1 Support Information

- 2 The basic chemical characteristics of Indulin ATTM are shown in Table S1, S2, and S3
- 3 [1]. More details can be found in the paper written by Hu, et al..

4 Preparation of catalysts

The $S_2O_8^2$ - K_2O/TiO_2 catalyst was prepared by the impregnation method. To prepare the 5 catalyst which contained 40 wt% $S_2O_8^{2-}$ and 40 wt% K_2O_1 g of TiO₂, 0.8586 g of KNO₃ 6 and 0.4754 g of (NH₄)₂S₂O₈ were added to 50 mL distilled water. The mixture was stirred 7 at 400 rpm for 48 h and then dried in an oven at 105 °C. After that, the catalyst was 8 calcined at 550 °C for 3 h in a tube furnace under air atmosphere in order to remove the 9 precursor. After grinding, the catalyst was stored in a dessicator before use. The $S_2O_8^{2-}$ -10 K₂O/TiO₂ modified by 5%Ni was prepared by the same method with an additional step of 11 adding 0.2477 g Ni(NO₃) $_2$ ·6H₂O to the distilled water. 12

13 Calculation of the volume ratio of the solvent

The volume ratio of the solvent was calculated through solubility coefficients. The solubility coefficient of Indulin AT is about 12 and other solubility coefficients can be easily got from open published literatures. According to the amount of substance of the two solvents (n_A and n_B), we can make the solubility coefficient of the mixed solvent equal 12. Then, we can get the volume ratio of the two solvents. The formula was as below:

$$n_A \times SC_A + n_B \times SC_B = 12 \tag{1}$$

$$n_A + n_B = 1 \tag{2}$$

22 SC_A and SC_B were the solubility coefficients of the two solvents.

23 n_A and n_B were the variables of amount of substance of the two solvents.

24 Depolymerization of lignin

20

25 Before the reaction, four kinds of solvents namely 30 mL 1,4-dioxane and 1 mL distilled water, 30 mL 1,4-dioxane and 6 mL methanol, 30 mL 1,4-dioxane and 0.5 mL 26 tetrahydrofuran or 30 mL 1,4-dioxane and 3 mL formic acid were respectively prepared. 27 The volume ratio of two solvents was calculated by dielectric constant. The 28 depolymerization reaction was conducted in a stainless steel autoclave reactor. 0.5 g of 29 lignin was first dissolved in a solvent under ultrasonic condition and 0.2 g of the catalyst 30 was added. The resulting mixture was transfered into the reactor. After passing a leak test 31 and completely purging out the air from the reactor, the reactor was pressurized to 4.0 32 MPa with H₂. The reactor was then heated to the reaction temperature for various times 33 (1 h, 6 h, 12 h, 24 h) under stirring at 900 rpm. The effects of different reaction times, 34 reaction temperatures, solvents and catalysts on lignin depolymerization were 35 investigated. At the end of a specified reaction time, the reactor was cooled down by 36 immersion in cold water, and the residual solid was separated from the liquid product by 37 filtration. For the liquid product, a tiny aliquot was set aside for GC and GC/MS analysis. 38

The monomers in liquid product were identified on a gas chromatography/mass spectrometry (GC/MS, QP2010S, Shimadzu, Japan) equipped with an Rtx-5MS column

 $(30 \text{ m} \times 25 \text{ mm} \times 0.25 \text{ µm})$. The oven temperature was programmed as 40 °C held for 3 41 min, ramped up to 180 °C with 4 °C/min and then to 260 °C with 10 °C /min. At last it 42 was held for another 10 min. Helium was the carrier gas. Quantitative analysis of the 43 monomer products was determined by GC-2010 gas chromatograph with a FID and a 44 WondaCAP5 column. The oven temperature was held at 50 °C for 3 min, ramped up to 45 250 °C at 10 °C/min and then held for another 10 min. The yield was calculated by using 46 acetophenone as an internal standard. The details of the internal standard method was 47 shown in SI. 48

49 All the reactions were done 3 times for the standard deviation analysis and get the 50 error bar.

51 The C, H, O, N and S contents (wt%) in the liquid product were measured by an 52 element analyzer (VarioELIII). The higher heating value (HHV) of the samples was 53 calculated by the Dulong's formula [45-46]:

54 HHV
$$(MJ/kg) = 0.335 \times C + 1.428 \times (H - O/8) - 0.145 \times N + 0.095 \times S$$

where C, H, O, N and S represent the weight percentages of carbon, hydrogen, oxygen,
nitrogen and sulphur respectively.

The liquid product was evaporated in a rotary evaporator at 40 °C, and was weighed and dissolved in 1 mL of acetone. The solution was then added dropwise into 200 mL petroleum ether with stirring at 400 rpm for 5 min. The sediment formed was separated from the supernatant by centrifuging at 10000 rpm for 5 min. The supernatant was evaporated with rotary evaporator at 40 °C. The remaining part of solution was weighed. 62 The yields of the liquid product, solid product, gas product, and PE-soluble product63 were calculated as follows:

64 % Yield of liquid product =
$$W_{LP}/W_L \times 100$$

65 % Yield of solid product =
$$(W_R - W_C)/W_L \times 100$$

66 % Yield of gas product = 100 - Yield of liquid product - Yield of solid product

67 % Yield of petroleum ether soluble = $W_P/W_L \times 100$

- W_{LP} : the weight of the liquid product
- $W_{\rm P}$: the weight of the PE-soluble product
- 70 W_R : the weight of the residual solid
- 71 W_L : the weight of the lignin (Indulin AT)
- 72 W_C : the weight of the catalyst

	Indulin AT
Klason lignin	88.8
Acid-soluble lignin	4.1
Total lignin	92.9
Arabinan	0.2
Galactan	0.56
Glucan	0.21
Xylan	0.56
Total Sugars	1.53
Ash	2.01

TABLE S1. Component compositions of Indulin ATTM (Wt %)

	Indulin AT
C (%)	65.5
H (%)	5.6
O (%)	25.2
N (%)	0.4
S (%)	3.3
MeO (%)	13.6

TABLE S2. Elemental and methoxyl contents

Substructures per 100 Ar*	Indulin AT	Pine milled wood lignin
Α: β-Ο-4'	8.2	41
Β: β-5'	1.1	9
C: Dibenzodioxocin	0.6	8
E: β-β' pinoresinol	1.2	2
F: β - β ' secoisolariciresinol	3.1	2
K: Enol ether	1.5	-
H: Stilbene	6.7	-
I: Coniferyl alcohol	0.3	4
J: G-CH(OH)-COOH	0.4	-
Primary aliphatic OH**	31	
Secondary aliphatic OH**	18	
Total aliphatic OH**	49	114
Phenolic OH**	63	28
OCH3**	68	95
Degree of condensation**	68	40

82 The monomer yield was calculated as follows (internal standard method):

- 83 Weight of one monomer = $\lambda * W_A / PA_A * PA_M$
- 84 W_A : the weight of acetophenone
- 85 PA_A: the peak area of acetophenone
- 86 PA_M : the peak area of the monomer
- λ : the correcting coefficient, calculated by the sample of the monomer through the above formula
- 89 There were some unknown peaks in the GC chromatograph. The correcting
- 90 coefficients of these unknowns cannot be determined. Therefore, these unknown peaks
- 91 were estimated using the average of all correcting coefficients of known monomeric
- 92 products [2]. All the correcting coefficients are shown in Table S4. The yield of total
- 93 monomers was calculated as follows:
- 94 Yield=Weight/Weight of lignin (0.5g)*100%
- 95 Yield of total monomers=Yield of all identified monomers+ Yield of all unknown96 monomers

97	Table S4	The	coefficients	of monom	iers

Monomer	Coefficient
Phenol	0.97
2-Methoxyphenol	0.91
Veratrole	0.87
4-Ethylphenol	0.84
4-Methylguaiacol	0.87
3,4-Dimethoxytoluene	0.90
4-Ethylguaiacol	0.90
Syringol	0.76
Eugenol	0.96
4-Propylguaiacol	0.98
Vanillina	0.69
Isoeugenol	0.69
Acetovanillone	0.52
2,6-Di-tert-butyl-4-methylphenol	1.28
4-Hydroxyl-3-Methoxypropiophenone	0.77
Homovanillic acid	0.21
Unknown monomer	0.83

100 **Table S5** The desorption of NH₃-TPD

	WA	SA	SSA
NH ₃ -TPD			
	/°C (μ mol·g ⁻¹)	/°C (μ mol·g ⁻¹)	$/^{\circ}C \ (\mu mol \cdot g^{-1})$
40%S ₂ O ₈ ² - 0%K ₂ O/TiO ₂	105-430 ^a (236.73) ^b	620-810 (157.03)	
40% S ₂ O ₈ ²⁻ -20%K ₂ O/TiO ₂	120-280 (39.115)	670-920 (211.13)	950-1100(794.71 ^d) + ^c
40% S2O82-40%K2O/TiO2	100-260 (122.54)		1020-1200(653.24 ^d)+ ^c
20% S ₂ O ₈ ²⁻ -40%K ₂ O/TiO ₂		620-790 (4304.8)	
$0\% S_2O_8^{2-40\%}K_2O/TiO_2$		540-745 (1924.5)	
20% S ₂ O ₈ ²⁻ -20%K ₂ O/TiO ₂	110-270 (104.72)		1060-1200(714.37 ^d)+ ^c

101 ^a Temperature range of the peak.

¹⁰² ^b Desorbed amount corresponding to the area of the peak.

- ¹⁰³ ^c The highest permitted temperature of the instrument is 1200 ^oC and the temperature was
 ¹⁰⁴ adjusted to 1100 ^oC to protect the instrument. It had no effect on the results.
- ¹⁰⁵ ^d It was the desorbed amount corresponding to the area of the partial peak.

107 **Table S6** The desorption of CO₂-TPD

	WB	SB	SSB
CO ₂ -TPD			
	$/^{\circ}C \ (\mu mol \cdot g^{-1})$	$/^{\circ}C (\mu mol \cdot g^{-1})$	/°C (μ mol·g ⁻¹)
40% S ₂ O ₈ ²⁻ - 0%K ₂ O/TiO ₂	190-370 ^a (87.618) ^b	620-830 (130.24)	
40% S ₂ O ₈ ² -20%K ₂ O/TiO ₂	200-360 (26.215)	680-870 (239.78)	940-1100(320.57°)+
40% S ₂ O ₈ ²⁻ -40%K ₂ O/TiO ₂	90-270 (56.294)		900-1100(367.59°)+
20% S ₂ O ₈ ²⁻ -40%K ₂ O/TiO ₂		580-765 (2123.1)	
0% S2O82-40%K2O/TiO2		540-730 (663.5)	
20% S ₂ O ₈ ²⁻ -20%K ₂ O/TiO ₂	90-410 (212.14)		930-1100(341.93°)+

108 ^a Temperature range of the peak.

¹⁰⁹ ^b Desorbed amount corresponding to the area of the peak.

¹¹⁰ ^c It was the desorbed amount corresponding to the area of the partial peak.

	S ₂ O ₈ ²	Ni-S ₂ O ₈ ²⁻ -	S ₂ O ₈ ²	Ni-S ₂ O ₈ ²⁻ -	S ₂ O ₈ ²⁻ -	Ni-S ₂ O ₈ ²
	K ₂ O/TiO ₂	K ₂ O/TiO ₂	K ₂ O/TiO ₂	K ₂ O/TiO ₂	K ₂ O/TiO ₂	K ₂ O/TiO ₂
	260 °C	260 °C	320 °C	320 °C	320 °C	320 °C
	1 h/%	1 h/%	1 h/%	1 h/%	12 h/%	12 h/%
Phenol	0.00±0.00	0.00±0.00	0.04±0.00	0.03±0.00	0.10±0.02	0.12±0.01
2-Methoxy-phenol	0.76±0.07	0.33±0.07	1.97±0.22	1.85±0.31	0.50±0.05	0.90±0.15
Veratrole	0.00 ± 0.00	0.14±0.03	$0.49{\pm}0.04$	0.05±0.01	0.37±0.02	0.39±0.08
4-Ethylphenol	0.00 ± 0.00	0.00 ± 0.00	0.20±0.02	0.04±0.01	0.44±0.06	0.08±0.03
4-Methyl-guaiacol	0.75±0.06	0.74 ± 0.08	0.88 ± 0.05	1.13±0.21	1.76±0.18	1.15±0.10
3,4-Dimethoxy-toluene	0.00 ± 0.00	0.00 ± 0.00	0.14±0.01	0.08±0.02	0.65±0.07	0.32±0.06
4-Ethyl-guaiacol	0.07±0.02	0.05±0.01	0.76±0.10	0.92±0.12	1.33±0.07	1.23±0.12
Syringol	0.00 ± 0.00	0.00 ± 0.00	0.15±0.02	0.22±0.05	1.38±0.18	0.52±0.13
Eugenol	$0.00{\pm}0.00$	0.03±0.00	0.16±0.01	0.16±0.05	0.04 ± 0.00	0.05±0.02
4-Propyl-guaiacol	0.00 ± 0.00	0.00 ± 0.00	0.19±0.04	0.32±0.03	0.08±0.03	0.36±0.06
Vanillina	0.27±0.05	0.36±0.02	0.06±0.01	0.23±0.08	0.13±0.01	0.18±0.04
Isoeugenol	0.22±0.06	0.28±0.06	0.22±0.03	0.38±0.07	0.33±0.05	1.16±0.13
Aceto-vanillone	0.17±0.05	0.14±0.02	0.08±0.02	0.31±0.08	0.52±0.01	0.36±0.06
2,6-Di-tert-butyl-4- methylphenol	0.04±0.01	0.03±0.00	0.06±0.01	0.06±0.02	0.59±0.07	0.22±0.02
4-Hydroxyl-3- Methoxypropiophenone	0.04±0.01	0.00±0.00	0.04±0.01	0.09±0.02	0.04±0.02	0.10±0.01
Homovanillic acid	0.70±0.09	1.00±0.12	0.38±0.10	1.66±0.23	0.63±0.07	0.66±0.03
Total unknown monomers/%	6.78±0.17	5.43±0.29	7.56±0.41	7.43±0.26	20.07±0.64	17.17±0.52
Total identified monomers	3.01±0.12	3.10±0.09	5.81±0.35	7.52±0.42	8.89±0.41	7.80±0.50
Total monomers	9.79±0.22	8.53±0.37	13.37±0.62	14.95±0.57	28.96±0.72	24.97±0.83

Table S7 The GC results of monomer products

			Reacti	Denation	Yield of	Yield of
Ref.	Lignin	Catalyst	on	Keaction	liquid	monomer
			time	temperature	products	products
[3/]	Organosolv	Pd/C + CrCl	5 h	280 °C	78 2%	20.8%
[]+]	lignin		5 11	200 C	/0.2/0	20.870
[25]	Organosolv	Ni/7rD	4 h	270 °C	87 20/	15 10/
[33]	lignin	111/211	4 11	270 C	07.570	13.170
[27]	Organosolv	NaOH +	4 h	260 °C	86 670/	12 60%
[37]	lignin	Ru/C	4 11	200 C	80.0770	12.0970
[29]	Organosolv	Ru/C +	2 h	250 °C	71 50/	17 510/
[30]	lignin	MgO/ZrO ₂	5 11	330 C	/1.370	17.3170
[29]	Kraft lignin	Ru/C +	2 h	250 °C	81 7 0/	10 7%
[30]	Klan nghin	MgO/ZrO ₂	5 11	550 C	01.770	10.770
This	Kraft lignin	$S_2O_8^{2-}$ -	10 h	220 °C	82 760/	28 06%
work	Kian ngulli	K ₂ O/TiO ₂	12 11	520 C	03.7070	20.70/0

Fig. S1 (a) SEM images of TiO₂. (b) SEM images of $S_2O_8^{2-}K_2O/TiO_2$. (c) EDS images of $S_2O_8^{2-}K_2O/TiO_2$



- 133 **Fig. S2** The adsorption of NH₃-TPD. (a) (1) Blank TiO₂. (2) 40% $S_2O_8^{2-}-0\%K_2O/TiO_2$.
- 134 (3) 40% $S_2O_8^{2-20\%}K_2O/TiO_2$. (4) 40% $S_2O_8^{2-40\%}K_2O/TiO_2$. (b) (1) Blank TiO_2. (2)
- $135 \quad 0\% \ S_2O_8^{2-}-40\% K_2O/TiO_2. \ (3) \ 20\% \ S_2O_8^{2-}-40\% K_2O/TiO_2. \ (4) \ 40\% \ S_2O_8^{2-}-40\% K_2O/TiO_2.$
- 136 (c) 20% $S_2O_8^2$ -20% K_2O/TiO_2 .
- 137 (a) (1) Blank TiO₂. (2) 40% S₂O₈²-0%K₂O/TiO₂. (3) 40% S₂O₈²-20%K₂O/TiO₂. (4) 40%
 138 S₂O₈²-40%K₂O/TiO₂.



(b) (1) Blank TiO₂. (2) 0% $S_2O_8^{2-40\%}K_2O/TiO_2$. (3) 20% $S_2O_8^{2-40\%}K_2O/TiO_2$. (4) 142 40% $S_2O_8^{2-40\%}K_2O/TiO_2$.





- 148 **Fig. S3** The adsorption of CO₂-TPD. (a) (1) Blank TiO₂. (2) 40% $S_2O_8^{22}-0\%K_2O/TiO_2$.
- 149 (3) 40% $S_2O_8^{2-20\%}K_2O/TiO_2$. (4) 40% $S_2O_8^{2-40\%}K_2O/TiO_2$. (b) (1) Blank TiO_2. (2)
- 150 0% $S_2O_8^{2-}40\%K_2O/TiO_2$. (3) 20% $S_2O_8^{2-}40\%K_2O/TiO_2$. (4) 40% $S_2O_8^{2-}40\%K_2O/TiO_2$.
- 151 (c) 20% $S_2O_8^2$ -20% K_2O/TiO_2 .
- 152 (a) (1) Blank TiO₂. (2) 40% $S_2O_8^{2-}-0\%K_2O/TiO_2$. (3) 40% $S_2O_8^{2-}-20\%K_2O/TiO_2$. (4) 40%
- 153 $S_2O_8^2$ -40%K₂O/TiO₂.



(b) (1) Blank TiO₂. (2) 0% $S_2O_8^{2-}40\%K_2O/TiO_2$. (3) 20% $S_2O_8^{2-}40\%K_2O/TiO_2$. (4) 157 40% $S_2O_8^{2-}40\%K_2O/TiO_2$.





163 Fig. S4 XRD patterns of the catalysts





164

- 165 The JCPDS file number for the peaks are as below.
- 166 Anatase tetragonal TiO₂^(a) JCPDS File No.21-1272
- 167 K₂Ti₂O₅^(b) JCPDS File No.13-0448
- 168 K₂Ti₈O₁₇^(c) JCPDS File No.41-1100
- 169 $K_2 Ti_6 O_{13}$ ^(d) JCPDS File No.40-0403
- 170 K₂SO₄ ^(e) JCPDS File No.05-0613
- 171 Brookite orthorhombic TiO₂^(f) JCPDS File No.29-1360

173 Fig. S5 The result of GC-MS Reaction conditions: 0.5 g lignin, 0.2 g 40% $S_2O_8^{2-}$ -

174 $40\%K_2O/TiO_2$, 4 MPa H₂, 320 °C, 12 h, 900 rpm.



176 References

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