


Supporting Information

Effect on the Antioxidant Capacity of Polypropylene by Vanillin:

A Natural Antioxidant Extracted from Cotton Stalk Lignin

Mingyu He, Han Dong, and Mamatjan Yimit[†] 

Key laboratory of Oil and Gas Fine Chemicals, Ministry of Education and Xinjiang Uyghur Autonomous Region,
College of Chemical Engineering, Xinjiang University, Urumchi 830046, China

Keywords: vanillin, UV photocatalysis, polypropylene, antioxidant capacity, mechanical properties

[†]Corresponding Author: Mamatjan Yimit

E-mail: mjan10@xju.edu.cn

Tel: (+) +86-181-1919-0465

Extraction of LG from cotton stalk

Firstly, 5 g collected cotton stalk powder was pretreated with 30 mL toluene/ethanol (2:1, V/V) solution for 8 hours. Then, 20 mL ionic liquid was added under the ultrasonic assisted environment for 40 minutes to obtain black liquid, which was centrifuged for several hours and then filtered to obtain crude LG products. Finally, the experiment used LG was centrifugally purified by 1, 4-dioxane for 8 hours. After centrifugation, the ionic liquid could be separated and recycled for further use.

Extraction of VA by UV photocatalysis from LG

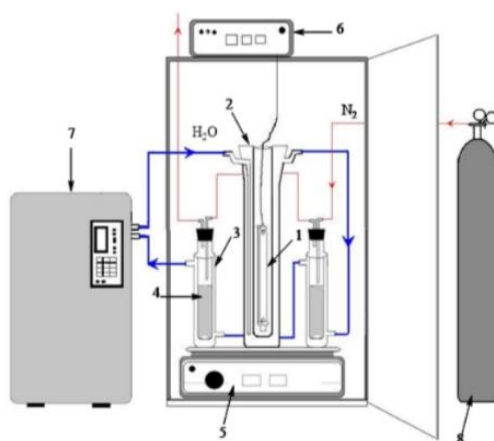


Figure S1 Photochemical reaction apparatus: ①UV lamp; ②quartz cylinder; ③quartz test tube; ④reactant; ⑤magnetic stirrer; ⑥power supply; ⑦temperature control device; ⑧N₂

Orthogonal test was designed to determine the optimal extraction process, which was shown in Table S1 and

Table S2. Four factors of VA production rate influence were 2.39, 2.95, 2.41, 1.86, respectively, which showed the influence degree was B>C>A>D. The optimum extracting conditions is A₂B₃C₁D₂, for the reaction temperature of 55 °C, the UV lamp wattage of 1000 W, the reaction time of 4 h, and the catalyst mass ratio of 15 wt%. Under the condition, the VA extraction yield was 89.01%.

Table S1 Factors and levels of orthogonal experiment

Level	A (Temperature/°C)	B (Wattage/W)	C (Time/h)	D (m _{catalyst} :m _{LG} /%)
1	45	300	4	10
2	55	500	6	15
3	65	1000	8	20

Table S2 The orthogonal test results of VA extracted by UV

No.	Factor				Extraction
	A	B	C	D	yield%
1	1	1	1	1	83.18
2	1	2	2	2	85.65
3	1	3	3	3	84.30
4	2	1	2	3	84.39
5	2	2	3	1	82.78
6	2	3	1	2	89.01
7	3	1	3	2	85.02
8	3	2	1	3	87.14
9	3	3	2	1	88.15
K1	253.13	252.59	259.33	254.11	
K2	256.18	255.57	258.19	259.68	
K3	260.31	261.46	252.10	253.83	
k1	84.38	84.20	86.44	84.70	
k2	85.39	85.19	86.06	86.56	
k3	86.77	87.15	84.03	85.28	
R	2.39	2.95	2.41	1.86	

Characterization between extracted VA and standard VA

The ¹H NMR and ¹³C NMR spectra of standard VA and extracted VA was shown in Figure S2, and the analyzed results of each hydrogen atom and carbon atom attribution were shown in Table S3. In the hydrogen spectrum, the displacement of 9.81 ppm belonged to the hydrogen atom on the aldehyde group, the displacement of 7.02~7.43 ppm belonged to 6 hydrogen atoms on the benzene ring, the displacement of 6.37 ppm and 6.36

ppm belonged to the hydrogen atom on the phenolic hydroxyl group, and the displacement of 3.95 ppm belonged to the 3 hydrogen atoms on the ether group. In the carbon spectrum, the displacement of 191.42 ppm and 191.38 ppm belonged to the aldehyde group carbon atom, the displacement of 152.12~109.04 ppm and 152.08~109.01 ppm belonged to 6 carbon atoms of the benzene ring, and the displacement of 56.02 ppm and 56.04 ppm belonged to the etheryl carbon atom.¹ The results showed that the NMR spectrum of the extracted VA were basically the same as those of the standard sample, indicating that the purity and structure of the extracted VA had good selectivity.

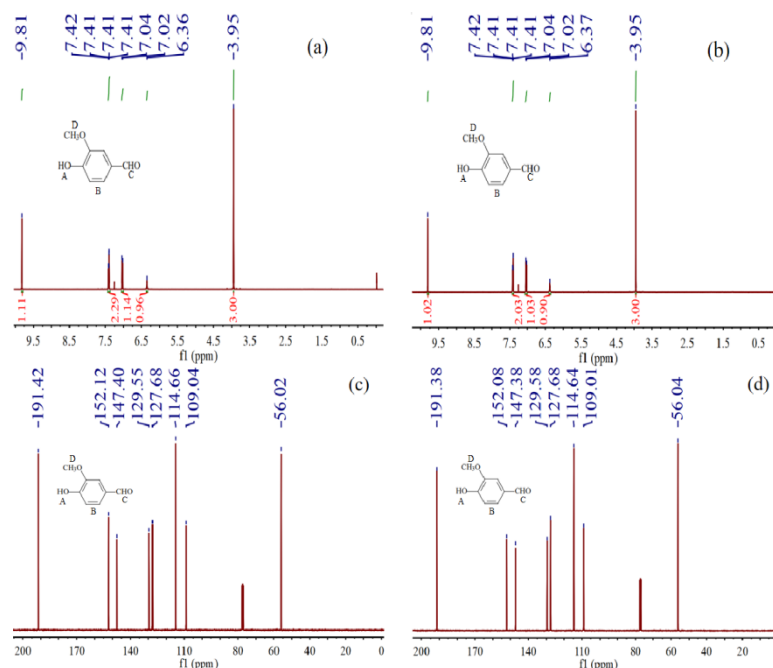


Figure S2 The NMR spectrum: (a) ¹H NMR of standard VA; (b) ¹H NMR of extracted VA; (c) ¹³C NMR of standard VA; (d) ¹³C NMR of extracted VA

Table S3 The attribution analysis of hydrogen and carbon atoms of VA

Displacement/ppm ^(a, b)	Belonging /Hydrogen	Displacement/ppm ^(c, d)	Belonging /Carbon
9.81 ^(a, b)	1 Hydrogen of C position	191.42 ^(c) , 191.38 ^(d)	1 Carbon of A p osition
7.02~7.43 ^(a, b)	3 Hydrogen of B position	152.12~109.04 ^(c)	6 Carbon of B p osition
6.36 ^(a) , 6.37 ^(b)	1 Hydrogen of A position	152.08~109.01 ^(d)	

3.95 ^(a, b)	3 Hydrogen of D position	56.02 ^(c) 、56.04 ^(d)	1 Carbon of D p osition
------------------------	-----------------------------	--	----------------------------

The structure and thermal properties of VA were shown in Figure S3. As shown in Figure S3(a), there was almost no difference in the position of the characteristic functional group peak in FTIR spectrum between the extracted VA and the standard VA, which was basically consistent with the industrial band, indicating high extraction purity and good selectivity. Other than, the VA sample had abundant functional groups, the characteristic peak of hydroxyl group (-OH) at 3414 cm⁻¹ was strong and wide, indicating the number of hydroxyl groups (-OH) was large. The characteristic peaks of functional groups in VA were mainly concentrated in the fingerprint bands at 1600~600 cm⁻¹. The band near 1655 cm⁻¹ was the absorption peak of C=O stretching vibration of conjugated carbonyl group. The absorption bands at 1524 cm⁻¹ could be attributed to the C=C stretching vibration of benzene ring skeleton. As for the band at 1458 cm⁻¹, it was the C-H bond characteristic peak of methyl bending vibration, whereas the band at 1374 cm⁻¹ was the C-H bond bending vibration of aromatic ring. The band observed near 825 cm⁻¹ was assigned to the out of plane bending vibration of aromatic ring.² As shown in Figure S3(b), the XRD patterns of extracted VA and standard VA were basically consistent. The main diffraction peak of (110) crystal plane of VA was found near 2θ=13.6°. The peak area of extracted VA was slightly smaller than that of standard sample, indicating that the crystallinity of the extracted sample was not as excellent as that of the standard sample, which might be caused by the destruction of the crystal structure by organic reagents in the purification process.³ The results of XRD showed that the crystal shape and structure of the extracted VA were basically the same as that of the standard sample, and there was no significant difference in structure.

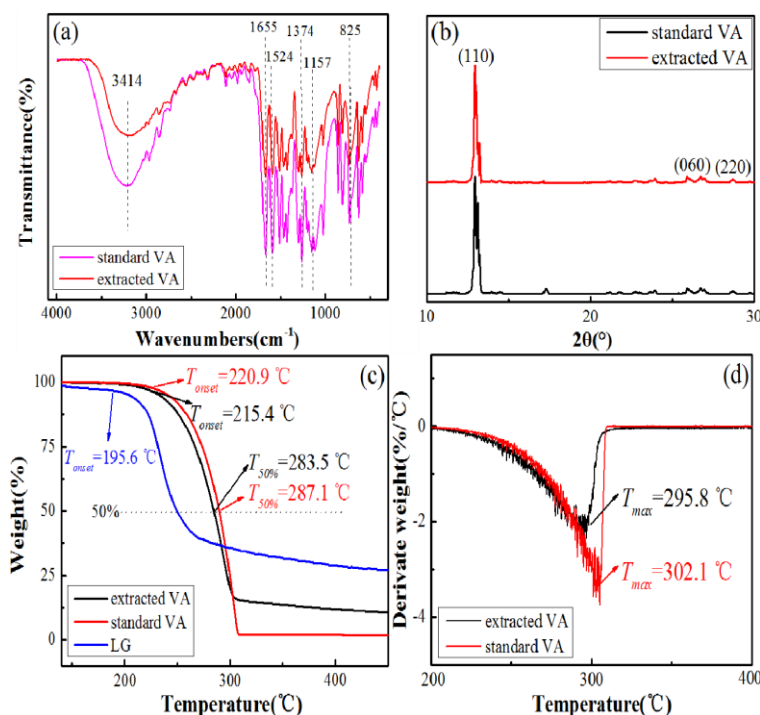


Figure S3 The structure and thermal properties of VA: (a) FTIR; (b) XRD; (c) TG; (d) DTG

As shown in Figure S3(c) and S3(d), the thermal properties of VA were studied by TGA. The initial temperature of main thermal decomposition stage (T_{onset}) and the maximum thermal decomposition rate temperature (T_{max}) were measured. Compared with LG, VA had a higher T_{onset} , but when the temperature exceeded 300 °C, the residual mass of VA was much lower than that of LG. This was because LG was a three-dimensional network amorphous macromolecular compound with strong intermolecular force, high Van Der Waals force and hydrogen bonding, so it had good thermal stability at high temperature.⁴ After UV degradation, however, VA had become a small molecule compound with reduced intramolecular interaction, and its thermal stability at high temperature was inferior to that of LG. The T_{onset} and T_{max} of the standard VA were about 220.9 °C and 302.1 °C, respectively, while the T_{onset} and T_{max} of extracted VA was 5.5 °C and 6.3 °C lower than that of standard VA, respectively, which proved that the thermal properties of the extracted VA were not significantly reduced, which was consistent with the characterizations of FTIR, NMR and XRD.

References

- [R1]Brisa P.; Louis-Charles D. M.; Ricard G. V.; Tania G. Characterization of Polysulfone and Polysulfone/Vanillin Microcapsules by ¹H NMR Spectroscopy, Solid-State ¹³C CP/MAS-NMR Spectroscopy, and N₂ Adsorption-Desorption. *ACS Appl. Mater. Inter.* **2011**, 3, 4420-4430.
- [R2]Tang B.; Yue T. X.; Wu J. S.; Dong Y. M.; Ding Y.; Wang H. J. Rapid and sensitive spectrofluorimetric determination of trace amount of Cr(III) with o-vanillin-8-aminoquinoline. *Talanta*. **2004**, 64, 955-960.
- [R3]Liu G. F.; Shi T. S.; Zhao Y. N. Infrared and Raman spectra of complexes about rare earth nitrate with Schiff base from o-vanillin and 1-naphthylamine. *J. Mol. Struct.* **1997**, 412, 75-81.
- [R4]Ando D.; Nakatsubo F.; Yano H. Thermal stability of lignin in ground pulp (GP) and the effect of lignin modification on GP's thermal stability: TGA experiments with dimeric lignin model compounds and milled wood lignins. *Holzforschung*. **2019**, 73, 493-499.