ARTICLE

# Supporting Information

## Hemicellulose integration enhances lignin valorization to sustainable high-performance potassium fulvic-like fertilizer

Kaixia Liang,[a] Jiale Yu,[a] Jialong Lv,[d] Qi Tang,[a] Zhiqian Meng,[a] Meng Liu,[a] Zhimin Chen,[ac] Lihang Guan,[ac] Qinqin Xia,[a] Shuo Dou,[a] Xiaoxue Song,[b] Haipeng Yu*[a] and Yongzhuang Liu*[ac]

[a]State Key Laboratory of Woody Oil Resources Utilization; Key Laboratory of Bio-based Material Science and Technology of Ministry of Education, Northeast Forestry University, Harbin 150040, China

[b]College of Home and Art Design, Northeast Forestry University, Harbin 150040, China

[c]School of Future Technology, Northeast Forestry University, Harbin 150040, China

[d]Tangshan Green Chemical Industry Technology Research Institute, Tangshan Sanyou Chemical Industry Co., Ltd，Tangshan 063305, China

E-mail: lyz@nefu.edu.cn; yuhaipeng20000@nefu.edu.cn

## Supporting Methods

According to the chemical industry standard HG/T 5334-2018 of China, five key indicators of potassium fulvic-like (KFA) substances were tested to determine compliance, including FA content, $K_2O$ content, water-insoluble matter, moisture content, and pH value.

## *1 Quantitative Method for Fulvic Acid*

The quantitative analysis of FA was still conducted according to the potassium dichromate oxidation method specified in the HG/T 5334-2018 standard. The specific steps were as follows.

Extraction of FA: A sample of m = 0.2 g was weighed, to which 100 ml of deionized water was added. The mixture was immersed in a boiling water bath for 2 hours. After cooling and filtration, the filtrate was diluted to a final volume of 250 ml.

Preparation of solution to be tested: 100 ml of test solution was accurately measured and transferred to a beaker, $H_2SO_4$ solution (4 mol $L^{-1}$) was acidified to pH = 1.5, left to stand and filtered and the filtrate was diluted to 250 ml.

Removal of metal ions: 50 ml of the acidified and diluted filtrate was taken, to which 7.5 ml of $Na_3PO_4$ solution (50 g $L^{-1}$) was added. After standing and filtration, the solution was diluted to a volume of 100 ml.

Oxidation: 10 ml of the solution to be tested was taken, and 5 ml of $K_2Cr_2O_7$ solution (0.4 mol $L^{-1}$) along with 15 ml of $H_2SO_4$ were added. The mixture was then heated and oxidized in a boiling water bath for 30 minutes.

Titration: The oxidized solution was cooled to room temperature. Then, 70 ml of water and 3 drops of the ferroin indicator solution (o-phenanthroline-ferrous ammonium sulfate mixture) were added. The mixture was titrated with a 0.1 mol $L^{-1}$ $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ standard solution until the endpoint was reached. V0 was the volume of ferrous ammonium sulfate consumed for oxidizing potassium dichromate in the blank sample, while V1 was the volume of ferrous ammonium sulfate consumed for oxidizing the remaining potassium dichromate in the control experiment (containing FA).

The mass fraction of fulvic acid content (on a dry basis) $FA_d$, expressed in %, was calculated using the following formula:

$$FA_d = \frac{37.5(V0 - V1)c\ (Fe^{2+})}{km}$$

$c(Fe^{2+})$**:** The concentration value of the ferrous ammonium sulfate standard titration solution, in mol $L^{-1}$.

k: The carbon coefficient for fulvic acid (bio-derived fulvic acid is calculated using 0.45).

m: Mass of the sample weighed after the hydrothermal humification reaction.

**Comparative analysis of the Chinese industry standard (HG/T 5334-2018) and classical methods for the isolation and purification of humic and fulvic acids:** The classical methods established by Thurman and Malcolm ,[S1] Swift ,[S2] André Van Zomeren et al. ,[S3] and Lamar et al.[S4] each possess distinctive features and demonstrate significant scientific value and broad applicability within their respective research fields. However, these methods are generally characterized by complex and labor-intensive procedures, placing high demands on experimental apparatus, specialized resin consumables, and the expertise of operators, thereby limiting their direct application as routine analytical tools under typical laboratory conditions. While we fully acknowledge the scientific merit of these classical approaches, the present study focuses on the standardized performance evaluation of the resulting products and is subject to certain limitations in experimental equipment and configuration. Therefore, we adopted the current Chinese industry standard, HG/T 5334-2018, as the basis for evaluation. This standard also draws upon the foundational studies of Cai et al. [8] and Kong et al. ,[29] ensuring the reliability of the analytical results. Notably, the accuracy of the method was validated using an FA analytical standard, yielding results consistently within the range of 97.67% to 99.43% (Fig. S7). Consequently, based on the existing research foundation and the experimental validation conducted in this study, the reliability of the methodology employed herein is substantiated.

## *2 Quantitative Method for $K_2O$*

The quantitative analysis of $K_2O$ was performed according to the potassium tetraphenylborate gravimetric method specified in the aforementioned standard. The specific steps are as follows.

Extraction of $K_2O$: A sample of m = 5 g was weighed, to which 150 ml of deionized water was added. The mixture was heated to boiling for 30 minutes, and after cooling, was diluted to a final volume of 250 ml.

Treatment of the test solution: 25 ml of the sample solution was taken, and 5 ml of bromine water (mass fraction 5%) was added. The mixture was heated to boiling until colorless. After cooling, it was filtered and washed. Then, 20 ml of EDTA solution (40 g $L^{-1}$) and 3 drops of phenolphthalein indicator (5 g $L^{-1}$ ethanol solution) were added and mixed well. Sodium hydroxide solution (400 g $L^{-1}$) was added dropwise until a red color appeared, followed by an additional 1 ml excess. The mixture was heated to boiling for 15 minutes and then cooled.

Precipitation and Filtration: Sodium tetraphenylborate solution (15 g $L^{-1}$) was added dropwise to the test solution under continuous stirring. After the appearance of a white precipitate, an additional 7 ml was added as an excess, and the mixture was allowed to stand for 15 minutes. The precipitate was filtered using a tared glass crucible filter (No. 4) and washed sequentially with sodium tetraphenylborate washing solution (1.5 g $L^{-1}$) and deionized water. The mass of the glass crucible filter was recorded as m2.

Drying: The crucible containing the precipitate was transferred to a drying oven set at 120 ± 5 °C and dried for 1.5 hours. After cooling to room temperature, it was weighed. The mass of the crucible containing the potassium tetraphenylborate precipitate was recorded as m1.

The potassium content $w_1$ was calculated according to the following formula:

$$w_1 = \frac{[(m1 - m2) - (m3 - m4)] \times 0.1314}{m \times {}^{25}\!/_{250}} \times 100$$

m3: The mass of the crucible containing the potassium tetraphenylborate precipitate in the blank experiment, in grams;
m4: The mass of the crucible in the blank experiment, in grams.
0.1314: The conversion factor from potassium tetraphenylborate mass to $K_2O$ mass.
25: The volume of the sample solution taken, in ml.
250: The total volume of the sample solution, in ml.

## 3 Determination of Water-Insoluble Matter Content

A sample of m = 1 g was weighed, and 100 ml of deionized water was added. The mixture was heated in a boiling water bath for 30 minutes. After cooling, it was subjected to vacuum filtration, and the precipitate was transferred to a drying oven set at 110 ± 5 °C to dry until constant weight was achieved.
The water-insoluble matter content $W_d$ (on a dry basis), expressed as a mass fraction (%), was calculated using the following formula:

$$W_d = \frac{m1}{m \times \left(\frac{100 - W_{ad}}{100}\right)} \times 100$$

m1: The mass value of the water-insoluble matter, in grams.
m: The mass value of the sample, in grams.
$W_{ad}$: The moisture content of the sample, expressed in %.

## 4 Determination of Moisture Content

A sample of m = 2 g was weighed and placed in a vacuum drying oven set at 50 ± 2 °C to dry for 2 hours ± 10 minutes. After cooling to room temperature, it was weighed.
The free water content $W_{ad}$, expressed as a mass fraction (%), was calculated using the following formula:

$$W_{ad} = \frac{m - m1}{m} \times 100$$

m: the mass value of the sample before drying, in grams;
m1: the mass value of the sample after drying, in grams.

## 5 Determination of pH Value

A sample of 1 g was weighed, and 100 ml of water was added. The mixture was stirred at room temperature for 10 minutes, and the pH value of the test solution was measured using a pH meter.

## Supporting Figures

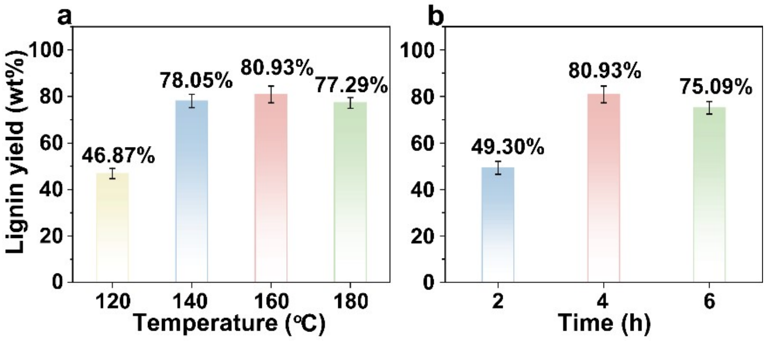

**Fig. S1** Separation efficiency of poplar lignin extraction via basic ethanol systems(NEL-1/1). (a) Fixed time (4 h), varying temperature (120-180°C). (b) Fixed temperature (160°C), varying time (2-6 h).

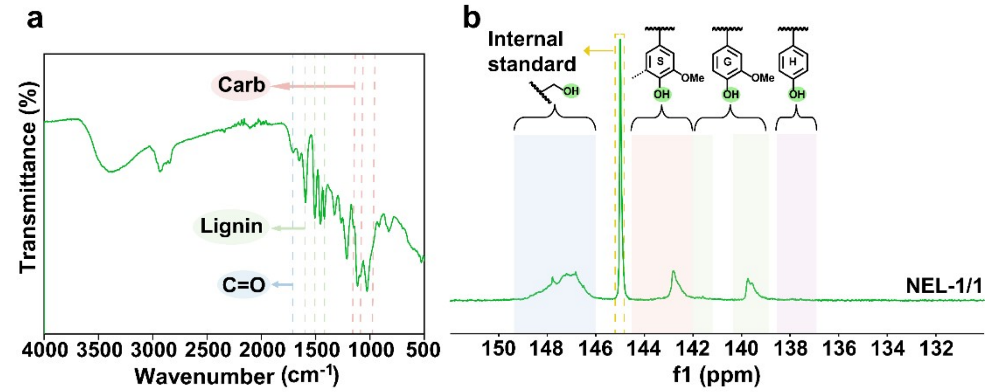

**Fig. S2** Structural analysis of lignin in basic ethanol systems(NEL-1/1). (a) FT-IR spectra. (b) $^{31}$P NMR spectra.

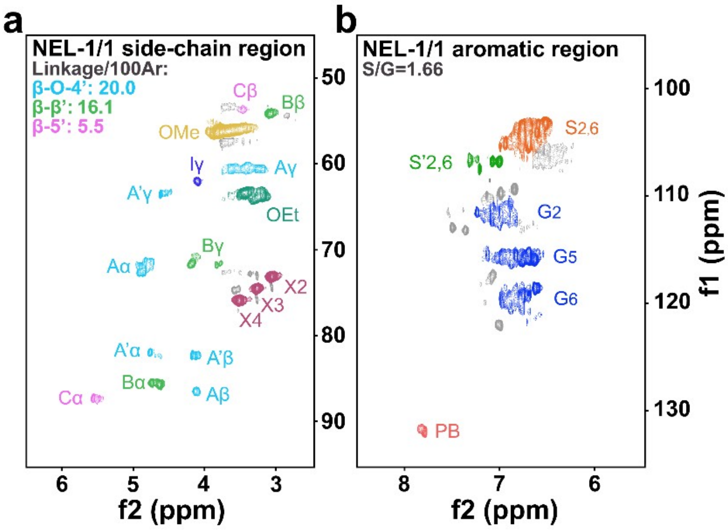

**Fig. S3** 2D HSQC NMR structural features of lignins from basic ethanol systems(NEL-1/1). (a) Side-chain region; (b) Aromatic region.

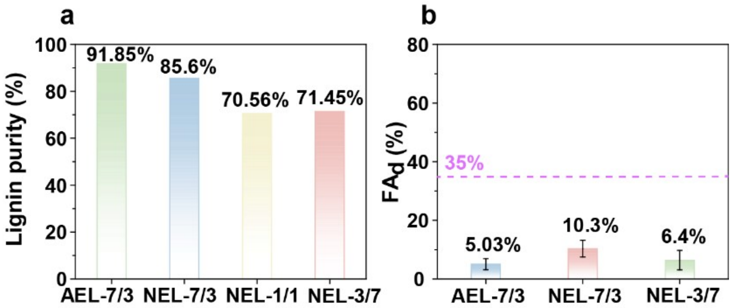

**Fig. S4** Purity (a) and fulvic acid content (b) of lignin from different systems.

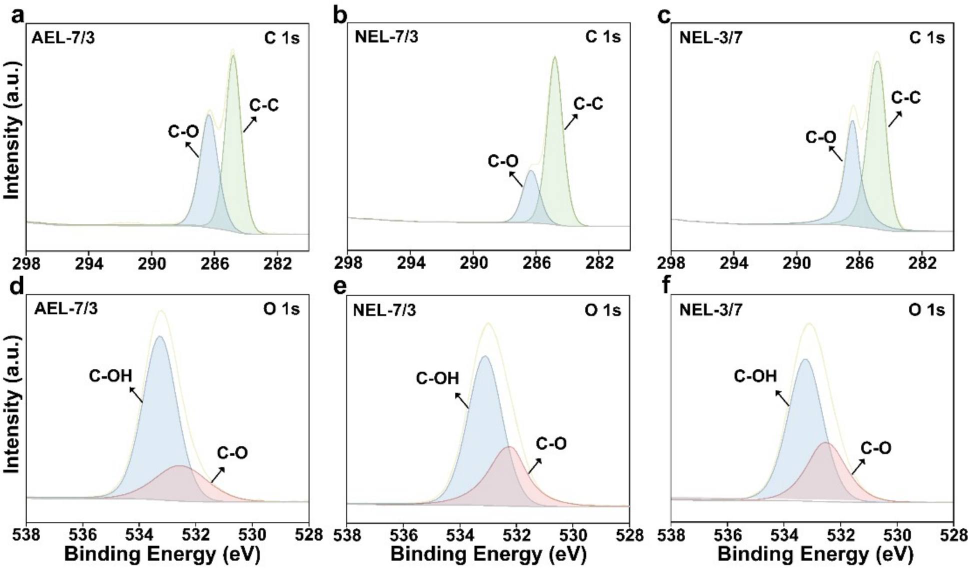

**Fig. S5** XPS spectra illustrating the structural characteristics of lignin. (Focus on C 1s and O 1s regions showing key functional group changes).

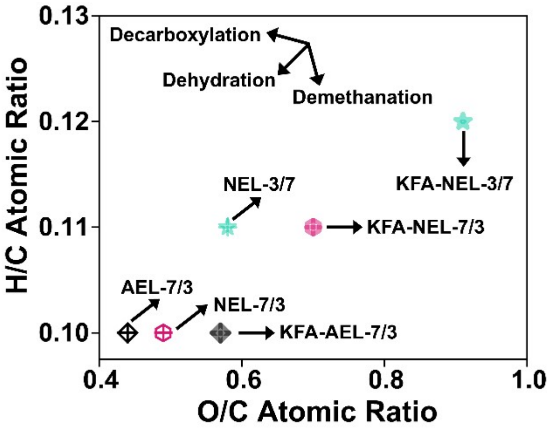

**Fig. S6** Van Krevelen diagram of lignin and KFA from different systems.

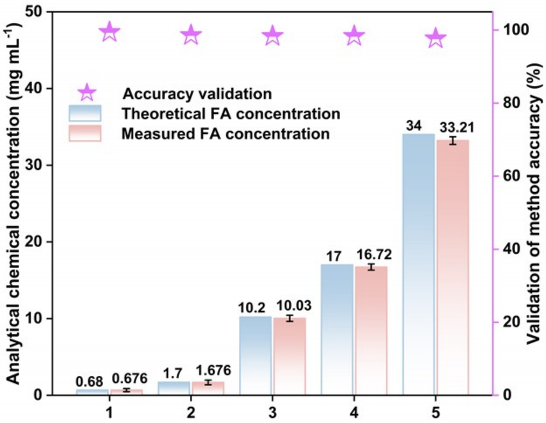

**Fig. S7** The accuracy of the analytical method was validated using an FA analytical chemical (85% purity) as a reference. (Accuracy of the method = Measured FA concentration / Theoretical FA concentration)

## Supporting Tables

**Table S1** Weight-average molecular weight (Mw), number-average molecular weight (Mn), and polydispersity index (Mw/Mn) of lignin from different systems.

| | Lignin samples | | | |
|---|---|---|---|---|
| | AEL-7/3 | NEL-7/3 | NEL-1/1 | NEL-3/7 |
| Mw | 1977 | 1474 | 1071 | 1559 |
| Mn | 552 | 749 | 458 | 883 |
| Mw/Mn | 3.6 | 2.0 | 2.3 | 1.8 |

**Table S2** Quantitative analysis of lignin (NEL-1/1) functional groups by $^{31}$P NMR.

| Lignin sample | Aliphatic OH mmol/g | Phenolic OH, mmol/g | | | COOH mmol/g |
|---|---|---|---|---|---|
| | | Syringyl | Guaiacyl | p-hydroxy phenyl | |
| NEL-1/1 | 3.65 | 1.26 | 1.03 | / | / |

**Table S3** Elemental analysis (EA) of lignin and KFA from different systems.

| Sample | C (%) | H (%) | O (%) | H/C | O/C |
|---|---|---|---|---|---|
| AEL-7/3 | 64.95 | 6.35 | 28.70 | 0.1 | 0.44 |
| NEL-7/3 | 63.01 | 6.36 | 30.63 | 0.1 | 0.49 |
| NEL-3/7 | 59.34 | 6.31 | 34.35 | 0.11 | 0.58 |
| KFA-AEL-7/3 | 59.19 | 5.96 | 33.80 | 0.1 | 0.57 |
| KFA-NEL-7/3 | 54.35 | 6.03 | 37.82 | 0.11 | 0.71 |
| KFA-NEL-3/7 | 46.74 | 5.75 | 45.08 | 0.12 | 0.91 |

**Table S4** An investigation into the FA content of lignins from different systems and the specific roles of various reagents in the humification process (using NEL-7/3 as a case study).

| Project/Sample | FA Content (dry basis, %) |
|---|---|
| Bio-based potassium fulvate (Standard) | ≥ 35 % |
| Mineral based potassium fulvate (Standard) | ≥ 50 % |
| AEL-7/3 | 5.03 % |
| NEL-3/7 | 6.4 % |
| NEL-7/3 | 10.3 % |
| NEL-7/3+KOH | 19.98 % |
| NEL-7/3+KOH+HO-$(CH_2O)_n$-H | 16.08 % |
| NEL-7/3+KOH+$Na_2S_2O_5$ | 37.00 % |
| KFA-NEL-7/3 | 49.44 % |

**Table S5** Compliance analysis of Kraft lignin quality based on HG/T 5334-2018 standard

| Project/Sample | FA Content (dry basis, %) | $K_2O$ Content (dry basis, %) | Water-Insoluble Matter (dry basis, %) | Moisture (%) | pH (1:100) |
|---|---|---|---|---|---|
| Bio-based potassium fulvate (Standard) | ≥ 35 % | ≥ 5 % | ≤ 5 % | ≤ 5 % | 4.0~ 7.0 |
| Mineral based potassium fulvate (Standard) | ≥ 50 % | ≥ 8 % | ≤ 8 % | ≤ 15 % | 4.0~ 11.0 |
| Kraft lignin | 21.55 % | / | / | / | / |
| KFA-$Na_2SO_3$ | 41.12 % | 11.17 % | 5.7 % | 1.94 % | 5.0 |
| KFA-$Na_2S_2O_5$ | 44.46 % | 11.20 % | 0.9 % | 3.18 % | 5.5 |
| KFA-$Na_2SO_4$ | 21.55 % | 11.29 % | 1.2 % | 2.58 % | 5.2 |
| KFA-$Na_2S_2O_5$ + hemicellulose | 52.82 % | 11.05 % | 2.16% | 0.03 % | 5.8 |

**Table S6** Comparative analysis of the mass/cost balance of the reagents and raw materials for 1t-scale KFA production in this study versus that of commercial KFA.

| Name | Dosage/Yield (t) | Unit price (￥/t )$^a$ | Cost (￥) |
|---|---|---|---|
| Kraft lignin | 1t | 3500 | 3500 |
| KOH | 0.115 | 6200-7200 | 770.5 |
| $Na_2S_2O_5$ | 0.0675 | 3200-4000 | 243 |
| $HO\text{-}(CH_2O)_n\text{-}H$ | 0.027 | 3500 | 94.5 |
| Hemicellulose | 0.01 | 7000 | 70 |
| **KFA-Kraft lignin** | 1.2195 | / | **4678**<br>**(3843￥/t)** |
| Commercial bio-based KFA | 1t | 4400-4700<br>(Average 4550) | - |
| Commercial mineral-based KFA | 1t | 9000-9800<br>(Average 9400) | - |

a: All the raw materials and chemicals cost are sourced from Alibaba (https://www.1688.com/)

## Supporting Information References

S1. E. M. Thurman and R. L. Malcolm, Preparative Isolation of Aquatic Humic Substances, *Environ. Sci. Technol.*, 1981, **15**, 463–466.

S2. R. S. Swift, Organic Matter Characterization *Soil Science Society of America Inc.*, 1996, DOI: https://doi.org/10.2136/SSSABOOKSER5.3.C35, 1011–1069.

S3. André Van Zomeren and R. N. J. Comans, Measurement of Humic and Fulvic Acid Concentrations and Dissolution Properties by a Rapid Batch Procedure, *Environ. Sci. Technol.*, 2007, **41**, 6755–6761.

S4. R. Lamar, D. Olk, L. Mayhew and P. Bloom, A New Standardized Method for Quantification of Humic and Fulvic Acids in Humic Ores and Commercial Products, *J. AOAC Int.*, 2014, **97**, 721–730.