

Upgrading Paper-Grade Bleached Hardwood Pulp Towards Dissolving Pulp Using γ -Valerolactone

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γ -Valerolactone (GVL) is a promising biomass-based platform compound that can be used for the removal of hemicellulose in pulp. In this study, a paper-grade pulp was treated using GVL to generate dissolving pulp for viscose production. The GVL concentration, treatment temperature, and reaction time had significant effect on the hemicellulose dissolution. The dissolving pulp with α -cellulose content of 92.3% and hemicellulose content of 5.45% was achieved with 60% GVL at 120 °C for 2 h. The Fock reactivity and intrinsic viscosity of the obtained dissolving pulp were 54.6% and 595 mL/g, which is comparable with the commercial product. In addition, GVL spent liquor was also recycled and reused to upgrade paper-grade pulp. By using purified recycled GVL to treat original pulp, the Fock reactivity of pulp was improved, and the cellulose content of as-prepared upgraded pulp increased to 92.1%, which was close to the cellulose content of dissolving pulp obtained from fresh GVL solution, while the intrinsic viscosity decreased significantly to 598 mL/g. Therefore, the efficient reuse of GVL not only ensured the high quality of dissolving pulp, but it also saved production costs and reduced environmental pollution.

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INTRODUCTION

Dissolving pulp is a typical high-value product derived from forest resources. It contains over 90% cellulose, less than 4% hemicellulose, and a small amount of impurities. It serves as a pivotal feedstock for the synthesis of viscose fiber, cellophane, carboxymethyl cellulose, and nanocellulose (Wang *et al.* 2020a). Viscose fiber predominates among the products resulting from the utilization of dissolving pulp, accounting for more than 65% of the overall output (Duan *et al.* 2017; Li *et al.* 2018). Prompted by the increasing bottlenecks of cotton, animal fiber, and petroleum-based fiber along with the escalating consumption of textile and apparel commodities, the demand for dissolving pulp has exhibited a significant growth trend (Liu *et al.* 2016; Li *et al.* 2018; Liu *et al.* 2019). Due to some technical and raw material issues, the quality of dissolved pulp is generally unstable and inferior. Therefore, the research on the preparation technology of high-quality dissolving pulp not only can realize the high-value utilization of forest resources, but also it can provide technical support for the transformation and upgrading of traditional papermaking enterprises, which has important application value and strategic significance.

To address the growing demand for dissolving pulp, it has been proposed to upgrade and convert paper-grade pulp into dissolving pulp. The primary purpose of the upgrading process is to remove hemicellulose and prepare a pulp containing high-purity cellulose (Yuan *et al.* 2017). A variety of techniques have been explored, including alkaline treatment (Li *et al.* 2015), enzyme treatment (Wang *et al.* 2016; Liu *et al.* 2020), nitren treatment (Janzon *et al.* 2008), ionic liquid treatment (Yang *et al.* 2020a), and so forth (Yang *et al.* 2021). Among these methods, alkaline treatment was proven to be effective in eliminating hemicellulose from chemical pulp and has been widely used in industry. Nevertheless, the alkaline amount used in the process of alkaline extraction is very high (equivalent to 8 to 10% of the oven-dried pulp), leading to high production costs and serious environmental pollution. Also, due to the mercerization reaction, the Fock reactivity of the pulp is decreased with the substantial alkaline consumption (Kim *et al.* 2019). Comparatively, enzyme treatment offers promise, due to its mild reaction conditions. Enzymatic treatment aims to destroy the hemicelluloses' macromolecular structures in the chemical pulp and degrade it into oligosaccharides using xylanase and mannanase, thereby removing hemicellulose from pulp (Duan *et al.* 2017). Regretfully, the hemicellulose removal rate of enzyme treatment has been reported to be only about 30%, and its reaction duration is very long, which prevents large-scale production of dissolving pulp (Qin *et al.* 2021).

Recently, ionic liquids have shown great potential in preparing dissolving pulp owing to their unique features such as nonflammability, thermostability and low vapor pressure (Xue *et al.* 2018). The imidazolium ionic liquids demonstrate good cellulose solubility. For example, Yang *et al.* (2020a) used 1-ethyl-3-methylimidazolium acetate-water to remove hemicellulose from paper-grade bleached pulp. It was shown that the α -cellulose content of the resulted pulp reached 92.2% under the optimal conditions, which indicated that 1-ethyl-3-methylimidazolium acetate-water system was an effective solvent to remove hemicelluloses. However, the toxicity and high price of ionic liquid severely limited its application in the industrial production of dissolving pulp. Alternatively, γ -valerolactone (GVL) with cheap and non-toxic characteristics is considered as a promising candidate for the upgrading of paper-grade pulp (Fang and Sixta 2015). GVL is a biomass-based platform compound that can be acquired by the conversion of cellulose and hemicellulose (Giselle *et al.* 2023; Granatier *et al.* 2023a; Marianna *et al.* 2023). Due to its non-toxicity, biodegradability, recyclability, and eco-friendliness, GVL has become an ideal solvent in the synthesis of some chemicals (Climent *et al.* 2011; Sorokina *et al.* 2022). Furthermore, in recent years, GVL has been extensively applied in the separation of biomass feedstock components, since it is miscible with water in any ratio (Sun *et al.* 2019; Shokri *et al.* 2022).

Luterbacher *et al.* (2014) first reported the study on the separation of biomass components using GVL solvent. They employed GVL/water as a medium for the degradation of biomass into monosaccharides in the presence of sulfuric acid catalyst, which greatly streamlined the conventional biomass pretreatment and enzymatic hydrolysis processes. It was found that high monosaccharide yields (70 to 90%) of corn stalk, hardwood, and coniferous wood were achieved under the specific conditions: 0.05% H₂SO₄, GVL/water ratio of 80/20, and temperatures ranging from 157 to 217 °C. Moreover, Lê *et al.* (2016) successfully separated three main lignocellulosic components using GVL/water mixture in one step. The obtained solid cellulose fraction was used to prepare regenerated cellulose fibers, while the liquid portion containing lignin and sugars could be further processed into valuable products. In the past, there have been numerous studies on

the utilization of GVL to separate lignocellulose components and then remove hemicellulose from pulp. However, there has been a lack of reports on the fate of using GVL for upgrading bleached hardwood into dissolving pulp.

Herein, the paper-grade bleached hardwood kraft pulp (P-BHKP) was upgraded to dissolving pulp using a green and eco-friendly organic solvent (GVL). The effects of GVL concentrations, treatment temperature, and duration on the hemicellulose removal were investigated. The Fock reactivity and intrinsic viscosity of the resulted pulp were analyzed. The physicochemical properties of dissolving pulp were characterized by multiple testing methodologies, including ion chromatography, scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR). Also, this study evaluated the recyclability of GVL and explored the recycling procedure of GVL-containing spent liquor to decrease the use of chemicals.

EXPERIMENTAL

Materials

The P-BHKP board was supplied by a pulp mill in China. The α -cellulose content, hemicelluloses content, Fock reactivity, and intrinsic viscosity of P-BHKP were 82.5%, 12.7%, 40.0%, and 658 mL/g, respectively. The fiber length of P-BHKP was 1.0 mm, and fines content was 19.5%. Prior to experiments, P-BHKP board was torn into small pieces and then soaked in deionized water for 4 h. The pulp was dispersed at 4000 rpm with a fiber disintegrator, followed by drying overnight at 120 °C and storing in a sealed bag for further use. γ -Valerolactone (GVL, 98%) and sulfuric acid (H₂SO₄, 98%) were purchased from Shanghai Macklin Biochemical Co., Ltd (China).

GVL Treatment

P-BHKP was treated with GVL in pressure-resistant glass bottles by oil bath method. The specific experimental steps were carried out as follows: 10 g of P-BHKP (o.d.) was put into the reaction container with 0.005 N sulfuric acid at liquid-to-solid ratio of 15 mL/g. The reaction was conducted with different treatment temperatures (80, 100, 120, 140, and 160 °C) at certain GVL concentrations (0, 20, 40, 60, and 80 wt%) for the scheduled times (0.5, 1, 2, 4, and 6 h). During GVL treatment, the pulp sample was shaken every 20 min. Once the reaction was completed, the glass bottle was taken out and then cooled under tap water. Afterward, the pulp sample was filtered using sand-core funnel and washed with hot water. Finally, the obtained solid pulp was dried overnight for further analysis.

GVL Recycling

The spent liquor after chemical pulp treatment contained a large amount of GVL. Two methods were chosen to reuse the spent liquor. One method is that the spent liquor was directly recycled by adding an appropriate amount of GVL and water, which is named as recycled GVL; the other one is that the spent liquor was allowed to sediment for 0.5 h to precipitate the fines, and then filtered and distilled to obtain GVL with high purity and then recycled for reuse, which is named as purified recycled GVL. The recycling reaction experiment was carried out with 60% GVL concentration at 120 °C for 2 h.

Characterization of Pulp

The hemicellulose content of pulp was tested by following the procedures from the National Renewable Energy Laboratory (NREL/TP-510-42618) (Sluiter *et al.* 2008) using ion chromatography unit equipped with CarboPacPA20 column with electrical-conductivity detector. Briefly, the pulp was hydrolyzed into mono sugars through two set hydrolysis steps, *i.e.*, first in a 72% H₂SO₄ at 25 °C for 1 h, and then diluted into 4% H₂SO₄ at 121 °C for 1 h. The hemicellulose content was calculated by summing of mono-sugars except glucose.

The Fock reactivity and α -cellulose content of pulp were determined as described previously (Tian *et al.* 2013; Wang *et al.* 2016; Liu *et al.* 2019). Briefly, the Fock reactivity of dissolving pulp was sequentially treated with NaOH, xanthation with CS₂, and regeneration with sulfuric acid, in which the xanthation of cellulose was performed at 19 °C in a water bath. The cellulose viscosity was determined in cupriethylenediamine (CED) solution at 0.5% cellulose concentration according to TAPPI T 230 om-94. Ash content was determined according to TAPPI T 244 om-93. Alkaline solubility, *i.e.* S10 and S18, was conducted using sodium hydroxide solution of 10% and 18% to extract pulp according to TAPPI T 235 cm-85. The S10 represents both degraded cellulose and hemicellulose, and the S18 represents mainly hemicellulose.

The surface morphology of pulp fibers was investigated by SEM (Hitachi Regulus 8220, Japan). The XRD pattern of pulp was analyzed on a D8-ADVANCE X-ray diffractometer (Bruker, Germany). The Segal equation was used to calculate the crystallinity index (CrI) (Segal *et al.* 1959). The chemical structure of pulp fibers was analyzed by a FTIR spectrometer (Bruker ALPHA, Germany) using ATR mode.

RESULTS AND DISCUSSION

Advantage of Using GVL for Pulp Upgrading

Hemicellulose combines tightly with cellulose, resulting in a much more compact and rigid structure for the original chemical pulp fiber, as shown in Fig. 1. However, the hemicellulose is a heteropolysaccharide, which differs from cellulose in its sugar moieties, branched chains, and lower molecular mass. It reacts with carbon disulfide preferentially rather than cellulose during viscose production, thereby affecting the cellulose processability and the final product. Therefore, the removal of residual hemicellulose in the chemical pulp is essential for the preparation of dissolving pulp (Janzon *et al.* 2008). Because of the excellent swelling properties of GVL, the compact structure of the fibers become loose after treating the chemical pulp with GVL (Shokoufeh *et al.* 2022; Granatier *et al.* 2021; Granatier *et al.* 2023b;). The hemicellulose hydrolyzes into much smaller fragments in a small amount of sulfuric acid, thus facilitating hemicellulose removal. In this study, 0.005 N sulfuric acid was introduced into GVL/water medium to remove hemicellulose from P-BHKP. The results indicated that the cellulose purity was increased from 82.5% into 93.2%, and the hemicellulose content decreased from 12.7% to 4.5%, which met the standard for dissolving pulp. The cellulose purity was slightly lower than the combination treatment of GVL and ionic liquid, which resulted in cellulose purity of 96% (Shokoufeh *et al.* 2022). The Fock reactivity related to the availability of free hydroxyl groups and the intrinsic viscosity associated with the cellulose chain were improved simultaneously. These changes enhance the downstream processability of pulp.

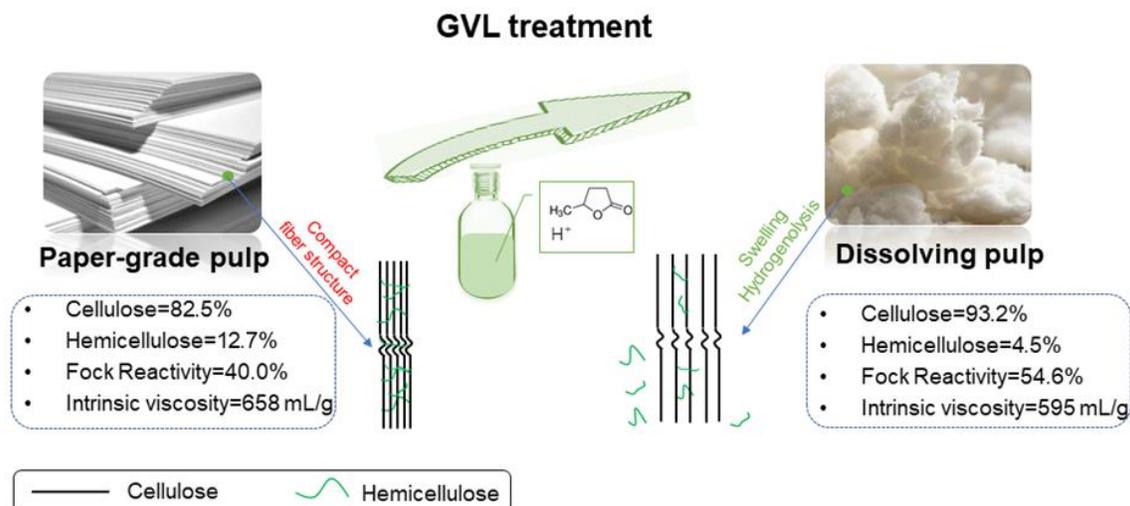


Fig. 1. Diagram of GVL treatment of paper-grade pulp (P-BHKP) towards dissolving pulp

Hemicellulose Removal during GVL Treatment of Pulp

With respect to the GVL treatment, the effects of GVL concentration, treatment temperature, and time on the removal of hemicellulose from P-BHKP were considered. The condition optimization of GVL treatment of paper-grade pulp is displayed in Fig. 2. As shown in Fig. 2A, with the increase of GVL concentration from 0 to 60%, the α -cellulose content in pulp was increased, while the hemicellulose content was decreased. When the GVL concentration reached 60%, the α -cellulose and hemicellulose contents were 91.0% and 6.12%, respectively. Further increasing the GVL concentration to 80%, the α -cellulose content of pulp was almost unchanged, which may be caused by the accompanying degradation of cellulose in such high GVL concentration (Duan *et al.* 2015). However, at this concentration, the dissolution of hemicellulose in the pulp was the highest, indicating that the swelling of GVL on the pulp reached a saturated state. Therefore, taking account of the cost of GVL solvent, 60% GVL concentration was selected for subsequent experiments.

Figure 2B reveals the change of α -cellulose and hemicellulose content in pulp at different treatment temperatures. With increasing temperature from 80 to 120 °C, the α -cellulose content of pulp rose gradually, and the hemicellulose content declined correspondingly. At the temperature of 120 °C, the α -cellulose and hemicellulose contents of pulp were 92.3% and 5.45%, respectively. However, the improvement of cellulose purity and hemicellulose removal was negligible with further increase of the temperature to 160 °C. Thus, considering the influence of temperature on GVL treatment conditions and energy consumption, 120 °C was chosen as the optimal reaction temperature.

Figure 2C presents the effects of different treatment times on the α -cellulose and hemicellulose contents of P-BHKP. The α -cellulose content of pulp was 89.2% when the treatment duration was only 0.5 h. Subsequently, the α -cellulose content was increased to 92.3% by prolonging the treatment time to 2 h. In addition, the hemicellulose content of pulp decreased from 9.38% at first 0.5 h to 5.45% at 2 h, with a change rate of 41.9%. Further increase time to 6 h, the improvement of pulp was slight. Based on the economic and technical standpoints, in this study, the GVL treatment condition was optimized as 60% GVL, 120 °C, and 2 h.

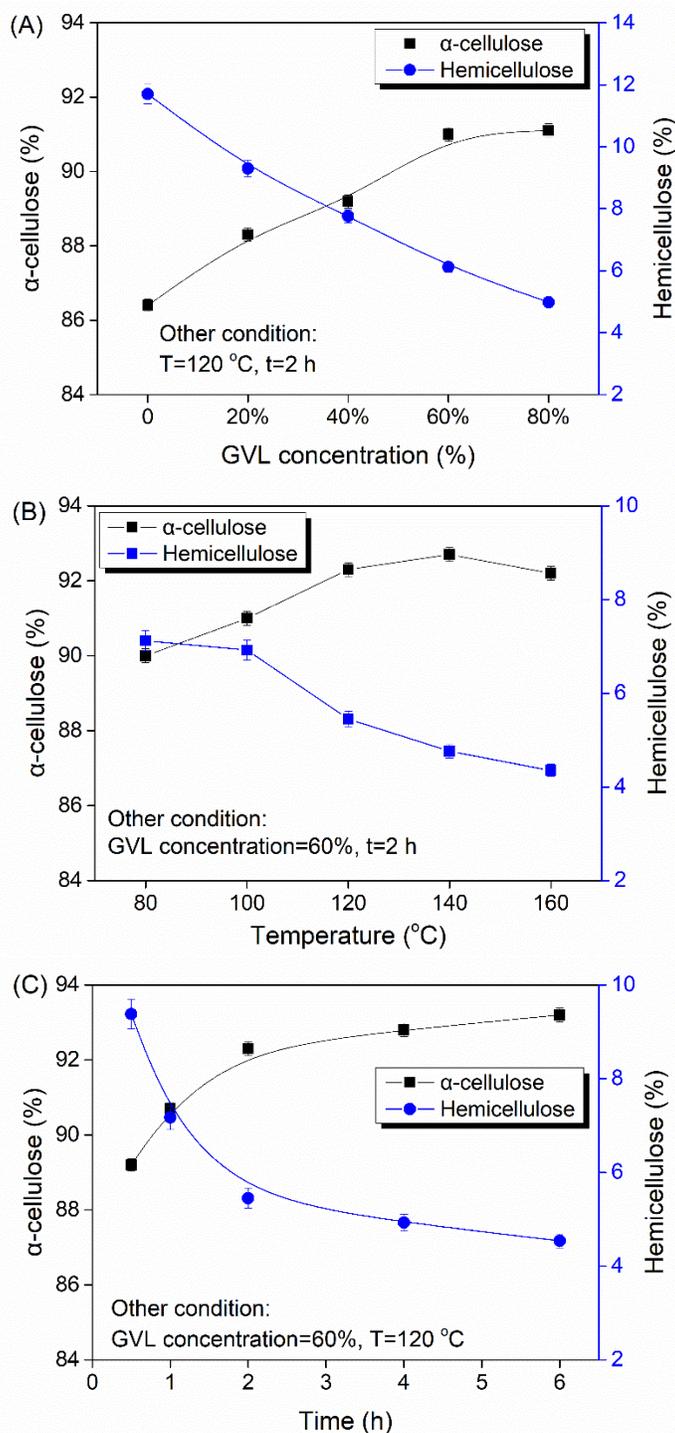


Fig. 2. Effects of GVL concentration (A), treatment temperature (B), and treatment time (C) on the α -cellulose and hemicellulose contents of pulp

Fock Reactivity and Intrinsic Viscosity of Pulp

Fock reactivity and intrinsic viscosity can influence the downstream processability (Duan *et al.* 2016). Fock reactivity represents the accessibility of free hydroxyl groups. The higher Fock reactivity would improve the reaction efficiency during viscose fiber production. Figure 3 shows the Fock reactivity and intrinsic viscosity of the original pulp,

upgraded pulp, and commercial dissolving pulp, which was produced from pre-hydrolysis kraft-based pulping process using hardwood as raw material. The Fock reactivity of pulp was improved from 40.1% to 54.6% by GVL treatment, which was comparable with the commercial dissolving pulp of 56.7%. Furthermore, intrinsic viscosity stands for the average length of cellulose chain. Too high or low intrinsic viscosity is not appreciated for dissolving pulp due to the homogeneous reaction that is required for viscose fiber production. It is noteworthy that the intrinsic viscosity of the pulp by GVL treatment led to a much faster reduction to 595 mL/g compared with that of the original pulp (658 mL/g), and similar results have been represented in previous literature (Duan *et al.* 2016; Yang *et al.* 2020b). To sum up, the intrinsic viscosity and Fock reactivity of the upgraded pulp obtained after GVL treatment were close to the commercial one, which basically achieved the standard of commercial dissolving pulp. In addition, the ash content of the upgraded pulp was 0.5%, which was decreased from the original pulp of 0.8%. The S_{10} and S_{18} values of the upgraded pulp was decreased to 8.9% and 5.7% from the original pulp of 13.5% and 10.7%, respectively.

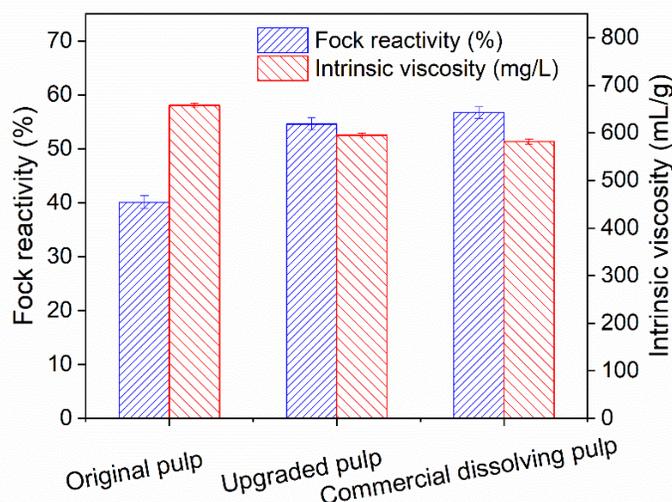


Fig. 3. The effect of GVL treatment on the Fock reactivity and intrinsic viscosity of pulp

SEM, XRD, and FTIR Analysis of Pulp

As exhibited in Fig. 4A, the surface of original pulp (P-BHKP) was relatively smooth, and the binding between the fibers was compact. After GVL treatment, the fiber was swollen obviously, which yielded more fiber filamentation, finally leading to the hemicellulose dissolution.

The XRD patterns of original pulp and upgraded pulp are depicted in Fig. 4B. As expected, the typical cellulose I diffraction peaks at 2θ of 15.5° , 22.6° and 34.5° (Wang *et al.* 2020b) were present in two pulp samples. This illustrated that GVL treatment preserved the main crystal structure of cellulose, such that the initial crystalline and amorphous areas coexisted. However, the intensity of diffraction peak in the pulp changed obviously. The crystallinity index (CrI) of original pulp was 82%, while the CrI of upgraded pulp was 71%. This decline in crystallinity may result from the swelling of the fibers as a result of the GVL treatment.

Moreover, the chemical structure of original pulp and upgraded pulp were analyzed by FTIR spectroscopy. As shown in Fig. 4C, the peak at 3275 cm^{-1} appeared in two pulps,

corresponding to the O–H stretching of cellulose (Diop *et al.* 2015). The peak located at 2915 cm^{-1} was attributed to the symmetric C–H stretching vibration of methyl (CH_2), and the peak at 1322 cm^{-1} was attributed to the CH_2 rocking vibration at C6 (Horseman *et al.* 2017). In addition, the characteristic peak of cellulose I structure (1025 and 1640 cm^{-1}) was prominent (Wang *et al.* 2022), which demonstrated that the upgraded pulp treated with GVL still retained the typical cellulose I structure.

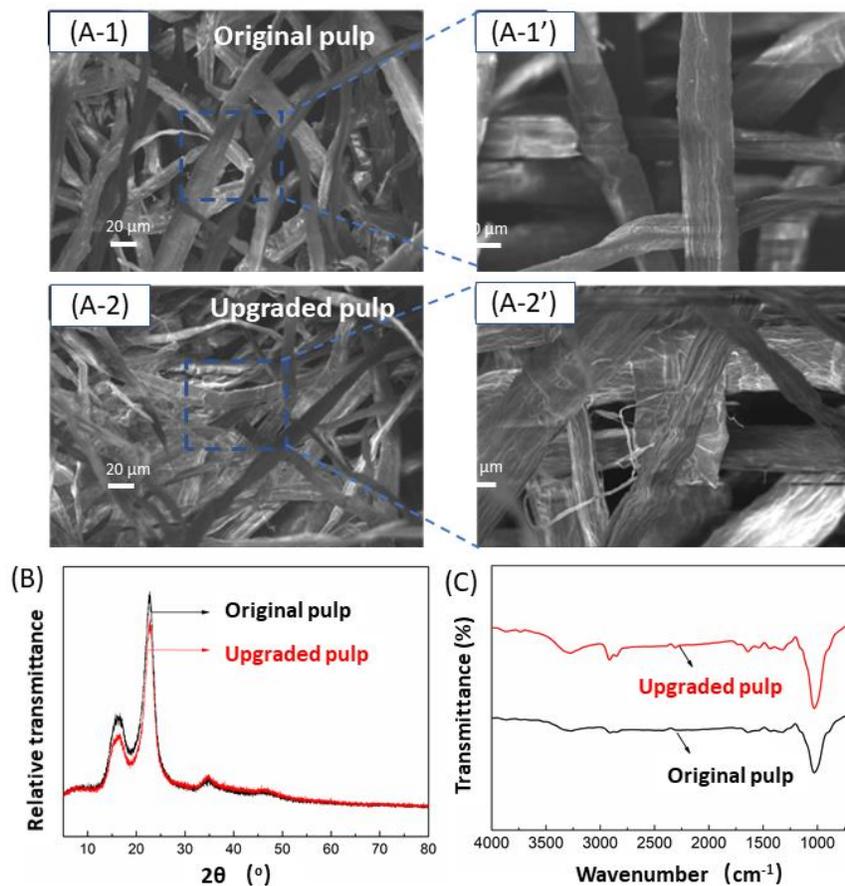


Fig. 4. SEM images (A), XRD patterns (B) and FTIR spectra (C) of original pulp and the upgraded pulp obtained by GVL treatment

GVL Recycling and Reuse

To reduce costs and achieve maximum economic value, the filtered GVL was recycled and reused to treat original pulp (P-BHKP) for producing dissolving pulp. The effects of different GVL recycling processes on the pulp properties were manifested in Fig. 5. As shown, the cellulose content, Fock reactivity, and intrinsic viscosity of recycled GVL treated pulp were increased to 90.4%, 52.1% and 615 mL/g from the original of 82.5%, 40.1%, and 658 mL/g, respectively. The purified recycled GVL resulted in a higher cellulose content (92.1%) and Fock reactivity (54.3%) along with lower intrinsic viscosity (598 mL/g) for the upgraded pulp. This indicated that the recycled GVL has a strong ability to dissolve the hemicellulose in pulp. Notably, the cellulose content and Fock reactivity of pulp increased after recycled GVL treatment, while the intrinsic viscosity decreased greatly. The purified recycled GVL was more favorable for the subsequent production of dissolving pulp.

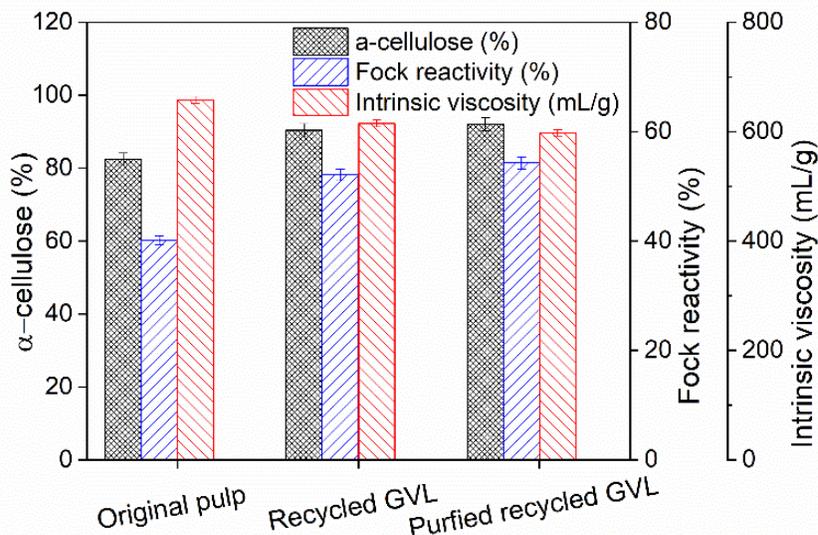


Fig. 5. The effects of two GVL recycling processes on the cellulose content, Fock reactivity and intrinsic viscosity of the pulp

CONCLUSIONS

1. γ -Valerolactone (GVL) was used to treat paper-grade bleached hardwood pulp for the removal of hemicellulose to form dissolving pulp for viscose production. The reaction parameters for GVL treatment, including GVL concentration, temperature, and time, were systematically optimized. Results showed that the dissolving pulp with α -cellulose content of 92.3% and hemicellulose content of 5.45% was obtained with 60% GVL at 120 °C for 2 h. Under these conditions, the Fock reactivity and intrinsic viscosity of the resulted dissolving pulp was comparable to that of commercial one. Also, SEM analysis displayed that after GVL treatment, the fiber was swollen, resulting in hemicellulose dissolution. Meanwhile, XRD and FTIR results demonstrated that GVL treatment maintained the native crystal structure of cellulose. Thus, the as-prepared dissolving pulp still exhibited the typical cellulose I structure.
2. GVL was recycled and reused to remove hemicellulose from original pulp successfully. These findings suggest that the green and efficient preparation of dissolving pulp will play an important foundation for the production of nanocellulose.

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