1.54 |
| 19.777 | Tetradecanoic acid | 2.58 |
| 20.069 | 1,3-diphenyl-1,3,5,5-tetramethyl-cyclotrisiloxane | 0.9 |
| 20.117 | 1,3-diphenyl-1,3,5,5-tetramethyl-cyclotrisiloxane | 0.99 |
| 20.661 | Cis-9-hexadecenal | 0.63 |

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| | | |
|---|---|---|
| 20.854 | Pentadecanoic acid | 2.96 |
| 21.101 | N-pentadecanol | 0.6 |
| 21.336 | Oxirane, heptadecyl- | 0.59 |
| 21.695 | 6-Pentadecenoic acid, 13-methyl-, (6Z)- | 2.58 |
| 21.893 | N-Hexadecanoic acid | 12.36 |
| 22.054 | 9-Octadecenamide, (z)- | 0.96 |
| 23.116 | n-Nonadecanol-1 | 0.74 |
| 23.608 | Oleic acid | 1.21 |
| 23.809 | Octadecanoic acid | 0.85 |
| 27.165 | Bis(2-ethylhexyl) phthalate* | 0.61 |
| 29.131 | Cholest-5-en-3-yl chloridocarbonate | 0.9 |
| 29.35 | Squalene | 23.55 |
| 29.998 | Cholest-5-en-3-yl chloridocarbonate | 0.64 |
| 30.322 | Cholesta-3,5-diene | 1.57 |
| 32.515 | 9-Hexadecenoic acid, eicosyl ester, (Z)- | 1.11 |
| 32.733 | Cholesterol | 4.63 |
| 33.645 | 1,3-Dioxolane, 4-ethyl-5-octyl-2,2-bis(trifluoromethyl)-, trans- | 0.53 |
| 33.695 | 5,6-Dihydro-2,3,10,11-tetramethoxyisoquino[1,2-b]quinazolin-8-one | 1.48 |
| 33.845 | Isophthalic acid, allyl dodecyl ester | 1.58 |
| 33.907 | Phthalic acid, undec-2-en-1-yl undecyl ester | 3.72 |
| 34.065 | Cholesta-3,5-dien-7-one | 1.42 |
| 34.281 | Bis(2-hydroxyethyl) phthalate * | 6.06 |
| 35.575 | 9-Hexadecenoic acid, eicosyl ester, (Z)- | 0.93 |

**Presence can be attributed to the plastic container used for storing the sample*

Table S2. Pyrolysates from Py-GC/MS of black liquor at 740 $^{o}$C.

| **Retention time (min)** | **Compound name** | **Area %** |
|---|---|---|
| 1.231 | 2-Butene | 0.96 |
| 1.339 | 1,2-diaminobutane | 1.38 |
| 1.4 | Dimethyl sulfide | 2.11 |
| 1.444 | 1,3-Cyclopentadiene | 1.41 |
| 1.642 | Butanal | 0.58 |
| 1.898 | Methycyclopenta-1,3-diene | 1.59 |
| 2.032 | Benzene | 2.08 |
| 2.09 | Thiophene | 0.61 |
| 3.051 | Benzene, methyl- | 1.77 |

| | | |
|---|---|---|
| 3.951 | 3-Cyclopentene-1-acetaldehyde, 2-oxo- | 1.44 |
| 4.498 | Benzene, 1,2-dimethyl- | 1.23 |
| 4.837 | Styrene | 1.6 |
| 5.042 | 2-Cyclopenten-1-one, 2-methyl- | 1.54 |
| 6.043 | 3-Methyl-2-cyclopenten-1-one | 0.82 |
| 6.289 | Phenol | 1.89 |
| 7.189 | 2-Cyclopenten-1-one, 2,3-dimethyl- | 0.8 |
| 7.46 | Phenol, 2-methyl- | 2.81 |
| 7.813 | Phenol, 3-methyl- | 2.27 |
| 7.996 | Phenol, 2-methoxy- | 7.86 |
| 8.313 | Phenol, 2,6-dimethyl- | 1.77 |
| 8.745 | Phenol, 2-ethyl- | 0.5 |
| 8.931 | Phenol, 2,4-dimethyl- | 1.09 |
| 9.2 | Phenol, 4-ethyl- | 0.64 |
| 9.258 | Phenol, 3,5-dimethyl- | 1.08 |
| 9.371 | Phenol, 2-methoxy-3-methyl- | 1.15 |
| 9.575 | Benzene, 1,4-dimethoxy- | 1.58 |
| 9.625 | Phenol, 3,4-dimethyl- | 0.43 |
| 10.575 | Phenol, 3-ethyl-5-methyl- | 0.64 |
| 10.771 | Phenol, 2,3,5-trimethyl- | 0.51 |
| 10.816 | Guaiacol, 4-ethyl- | 1.33 |
| 11.344 | 2-Methoxy-4-vinylphenol | 2.35 |
| 11.845 | Phenol, 2,6-dimethoxy- | 7.12 |
| 13.086 | 3,5-Dimethoxy-4-hydroxytoluene | 0.9 |
| 13.185 | Phenol, 2-methoxy-4-(1-propenyl)-, (e)- | 0.7 |
| 15.269 | 1-Naphthalenol, 2-methyl- | 6.47 |
| 17.003 | 1-Naphthol, 6,7-dimethyl- | 9.83 |
| 17.833 | 1-Naphthol, 2,5,8-trimethyl- | 1.58 |
| 18.994 | n-Hexadecanoic acid | 16.67 |
| 20.836 | Octadecanoic acid | 5.91 |

Table S3. Selectivity to phenols detected via GC/MS, total phenolic OH content estimated via Δε-IDUS spectrophotometry, and other properties of liquid product.

| Exp ID | Methoxy phenols (A) (GC/MS area %) | Dihydroxy-benzenes (B) (GC/MS area %) | Alkyl phenols (C) (GC/MS area %) | Phenol (D) (GC/MS area %) | Other phenolics (E) (GC/MS area %) | Total phenol selectivity (A+B+C +D+E) (GC/MS area %) | Total phenolic OH groups (mmol $g^{-1}$) | pH | $[OH^-]$ # × $10^{-5}$ mol $L^{-1}$ | Total suspended solids (TSS) (mg $mL^{-1}$) | Total dissolved solids (TDS) (mg $mL^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **E1** | 87.2 | 1.3 | - | 0.2 | 2.7 | 91.4 | 0.57 | 11.16 | 144.5 | 47.1 | 132.7 |
| **E2** | 70 | 6.1 | - | 1.9 | 4.3 | 82.3 | 0.41 | 10.79 | 61.7 | 70.4 | 93.6 |
| **E3** | 35.8 | 1.5 | 0.9 | 12.4 | 9 | 59.6 | 0.38 | 10.68 | 47.9 | 55.3 | 126.2 |
| **E4** | 2.4 | 33.6 | 7.7 | 3.8 | 13.4 | 60.9 | 0.28 | 10.19 | 15.5 | 64 | 111.4 |
| **E5** | - | 1 | 13.5 | 7 | 6.3 | 27.8 | 0.24 | 9.65 | 4.5 | 79.3 | 283.5 |
| **E6** | - | 0.4 | 18.4 | 7.6 | 7.1 | 33.5 | 0.19 | 9.45 | 2.8 | 34.9 | 81.3 |
| **E7** | - | - | 31.8 | 12.5 | 8.3 | 52.6 | 0.29 | 9.49 | 3.1 | 44.6 | 94.3 |
| **T1** | - | - | 2.3 | 6.3 | 14.7 | 23.3 | 0.13 | 9.77 | 5.9 | 178.5 | 337.4 |
| **T2** | - | 1 | 13.5 | 7 | 1 | 22.5 | 0.32 | 9.65 | 4.5 | 79.3 | 283.5 |
| **T3** | - | 0.6 | 12.4 | 17.8 | 11 | 41.8 | 0.33 | 9.61 | 4.1 | 181 | 218 |
| **T4** | - | - | 10.4 | 7.9 | 13.3 | 31.6 | 0.23 | 9.59 | 3.9 | 112.2 | 151.3 |
| **S1** | - | - | 20.8 | 11.8 | 19.8 | 52.4 | 0.22 | 9.58 | 3.8 | 78.4 | 105.2 |
| **S2** | - | 0.6 | 12.4 | 17.8 | 0.6 | 31.4 | 0.33 | 9.61 | 4.1 | 181 | 218 |
| **S3** | - | - | 7.9 | 11 | 10.7 | 29.6 | 0.35 | 9.86 | 7.2 | 121.4 | 232.4 |
| **S4** | 0.5 | 0 | 15 | 23.7 | 16.2 | 55.4 | 0.35 | 10.21 | 16.2 | 158.9 | 322 |

# $[OH^-] = \frac{1 \times 10^{-14}}{10^{-pH}}$

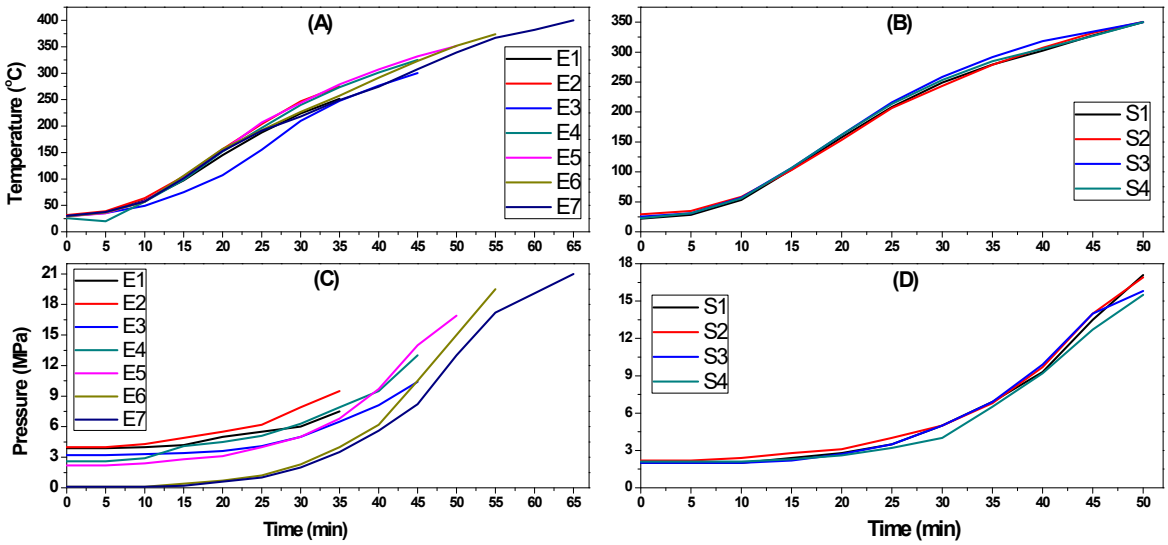


Fig. S1. Temperature and pressure profiles recorded for different HTL experiments.

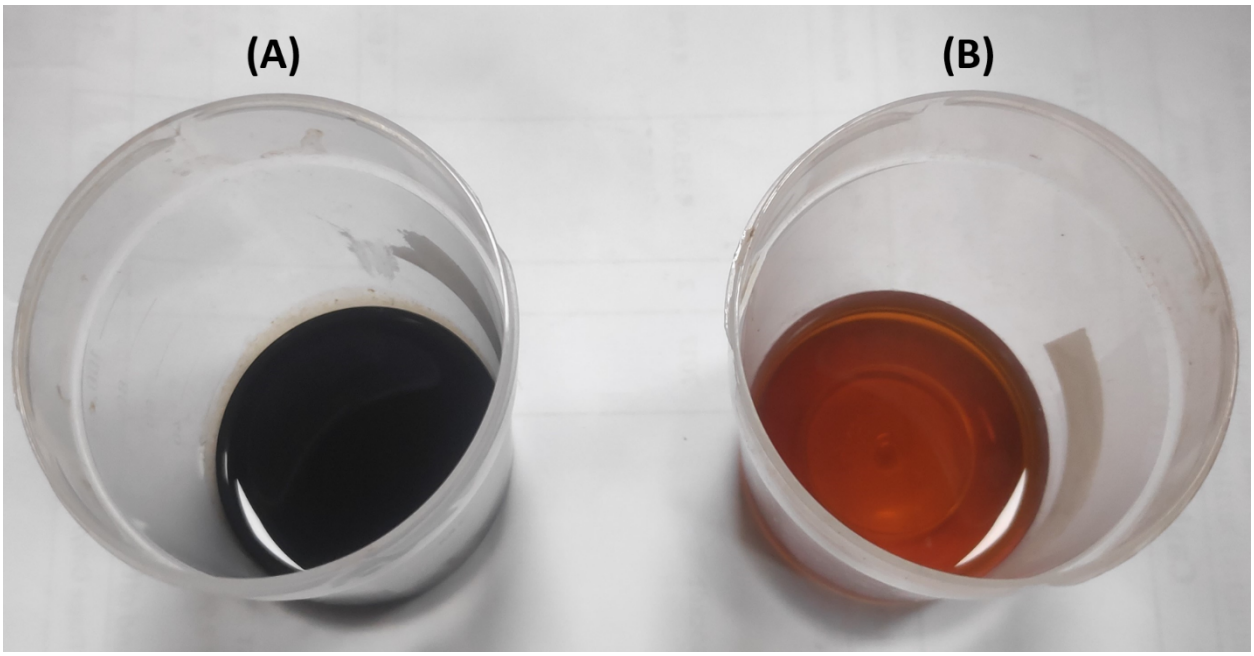


Fig. S2. Liquid products from experiment (A) E1 (black) and (B) E7 (reddish brown).

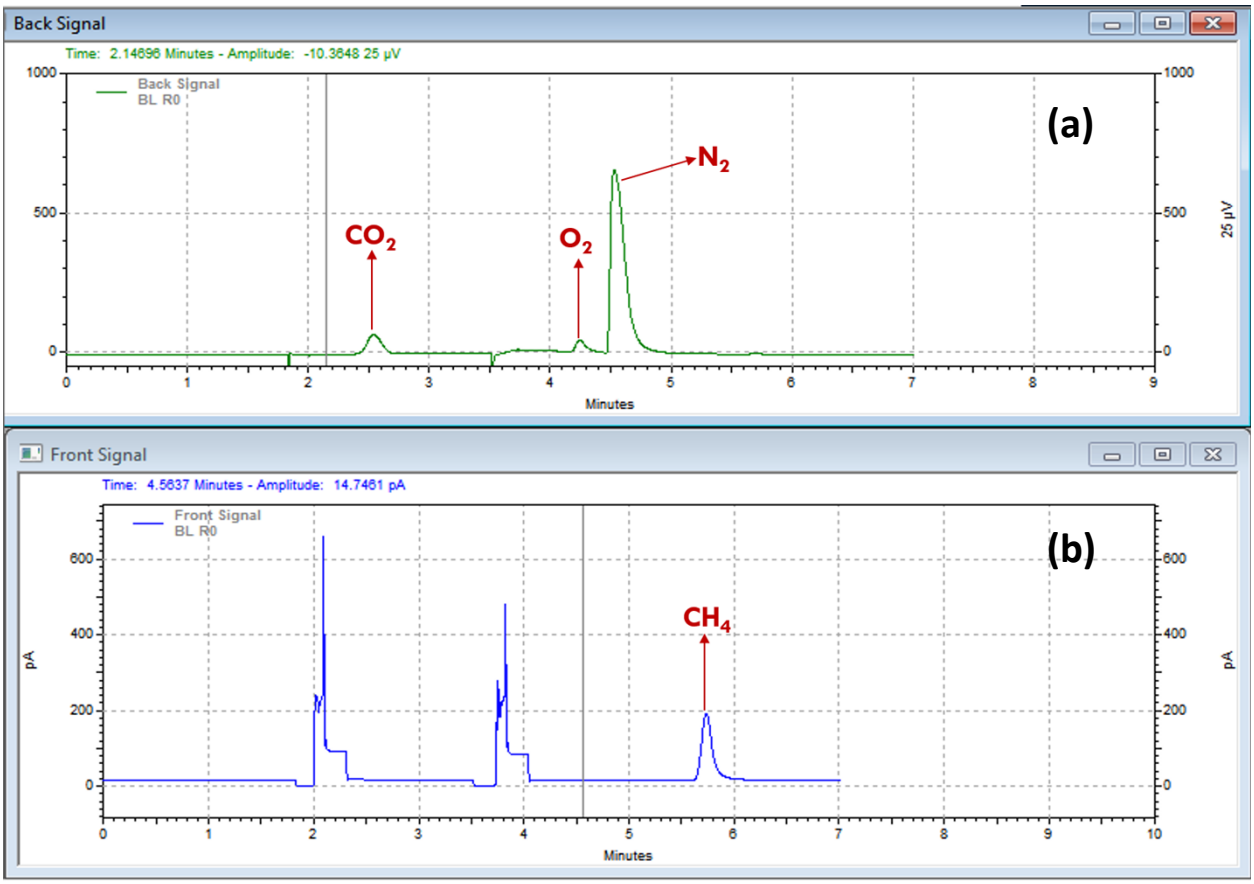


Fig. S3. GC trace of the gas phase from experiment E7 (400 °C, 30 min, 15 wt.% solid loading).

Output of (a) TCD, and (b) FID.

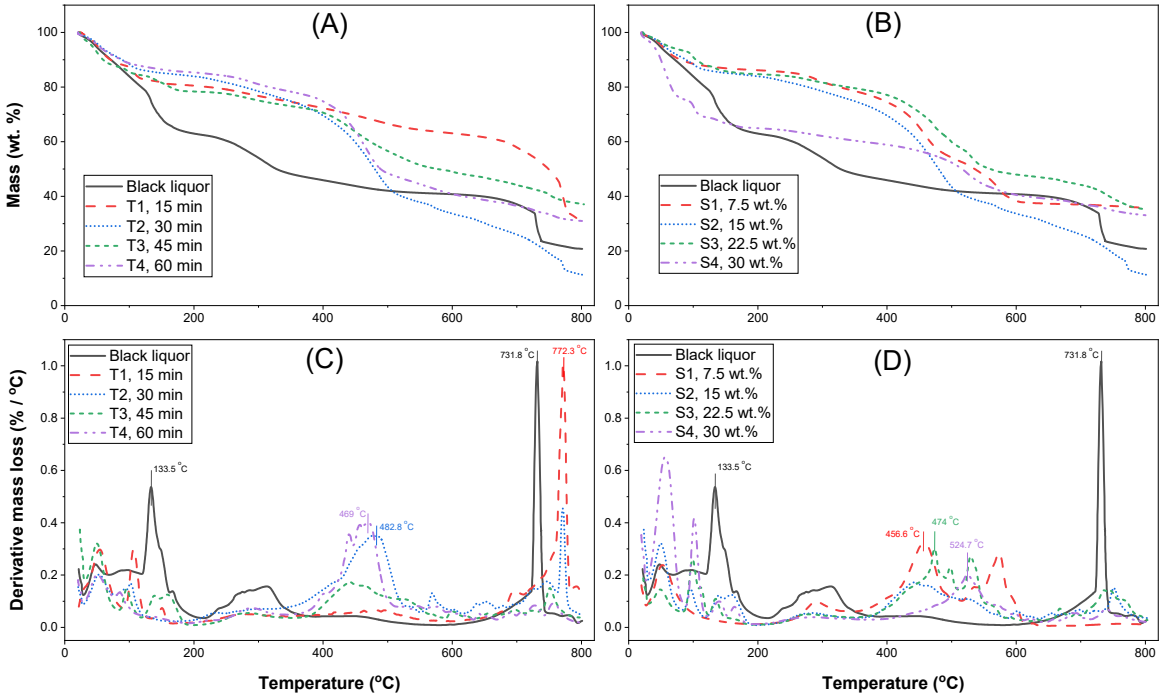


Fig. S4. Thermogravimetric mass loss (A,B) and differential thermograms (C,D) of black liquor and hydrochars from different experiments.

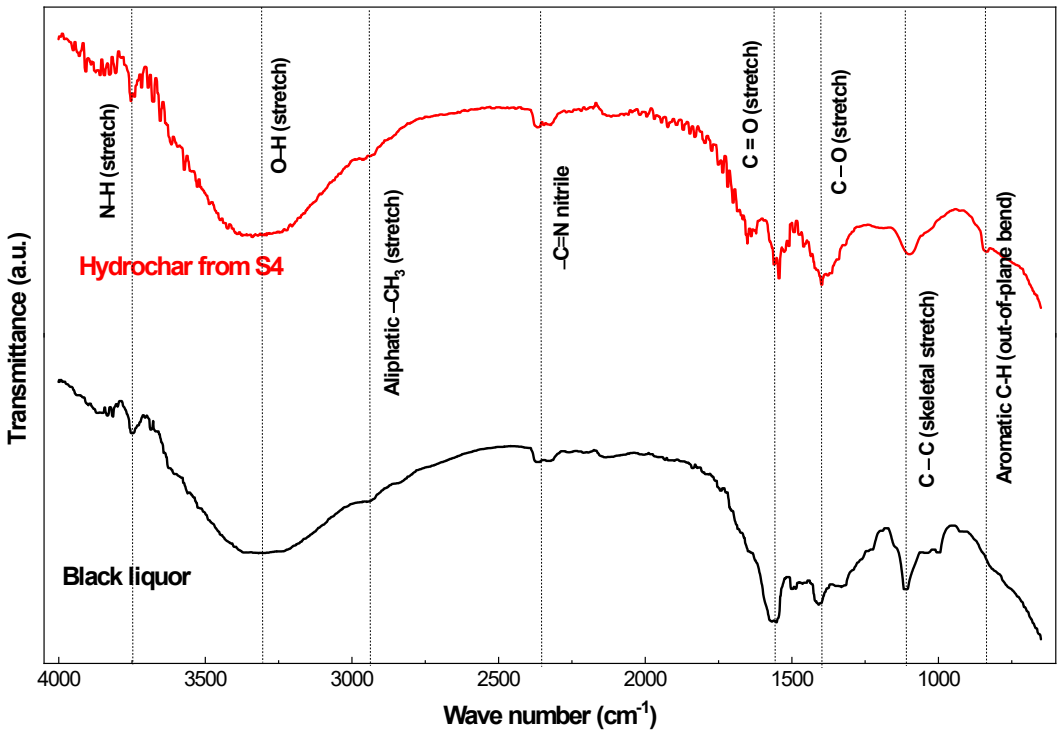


Fig. S5. FTIR spectra of black liquor and hydrochar from experiment S4 (30 wt.% loading).

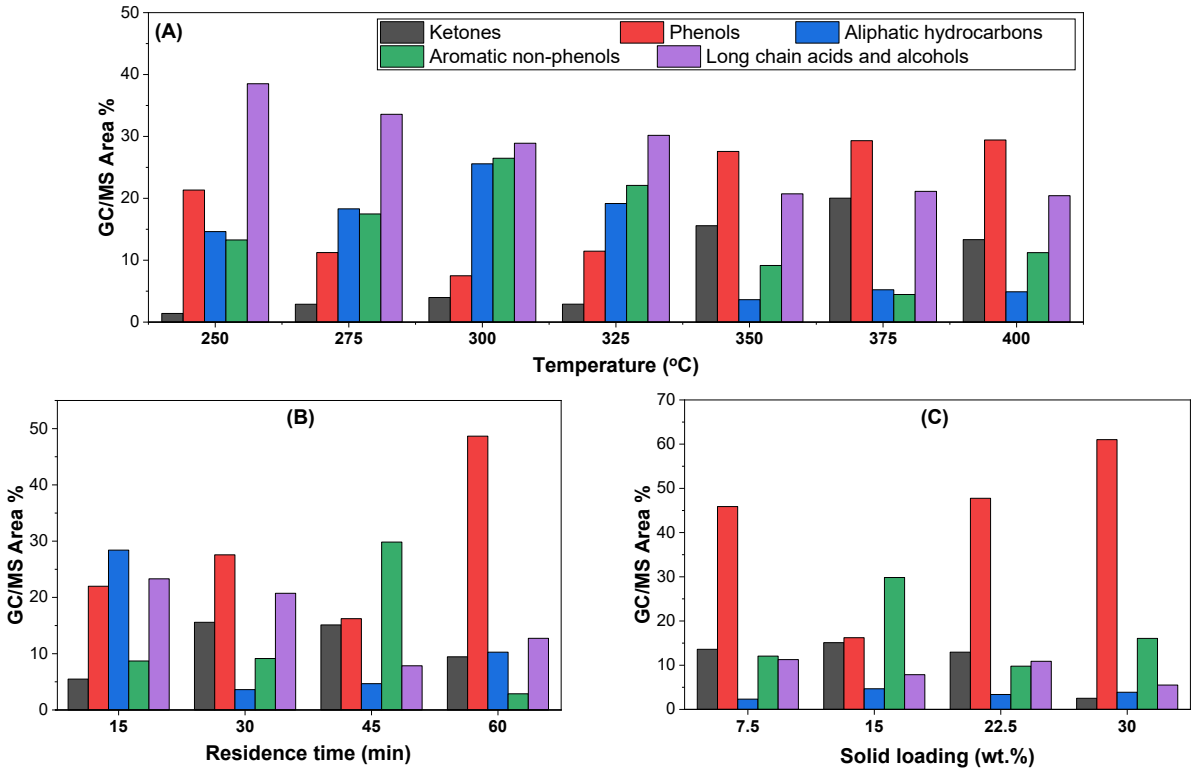


Fig. S6. Pyrolysates from Py-GC/MS of hydrochars at 740 °C from different experiments by varying (A) temperature at 30 min residence time and 15 wt.% solid loading, (B) residence time at 350 °C and 15 wt.% loading, and (C) solid loading at 350 °C and 30 min.

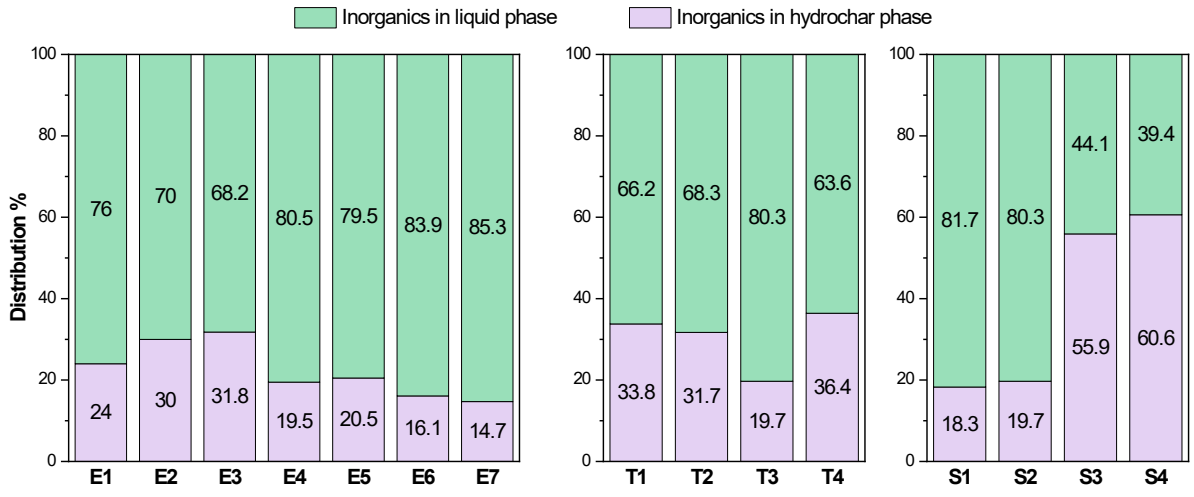


Fig. S7. Distribution of inorganics (%) between liquid and hydrochar phase.

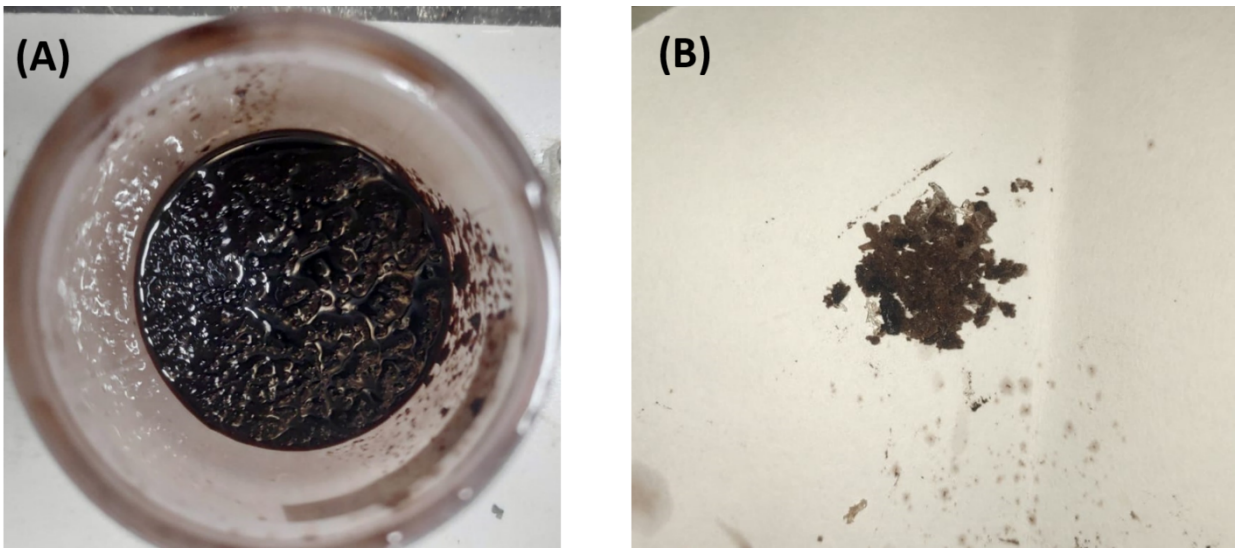


Fig. S8. (A) Precipitated salt at the bottom of the storage vessel for the liquid product from experiment S4, and (B) filtered salt crystals.