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## **Supporting Information**

# Esterification mechanism of lignin with different catalysts based on lignin model compounds by mechanical activation-assisted solid-phase synthesis

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### 1. Detailed analytical conditions

The FTIR measurements were performed with a FTIR-7600 Spectrometer (Lambda Scientific Pty Ltd, Australia). Mixture powders of sample (2.0 mg) and KBr (200.0 mg) were pressed into a disk for testing. The spectra were recorded with 32 scans in the frequency range of 4000–400 cm<sup>-1</sup> with a resolution of 1 cm<sup>-1</sup>. NMR spectra were accumulated on an AVANCE III HD 600 spectrometer (Bruker, Switzerland). Approximate 100-300 mg of sample was dissolved in 1 mL of DMSO-d6 (99.9% deuterated, 0.05% tetramethylsilane) and left overnight to obtain complete dissolution. The solution was filtered with microporous filter membrane of 0.45 µm before <sup>1</sup>H and <sup>13</sup>C NMR analyses. Ultraviolet/Visible (UV/Vis) spectroscopy analysis was performed with a 2802s UV/Vis spectrometer (UNIC, USA) in the wavelength range of 200-600 nm, at a slit width of 1 nm and a moderate scan velocity. About 0.010-0.015 g of sample was dissolved in 10 mL of water and 1,4-dioxane mixture (volume ratio of water:1,4-dioxane = 1:9). The neutral solution was got by diluting 2.0 mL of the solution to 50.0 mL with pH 6 phosphate buffer, while the alkaline solution was got by diluting 2.0 mL of the solution to 50.0 mL with pH 12 sodium borate buffer. The pH 6 and pH 12 buffers were prepared according to method of Goldschmid, Otto.<sup>1</sup> The difference spectra were directly determined by measuring the absorbance of the alkaline solution relative to the neutral solution, and the maximum absorption were selected for the calculation of DE.

## References

1 O. Goldschmid, Anal. Chem., 1954, 26, 1421-1423.

### 2. NMR analysis——Supplement for Table 2

The calculation of ester content of acetylated lignin model compounds from integration of

## <sup>1</sup>H-NMR spectra:

Supposing the degree of esterification (DE) were  $x_1$ ,  $x_{21}$  (phenol ester),  $x_{22}$  (alcohol ester),  $x_3$ , and  $x_4$  for vanillin, vanillyl alcohol, p-hydroxy benzaldehyde, and syringaldehyde respectively, then the number of H in CH<sub>3</sub>COO and the esters content of the products from 1 mol of raw material can be expressed in Table S1. Integral area can be gotten from NMR spectra.

	Products						
		-	In th	eory	NMR ar		
Sample	Structure	DE	Number of Ar-H	Number of H in CH <sub>3</sub> COO	Integral area of Ar- H	Integral area of H in CH <sub>3</sub> COO	Content of ester
Vanillin	СНО ОСН <sub>3</sub>	$x_1$	3	3 <i>x</i> <sub>1</sub>	1	A <sub>1</sub>	$x_1$
Vanillyl alcohol		<i>x</i> <sub>21</sub> + <i>x</i> <sub>22</sub>	3	$3x_{21}+3x_{22}$	1	A <sub>2</sub>	<i>x</i> <sub>21</sub> + <i>x</i> <sub>22</sub>
p-hydroxy benzaldehyde	СНО	<i>x</i> <sub>3</sub>	4	3 <i>x</i> <sub>3</sub>	1	A <sub>3</sub>	<i>x</i> <sub>3</sub>
Syringaldehyde	H <sub>3</sub> CO OCH <sub>3</sub>	<i>x</i> <sub>4</sub>	2	3 <i>x</i> <sub>4</sub>	1	$A_4$	$x_4$

Table S1 The amount of hydrogen in the products in theory and NMR analysis

#### 3. UV/Vis analysis

The calculation of phenolic hydroxyl content of vanillin and vanillyl alcohol after esterification:

One mol of raw material as the basis of calculation, supposing the amount of each component for vanillyl alcohol after esterification were a, b, c, and d, respectively. If DE of phenolic hydroxyl and aliphatic hydroxyl were x and y, for vanillin and vanillyl alcohol, the constituents and phenolic hydroxyl contents before and after esterification in theory could be expressed as Table S2. According to the material balance, equations S1–3 were gotten.

a+b+c+d=1 (S1) b+c=x (S2) b+d=y (S3)

Combining Table S2 and the above equations, it is easy to see that the phenolic hydroxyl contents of vanillyl alcohol and vanillin were 17/154 and 17/152 before esterification, and were 17(1-x)/(154+43x+43y) and 17(1-x)/(152+43x) after esterification.

	Before esterification			After esterification					
Sample	Constituents	mol	Molecular weight	Content of phenolic hydroxyl(C <sub>1</sub> )	Constituents	mol	Molecular weight	The amount of phenolic hydroxyl	Content of phenolic hydroxyl(C <sub>2</sub> )
Vanillin	$V_1$	1	152	17/152	$V_1 V_2$	1-x x	152(1-x)+(152+43)x	17(1- <i>x</i> )	17(1-x)/(152(1-x)+(152+43)x)
Vanillyl alcohol	VA <sub>1</sub>	1	154	17/154	$\begin{array}{c} VA_1\\ VA_2\\ VA_3\\ VA_4 \end{array}$	a b c d	154 <i>a</i> +(154+43+43) <i>b</i> +( 154+43) <i>c</i> +(154+43) <i>d</i>	17(1 <i>-b-c</i> )	17(1- <i>b</i> - <i>c</i> )/(154 <i>a</i> +(154+43+43) <i>b</i> +(1 54+43) <i>c</i> +(154+43) <i>d</i> )
Note: struct	ures of the consti	tuents	were as foll	оw: Э СН <sub>3</sub>	СН2ОН			СН <sub>2</sub> ОН	CH2OCH3

Table S2 The amount of phenolic hydroxyl before and after esterification in theory



Fig. S1 Structure of lignin model compounds



**Fig. S2** FTIR spectra of acetylated lignin model compounds catalyzed by sodium acetate: (a) acetylated vanillin, (b) acetylated vanillyl alcohol, (c) acetylated p-hydroxy benzaldehyde, and (d) acetylated syringaldehyde



**Fig. S3** FTIR spectra of acetylated lignin model compounds catalyzed by sulphuric acid: (a) acetylated vanillin, (b) acetylated vanillyl alcohol, (c) acetylated p-hydroxy benzaldehyde, and (d) acetylated syringaldehyde



**Fig. S4** <sup>1</sup>H-NMR spectra of acetylated lignin model compounds catalyzed by sodium acetate: (a) acetylated vanillin, (b) acetylated vanillyl alcohol, (c) acetylated p-hydroxy benzaldehyde, and (d) acetylated syringaldehyde



**Fig. S5** <sup>13</sup>C-NMR spectra of acetylated lignin model compounds catalyzed by sodium acetate: (a) acetylated vanillin, (b) acetylated vanillyl alcohol, (c) acetylated p-hydroxy benzaldehyde, and (d) acetylated syringaldehyde



Fig. S6 <sup>1</sup>H-NMR spectra of acetylated lignin model compounds catalyzed by H<sub>2</sub>SO<sub>4</sub>:
(a) acetylated vanillin, (b) acetylated vanillyl alcohol, (c) acetylated p-hydroxy
benzaldehyde, and (d) acetylated syringaldehyde



**Fig. S7** <sup>13</sup>C-NMR spectra of acetylated lignin model compounds catalyzed by H<sub>2</sub>SO<sub>4</sub>: (a) acetylated vanillin, (b) acetylated vanillyl alcohol, (c) acetylated p-hydroxy benzaldehyde, and (d) acetylated syringaldehyde