Supplementary material for

Experimental Studies on the Hydrotreatment of Kraft lignin to Aromatics and Alkylphenolics using economically viable Fe-based catalysts

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Table S1 Oil yields and mass balances at different temperatures in the absence of catalyst*

Reaction temperature (°C)	DSP (%)	ASP (%)	GP (%)	Water (%)	Residue (%)	Mass balance (%)
350	3.9	1.4	4.2	-	68.0	78
400	9.4	2.2	10.4	7.5	50.0	79
450	6.7	3.4	17.1	15.5	38.0	82

Reaction conditions: Kraft lignin, 15 g; hydrogen pressure of 100 bar at RT; 1200 rpm
DSP-DCM soluble products, ASP-Acetone soluble products, GP-gaseous products
*Yields are on wt.% of lignin intake

Table S2 Monomers yield at different temperatures in the absence of catalyst*

Reaction temperature (°C)	Phenolics (%)	Aromatics (%)	Alkanes (%)	Others (%)	Total monomers (%)
300	0.7	0.1	0	1.3	2.1
400	5.1	1.5	0.2	0.5	7.3
450	3.2	1.5	0	0.3	5.0

*Yields are on wt.% of lignin intake

Table S3: Overview of the catalytic hydrotreatment experiments of Kraft lignin [a]: Conversions, product yields, mass balance and elemental composition

Catalyst	Limonite	Fe_2O_3-NiO	Fe_2O_3
Organic phase (wt%)[b]	33.97	39.08	31.13
Aqueous phase (wt%)[b]	21.5	18.31	15.13
Gas phase (wt%)[b]	18.3	15.47	15.98
Residue/Coke (wt%)[b]	24.7	21.97	30.20
Total mass balance (wt%)[b]	98.1	94.83	92.45
Water content organic phase (wt%)	2.3	1.89	3.64
Carbon content aqueous phase (wt%)	1.3	1.07	1.50
Monomer product yield (wt%) [b]			
Alkylphenolics	16.7	17.69	13.48
Aromatics	4.1	3.78	3.67
Napthalenes	3.2	3.3	1.52
Ketones	0.4	0.34	0.76
Cyclic/linear alkanes	5.0	3.54	1.73
Catecholics	1.6	1.44	0.65
Guaiacolics	0.1	1.02	0.10
Total Yield (wt%) [b]	30.9	31.12	21.93

[a] Reaction conditions: 450 °C, 4h, 100 bar H_2 initial pressure, 5 wt% catalyst and 2.5 wt% sulphur source (DMDS)

[b] wt% on lignin intake

Table S4: Gas phase composition after catalytic hydrotreatment experiments of Kraft lignin.

Gas Phase	Limonite 350 °C	Limonite 400 °C	Limonite 450 °C	$CoMo/Al_2O_3$ 450 °C	FeS_2, 450 °C	Goethite 450 °C
Carbon dioxide (mol%)	6.2	9.6	9.7	7.9	8.0	8.5
Ethylene (mol%)	0.0	0.0	0.0	0.0	0.0	0.0
Ethane (mol%)	0.7	3.5	6.1	6.2	5.8	5.6
Propylene (mol%)	0,0	0.0	0.0	0.0	0.0	0.0
Propane (mol%)	0.3	1.4	2.6	2.6	2.6	2.6
Hydrogen (mol%)	80.9	60.1	42.9	35.9	51.2	50.5
Methane (mol%)	11.5	25.1	38.3	47.3	31.5	32.1
Carbon monoxide (mol%)	0.4	0.3	0.4	0.1	0.8	0.7
Total H_2 consumption %	52	67	75	84	64	69

Table S5: Elemental analyis of solid products obtained after catalytic hydrotreatment experiments of Kraft lignin.

Sample	**Catalyst and reaction temperature**	**C %**	**H %**	**O %**	**N %**	**S %**
Kraft lignin	-	61.1	5.6	30.6	<0.01	1.6
Solid phase	Limonite, 350 ^{o}C	63.3	4.2	24.6	1.2	6.7
Solid phase	Limonite, 400 ^{o}C	71.3	3.6	18.6	1.2	5.3
Solid phase	Limonite, 450 ^{o}C	74.3	2.8	21.7	1.1	4.9
Solid phase	$CoMo/Al_2O_3$ 450 ^{o}C	72.7	2.9	22.1	1.1	2.6
Solid phase	FeS_2, 450 ^{o}C	80.1	2.9	16.0	1.0	4.6
Solid phase	Goethite 450 ^{o}C	75	2.8	14.7	1.0	6.4

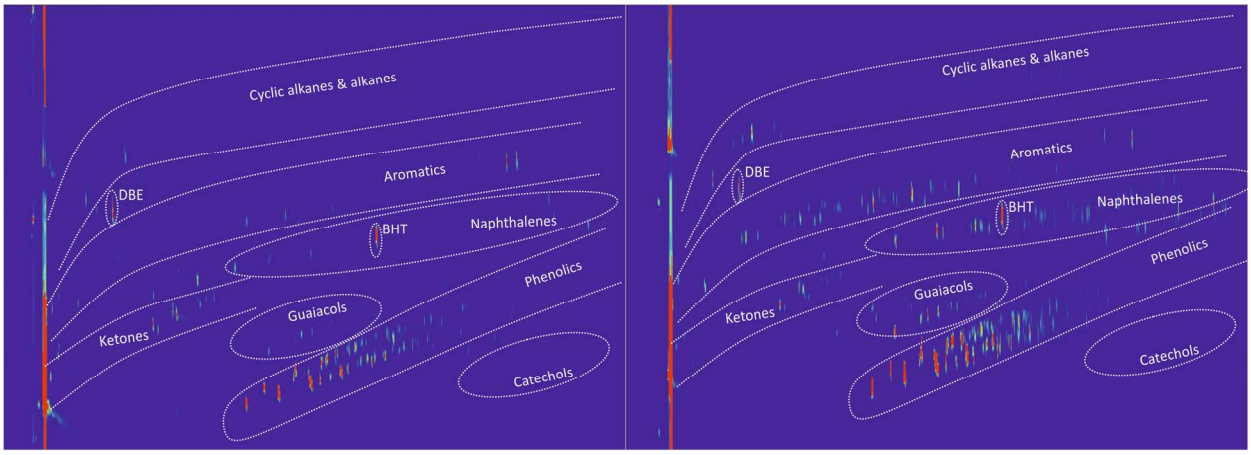

Figure S1: GCxGC-FID chromatogram for the lignin oil obtained at 350 (right plot) and 400°C (left plot)

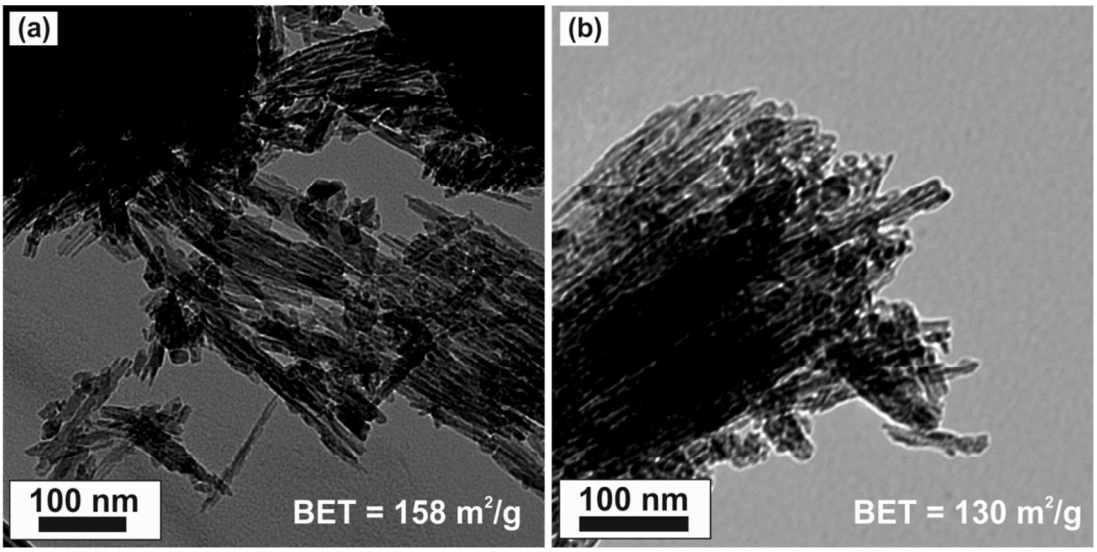

Figure S2: TEM images of the limonite catalyst before (a) and after (b) calcination.

Calibration of GC×GC-FID chromatograms

The first step in the quantification procedure involved determination of the RRF value for a number of representative model components belonging to the various compound groups (alkylphenolics, aliphatic hydrocarbons, aromatics,). The following equation was used to calculate the RRF for an individual model component:

$$RRF = \frac{C_{IS}A_C}{C_c A_{IS}} \quad (1)$$

Where C_{IS} is the concentration of the internal standard, A_{IS} the area of the internal standard (di-nbutylether, DBE), C_C the concentration of the component C, A_C is the area of the component, and RRF is the relative response factor for compound C.
The RRF value for an individual model component was determined by plotting the ratio C_c/C_{IS} versus the ratio A_c/A_{IS}. In such a plot, (see Figures S3-S5 below), the slope is the RRF value for the individual model component.

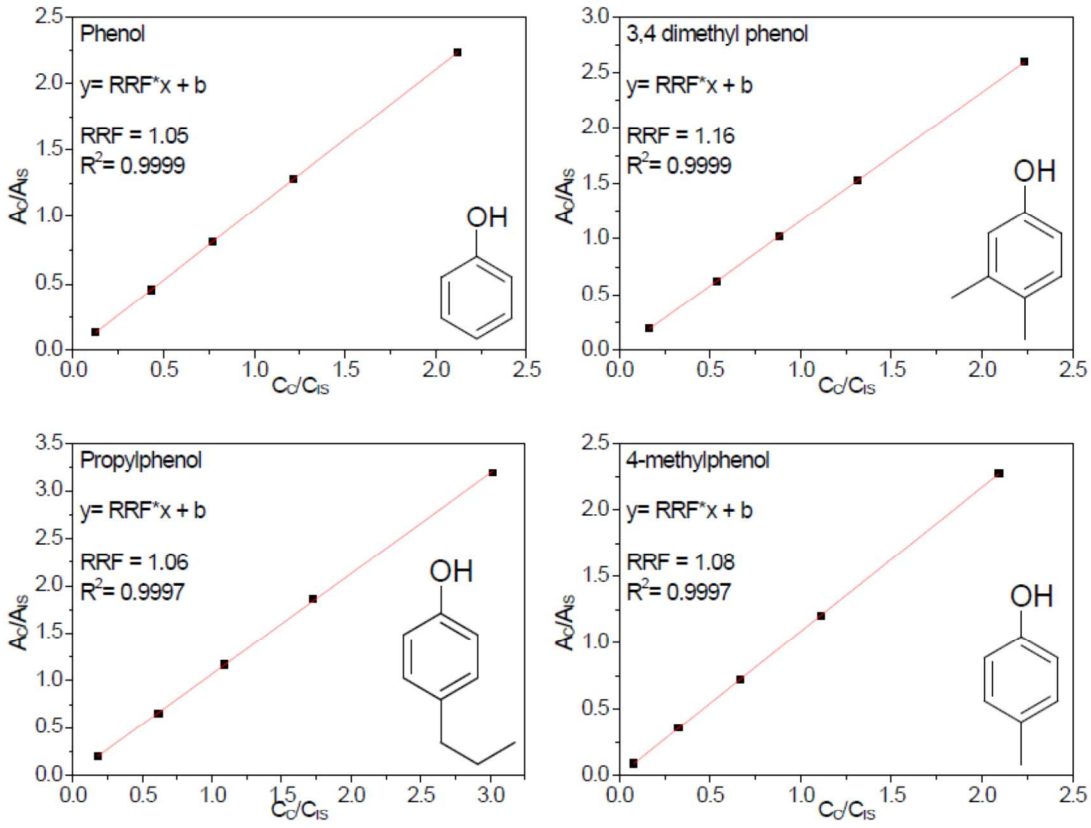

Figure S3. RRF values for several (alkylated) phenolics

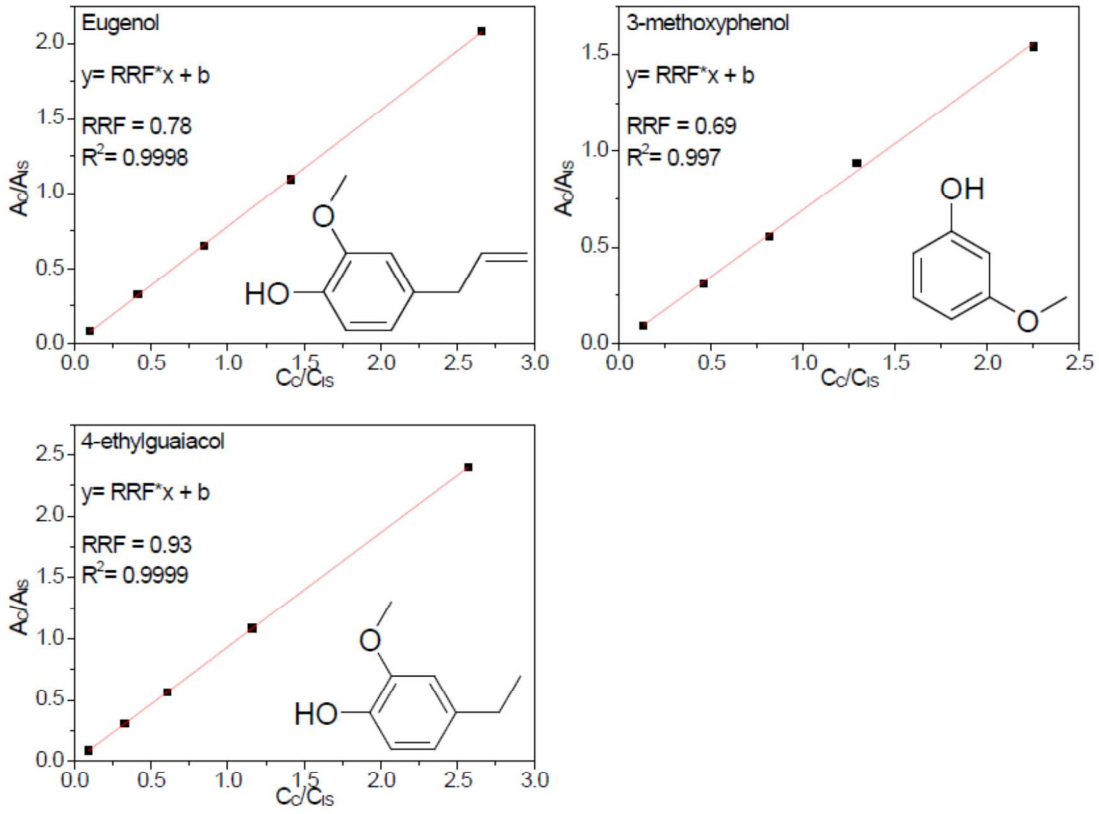

Figure S4: RRF values for several alkylated methoxy phenolics.

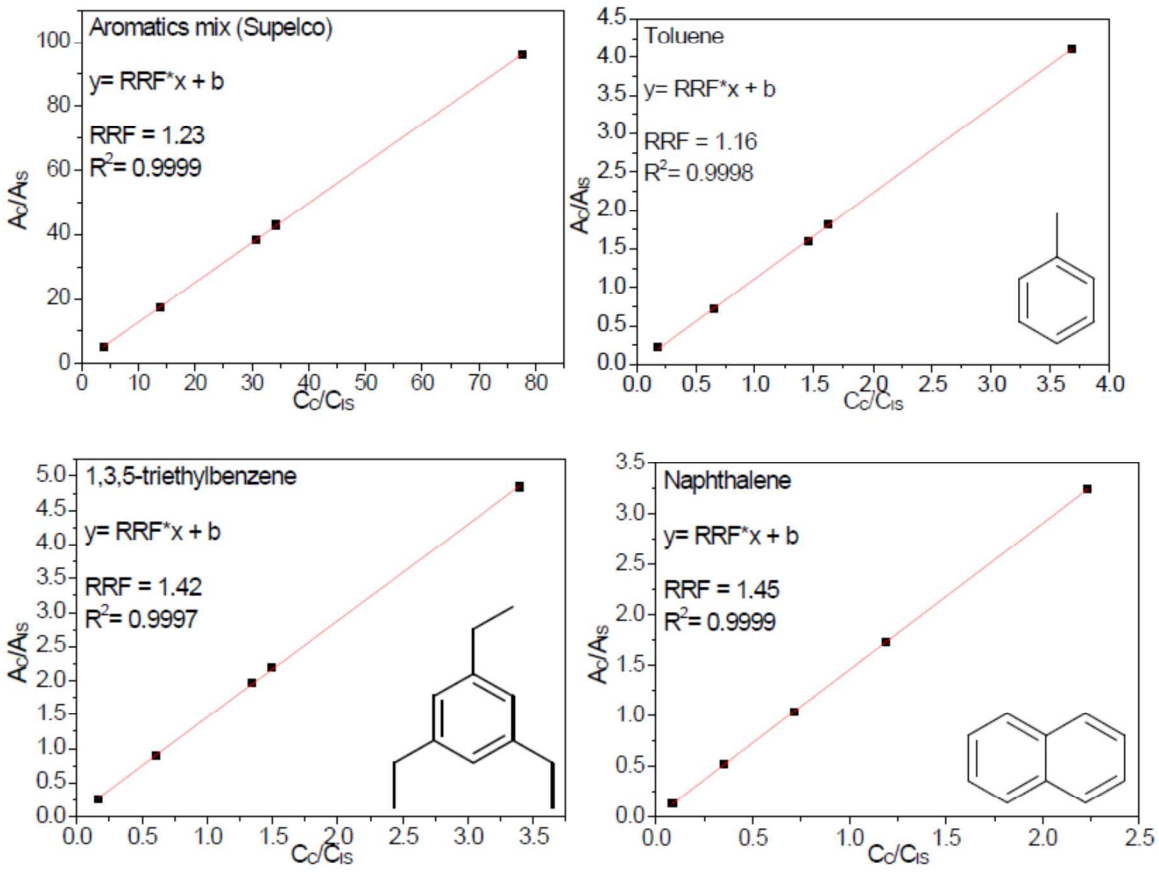

Figure S5. RRF values for several aromatics.

For the quantification based on compound groups, the total compound group area was calibrated over a concentration range of 10 to 100 mg/kg by using 5 calibration mixtures. From these calibrations, an average RRF is calculated for each compound group, see Table S6 below.

Table S6. Average RRF values for various compound groups

Compound group	RRF (DBE)
Alkylated phenolics	1.1
Methoxylated alkylated phenolics	0.9
Aromatics/Naphthalenes	1.23
Linear/branched alkanes	1.6
Cyclic alkanes	1.5
Ketones/Alcohols	1