Supplementary information:

Elucidating transfer hydrogenation mechanisms in non-catalytic lignin depolymerization

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Table S.1. State of art of the transfer hydrogenation of lignin

Lignin sources	**Solvent**	**Cat.**	**Temp, K.**	**Reaction time, h**	**Oils yields wt%**	**Solids yields wt%**	**Composition and observation**	**Ref.**
Hydrolytic Eucalyptus	Water	No Cat. Sodium formate	543	0.5	44[a]	n.d.	Main products were guaiacol, syringol C:H:O (67.2/6.3/26.3) 400-800g/mol	1
Various Lignin	Water or Ethanol	No Cat	633-663	4-18	48-76	2-9	Alkylation of the lignin oil in presence of ethanol as solvent increased the oil yields by 5 to 10 %	2
Lignin dimer models	Ethanol	No Cat	653	24	48-83[b]	n.d.	More realistic lignin model led to lower oil yield (48wt%) due to secondary reaction	3
Various Lignin	Water	No Cat Rh/Al_2O_3 Ru/ Al_2O_3 Pd/ Al_2O_3	613	6	58.2 90.0 81.0 81.7	22.4 5.1 4.8 2.8	Catalyzed reaction showed lower char formation and higher oils yields	4
Alkali Lignin	Water	No Cat Pd/ Al_2O_3	538 and 623	1 and 5	18.0[c] 16.6	5.1[c] 12.8	No catalyzed conditions gave higher diethylether extract and more than two-fold lesser solid fraction	5
Hardwood Alcell	Isopropanol	No Cat Ru/C	673	4	18.2 71.2	46.0 [d] 1.0	Oil C/H/O: 79.9/8.9/11.2 Oil C/H/O: 80.8/10.2/8.9 The presence of catalyst reduced the solid formation and increase the deoxygenation of the oil Aldo condensation of the isopropanol virtually increased the oil yields.	6
Low sulfonated Akali Lignin	Water	No Cat Pd/C	538	6	33.1 [e] 25.7	1.1 22.9	Higher char formation in presence of Pd/C cat. Formic acid alone prevented the lignin repolymerization Pd/C does not affect the products distribution Longer reaction time affected products distribution, increasing the catechol yield while decreasing the guaiacol yield	7

[a]: Mass of extract in Chloroform/Ethanol (v/v: 3/1), [b]: Yields of GC quantified products, [c] : In percent of the total feed (including the Formic acid), [d] : Acetone insoluble fraction, [e] : Ether extractable fraction.

Table S.2. List of reference products used for the calibration

[Coefficient response defined as α = (Area $_{\text{product (i)}}$/ Area $_{\text{IS}}$)/ (mass $_{\text{products (i)}}$/mass $_{\text{IS}}$) with IS = 1,3,5-tri tert-butylbenzene]

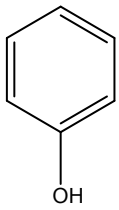
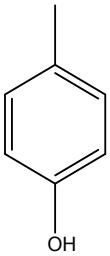
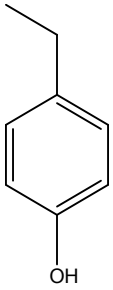
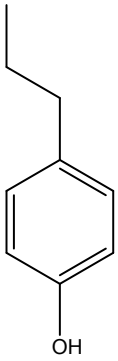
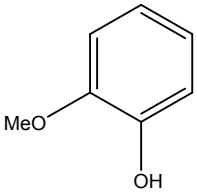
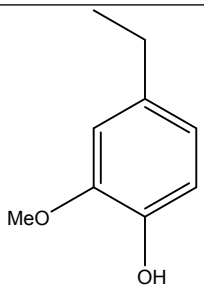
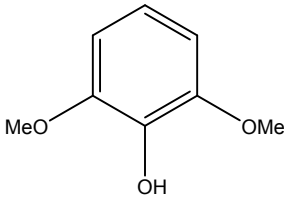
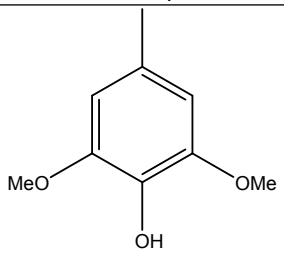
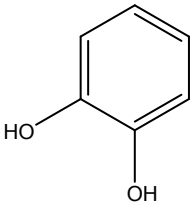
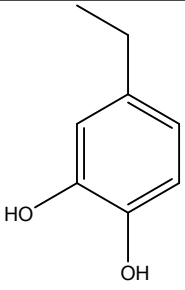
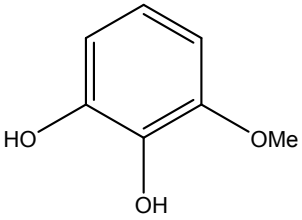
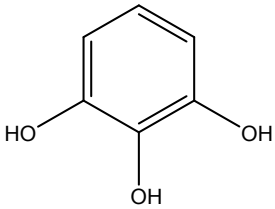
			
Phenol (α = 1.35)	*p*-cresol (α = 1.29)	*p*-ethyl phenol (α = 1.29)	*p*-propyl phenol (α = 1.25)
			
Guaiacol (α = 1.25)	*p*-ethyl guaiacol (α = 1.21)	Syringol (α = 1.19)	*p*-methyl syringol (α = 1.13)
			
Catechol (α = 1.31)	*p*-ethyl catechol (α = 1.31)	*o*-methoxy catechol (α = 1.3)	Pyrogallol (α = 1.90)

Table S.3. List of the products with IUPAC names and CAS numbers

	IUPAC Name	CAS number
Anisole	methoxybenzene	100-66-3
2-methylanisole	1-methoxy-2-methylbenzene	578-58-5
4-methylanisole	1-methoxy-4-methylbenzene	104-93-8
Phenol	Phenol	108-95-2
4-ethyanisole	1-ethyl-4-methoxybenzene	1515-95-3
2-cresol	2-methylphenol	95-48-7
1,2-dimethoxybenzene	1,2-dimethoxybenzene	91-16-7
4-cresol	4-methylphenol	106-44-5
guaiacol	2-methoxyphenol	90-05-1
4-ethylphenol	4-ethylphenol	123-07-9
4-methylguaiacol	2-methoxy-4-methylphenol	93-51-6
Cyclohexane-1,2-diol	(cis/trans)-1,2,-cyclohexanediol	1792-81-0 (cis) 1460-57-7 (trans)
1,2,3-trimethoxybenzene	1,2,3-trimethoxybenzene	634-36-6
catechol	1,2-dihydroxybenzene	120-80-9
4-propylphenol	4-propylphenol	645-56-7
4-methylcatechol	1,2-dihydroxy-4-methylbenzene	452-86-8
3-methylcatechol	1,2-dihydroxy-3-methylbenzene	488-17-5
4-ethylguaiacol	4-ethyl-2-methoxyphenol	2785-89-9
syringol	2,6-dimethoxyphenol	91-10-1
4-ethylcatechol	1,2-dihydroxy-4-ethylbenzene	1124-39-6
methyl-ethylguaiacol	methyl-ethyl-2-methoxyphenol	n.a.
4-propylguaiacol	4-propyl-2-methoxyphenol	2785-87-7
3-methoxycatechol	1,2-dihydroxy-3-methoxybenzene	934-00-9
4-methylsyringol	2,6-dimethoxy-4-methylphenol	6638-05-7
ethyl-methylcatechol	Ethyl-methyl-1,2-dihydroxybenzene	n.a.
4-propylcatechol	1,2-dihydroxy-4-propylbenzene	2525-02-2
pyrogallol	1,2,3 trihydroxybenzene	87-66-1
5-methyl-3-methoxycatechol	1,2-dihydroxy-5-methyl-3-methoxybenzene	n.a.
4-ethylsyringol	2,6-dimethoxy-4-ethylphenol	14059-92-8
2-phenol-ethanol	4-(2-hydroxyethyl)phenol	501-94-0
5-ethyl-3-methoxycatechol	1,2-dihydroxy-5-ethyl-3-methoxybenzene	n.a.
4-propylsyringol	2,6-dimethoxy-4-propylphenol	6766-82-1
5-propyl-3-methoxycatechol	1,2-dihydroxy-5-propyl-3-methoxybenzene	n.a.
alpha-methylvanillyl alcohol	4-hydroxy-3-methoxy-a-methylbenzyl alcohol	2480-86-6
acetoguaiacol	4-hydroxy-3-methoxyacetophenone	498-02-2

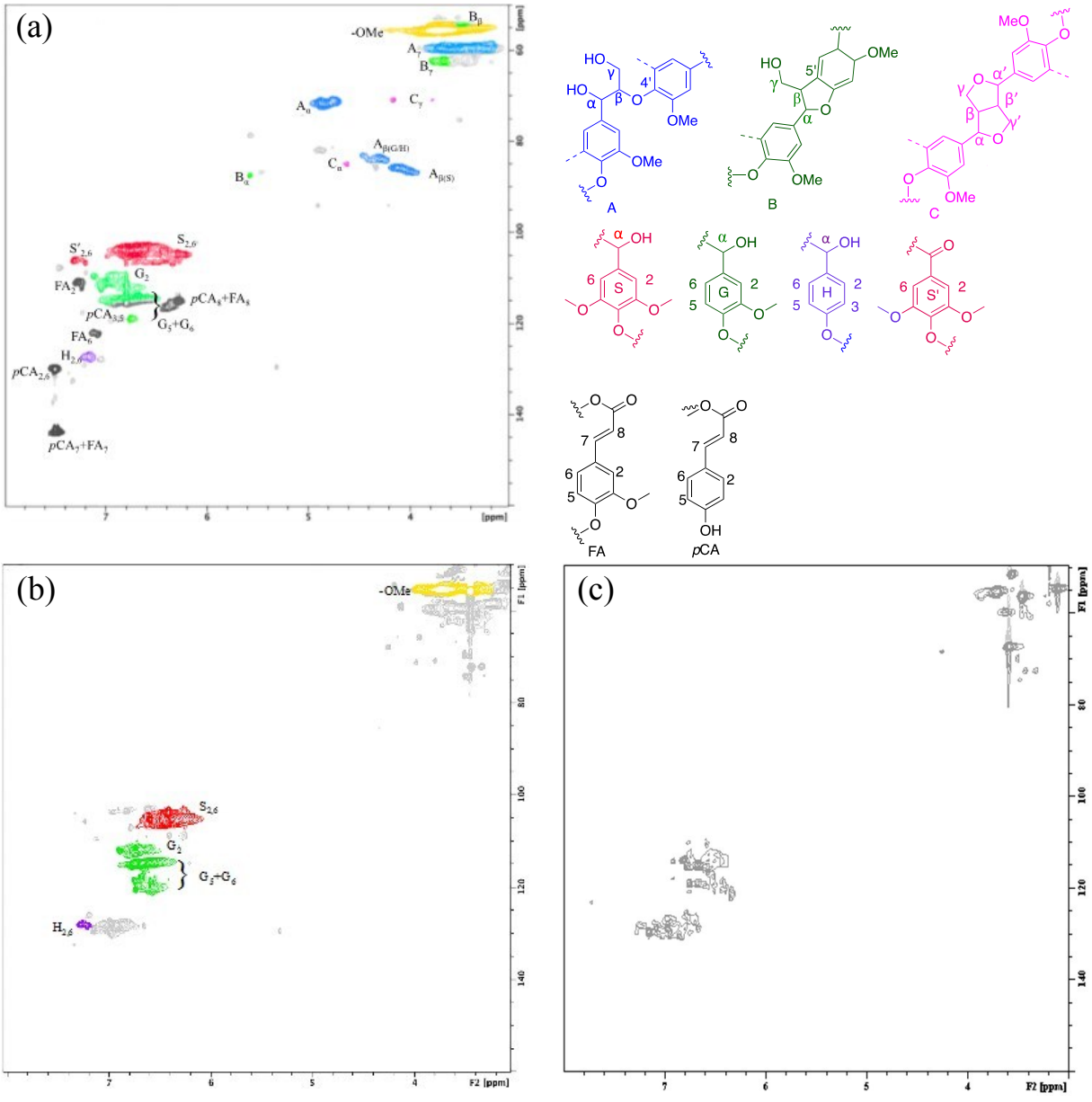


Fig. S.1. 2D HSQC NMR spectra of Sugarcane bagasse (a) and Lignin oil after reaction up to 270°C (b) and 4h at 300°C (c)
[**A**, β-ether (β-O-4′) unit; **B**, phenylcoumaran (β-5′) unit; **C**, resinol (β-β´) unit; ***p*CA**, *p*-coumarate unit; **FA**, Ferrulate unit;
G, guaiacyl unit; **S**, syringyl unit; **S′**, benzyl-oxidized **S** unit; **H,** *p*-hydroxyphenyl unit.]

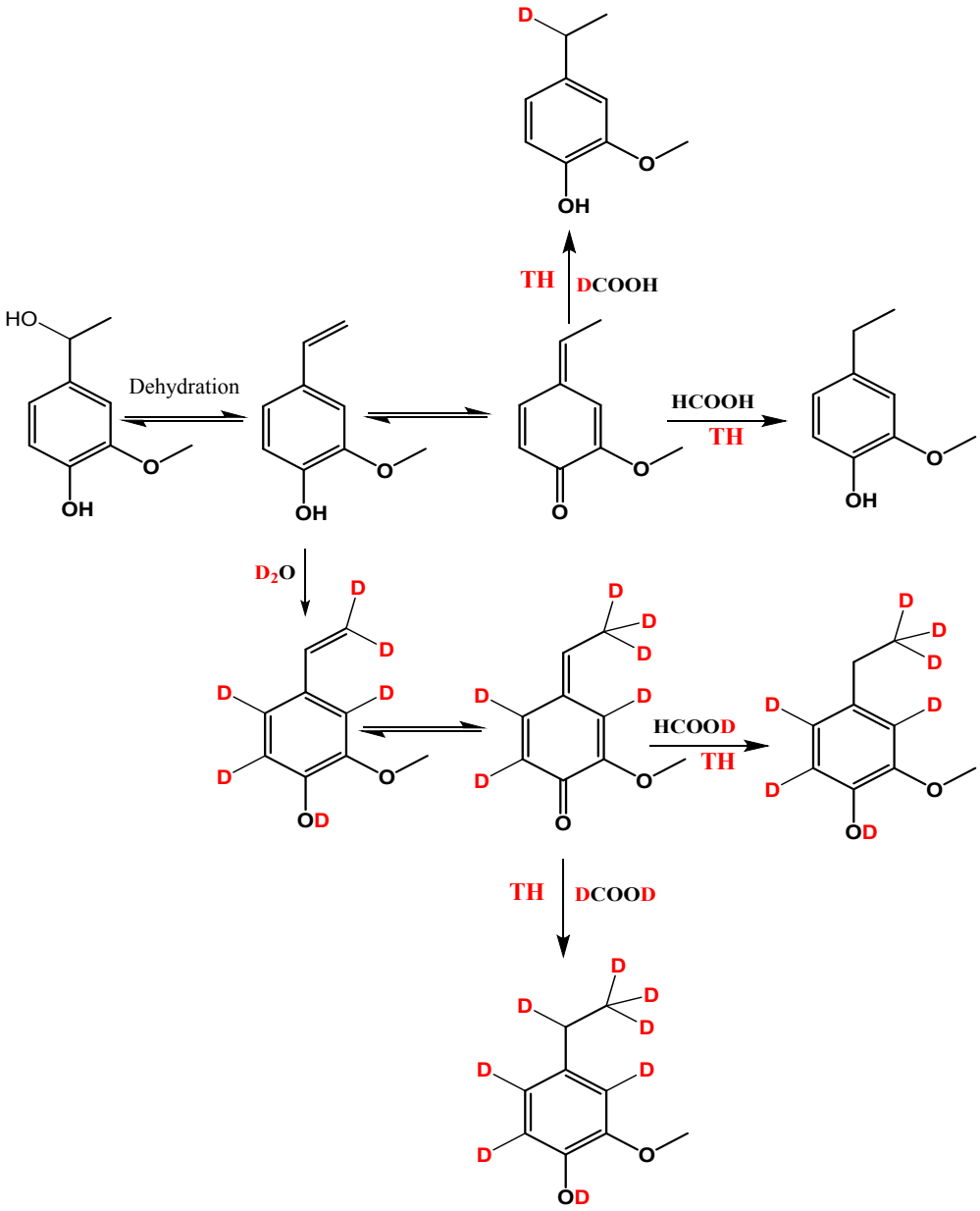


Fig. S.2. Deuterium incorporation on the ethylguaiacol as function of the H/D exchange of D_2O and transfer hydrogenation of d-formic acid [TH : Transfer hydrogenation; Reaction pathways: HCOOH for FA/H_2O; DCOOH for *d*-FA/H_2O; HCOOD for FA/D_2O and DCOOD for *d*-FA/D_2O]