## **Supporting Information**

# Role of peracetic acid on disruption of lignin packing

structure and its consequence on lignin depolymerisation

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### 1. List of Acronyms

DACSL – <u>D</u>ilute <u>A</u>cid <u>C</u>orn <u>S</u>tover <u>L</u>ignin

 $PAA - \underline{P}er\underline{a}cetic \underline{A}cid$ 

MPC – <u>M</u>onomeric <u>P</u>henolic <u>C</u>ompounds

 $F\text{-}C-\underline{F}olin\text{-}\underline{C}iocalteu$ 

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 $NMR - \underline{N}uclear \underline{M}agnetic \underline{R}esonance Spectroscopy$ 

 $XRD - \underline{X} - \underline{R}ay \underline{D}iffraction$ 

## 2. Supplemental Results

	Acid Soluble	Acid Insoluble	I. i i.e.			Maintana	T . 4 . 1
	Lignin,	Lignin,	Lignin,		. 1 0/	Moisture,	l otal,
	%	%	%	Sugar, %	Ash, %	%	%
DACSL	1.36	65.57	66.93	16.84	1.10	13.24	98.14

Table S1. Determination of Klason Lignin Purity.

#### **Calculation of Mass Balance**

In the present article, the total yield of the monomeric phenolic compounds (MPCs) was determined by the FC analysis wherein the absorbance of the solution was determined by UV-visible spectroscopy and the corresponding yield of the MPCs was calculated based on the calibration curve using isoeugenol as the standard. The mass balance was calculated as follows:

$$Mass \ Balance \ (\%) = \frac{g \ products}{g \ reactant} X \ 100 \tag{1}$$
$$Mass \ Balance \ (\%) = \frac{(g \ in \ solid + g \ in \ solution)}{g \ DACSL} X \ 100 \tag{2}$$

Upon PAA-mediated oxidation of DACSL, we obtained both solid and liquid phases. The solid phase contained insoluble oligomeric/polymeric structures while the quantified MPCs were present in the solution phase. In equation (1), "g products" includes the weights for both the oligomeric/polymeric materials and the MPCs. As both the solid products obtained after oxidation, washing and subsequent freeze-drying of the residue and the starting material can be directly weighed, the terms "g solid" and "g DACSL" in equation (2) were weights obtained gravimetrically and unambiguously. On the other hand, "g solution" corresponding to the yield of MPCs was obtained from FC analysis. The good mass balance (80-90%) obtained during the oxidation suggests that the FC method provides satisfactory results for the yield determination of the phenolic compounds for this application.

Sample	wt. of the starting solid (g)	Yield of solid isolated after oxidation (g)	Yield of MPC present in the liquid after oxidation (g)*	Total amount (solid + solution) (g)	Mass Balance (%)
0.1 g PAA/g lignin	3.01	1.96	0.81	2.77	90.8
0.2 g PAA/g lignin	2.93	1.80	0.55	2.35	80.2

Table S2. Mass balance obtained during the oxidation of lignin with different amounts of peracetic acid

\* Yield of MPC present in the liquid after oxidation was calculated based on the FC-analysis



Figure S1. Comparison of DACSL and partially oxidised DACSL samples. The oxidation was carried out in 1,4-dioxane.

Table S3. Details of the oxidised lignin wherein the oxidation was carried out at 1,4-dioxane.

Sample	Oxidation time (h)	Weight (g) of the sample shown in	
		Figure S2	
DACSL	0	0.6220	
LO-Dioxane – 1	1	0.5887	
LO-Dioxane – 2	3	0.6167	
LO-Dioxane – 3	5	0.6475	
LO-Dioxane – 4	18	0.6168	



Figure S2. Comparison of DACSL and partially oxidised DACSL samples. The oxidation was carried out in n-hexane.

Table S4. Details of the oxidised lignin wherein the oxidation was carried out in n-hexane.

Sample	Oxidation time (h)	Weight (g) of the sample shown in Figure S3
DACSL	0	0.7820
LO-Hexane – 1	1	0.7801
LO-Hexane – 2	3	0.7700
LO-Hexane – 3	5	0.8271
LO-Hexane – 4	18	0.7828

Table S5. Quantitative <sup>13</sup>C NMR study to determine the carbonyl carbon in the acetyl group connected to primary, secondary, and phenolic hydroxyl group per aromatic ring in DACSL and different partially oxidised DACSL samples.

$\delta_{\rm C}(\rm ppm)$	Assignment	Number of moieties per Ar ring				
range		DACSL	LO-1	LO-2	LO-3	LO-4
171.2-	C attached to Primary OH	0.60	0.60	0.62	0.61	0.61
170.2						
170.2-	C attached to Secondary OH	0.63	0.58	0.55	0.55	0.55
169.5						
169.5-	C attached to Phenolic OH	0.42	0.50	0.52	0.54	0.56
167.8						



Figure S3. Comparison of diffraction patterns of DACSL and Na<sub>2</sub>SO<sub>4</sub>.



Figure S4. <sup>13</sup>C NMR spectrum of DACSL.



Figure S5. <sup>13</sup>C NMR spectrum of LO-1.



Figure S6. <sup>13</sup>C NMR spectrum of LO-2.



Figure S7. <sup>13</sup>C NMR spectrum of LO-3.



Figure S8. <sup>13</sup>C NMR spectrum of LO-4.

#### Side-chain Replacement pathway



Scheme S1. Stepwise reaction mechanism corresponding to the side chain replacement pathway observed during the Baeyer-Villiger oxidation.



Scheme S2. Baeyer-Villiger oxidation of 4-methoxy acetophenone in presence of PAA. Reaction condition: PAA, 60°C, 2 h, 1 atm.



#### 2.1 Baeyer-Villiger oxidation of unsymmetrical ketone by peracetic acid

Scheme S3. Reaction mechanism of Baeyer-Villiger oxidation of unsymmetrical ketone (substituted acetophenone was taken as an example).

Baeyer-Villiger oxidation proceeds via the addition of peracetic acid to the carbonyl group to generate a hydroperoxide-type intermediate. As oxygen-oxygen single bond is weak and monovalent oxygen cannot bear a positive charge, the intermediate undergoes loss of carboxylates with a concomitant migration of either phenyl or alkyl group to the oxygen which resulted to the corresponding ester. The ester thus generated can further be hydrolysed to produce the corresponding acid. The transition state of the Baeyer-Villiger oxidation is cationic due to the loss of carboxylates as the leaving group. As the phenyl group stabilises the cationic intermediate better compared to alkyl group, migration of the former is preferable. Thus, considering the example of aromatic ketone shown above, phenolics (resulting from phenyl migration) are expected as major product compared to the phenolic

acid (resulting from alkyl migration). However, in case of lignin oxidation, phenolic acid was obtained as the major product. This could be explained by invoking the significant steric interaction posed by the bulky phenyl group (as it is connected to lignin polymeric structure) of the ketone (3) which alters the expected order of the migratory aptitude based on their electronic effect.

Peracetic Acid Oxidant	0.2 g/g lignin	-44%				
Loading (1 g/ g lignin)	2 g/g lignin				55	5%
	1.25 \$/lb		-6%			
MPC Value (\$1/Ib)	0.5 \$/lb			13%		
MDC Vield on Linnin (42 ud%)	60		-10%			
MPC field on Lignin (42 wt%)	30			6%		
A set is A sid Solvent Loading (17 ml/s)	1 ml/g lignin		-6%			
Acetic Acid Solvent Loading (17 mi/g)	20 ml/g lignin			1%		
Acetic Acid Solvent Loss (2 wt%)	0.10%		-6%			
	3%			3%		
Lignin to MPC Capex (32 mm\$)	-50%		-2%			
Light to the couper (of hinty)	+50%			■ 2%		
MDC Future starts Lang (20% Ethical Association)	0%		0%			
MPC Extractant Loss (2% Ethyl Acetate)	5%			0%		
MPC Extractant Loading (100% of MPC rate)	25% of MPC		0%			
	200% of MPC			0%		
	\$5/lb		0%			
Catalyst Cost (\$60/10)	\$90/lb			0%		
Catalyst Life (1 year)	2 years		0%			
	0.2 years			0%		
	-	55% -35	% -15%	5% 2	5% 45%	

#### % Change in Minimum Fuel Selling Price based on 2013 SOT (\$8.6/gge) (numbers at left in parenthesis are the 2013 SOT values)

Figure S9. Tornado plot obtained from preliminary techno-economic analysis corresponding to PAA depolymerization of lignin to MPCs.