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ORIGINAL ARTICLE

Preparation of flocculant for optimizing glycol lignin manufacturing process by cationization of glycol lignin

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Abstract

Glycol lignin possessing thermoplastic and fusible properties can be a biorefinery platform material; however, glycol lignin is obtained as very small particles in suspension and the low dewatering efficiency is a major difficulty for the mass production. To improve the productivity of glycol lignin in the refinery plant, glycol lignin-based flocculants were prepared and their flocculation performance was examined. The flocculants (cationized glycol lignins) were synthesized by a reaction with glycidyltrimethylammonium chloride (GTA) in various reaction conditions. The prepared flocculants exhibited high flocculation performance and successfully economized the production cost of glycol lignin. Their flocculation efficiency was affected by the precipitation temperature, the length of the glycol chain, the molecular weight and the functional group of the glycol lignin. The flocculation behavior was interpreted by phase separation theory at a lower critical solution temperature (LCST).

Keywords Lignin · Polyethylene glycol (PEG) · Acid-catalyzed solvolysis · Flocculant · Glycidyltrimethylammonium chloride (GTA)

Introduction

The Paris agreement was adopted in COP21, and limiting the availability of petroleum chemicals was commonly accepted to prevent global warming. Lignocellulose is an alternative to fossil resources that is expected to provide a solution to the global warming problem, given its carbon neutrality. Lignocellulose materials are mainly composed of two parts: polysaccharides and lignin. Currently, large amounts of polysaccharides are used for the industrial preparation of materials like paper. On the other hand, effective utilization of lignin is yet to be achieved. Thus, lignin is a key material to promote a sustainable social system. Large amounts of lignin (an estimated 2×10^{10} t per year) are biosynthesized annually, and the excess that is currently leached is ~3×10^{11} metric tons [1].

To utilize lignin, separation treatments, such as pulping procedures, are required for lignocellulosic materials. Lignin is connected to polysaccharides through the lignin–carbohydrate complex linkage. The chemical structure of the obtained lignin (technical lignin) is affected in various degrees by the chemical reactions during the separation from lignocellulose; thus, the chemical structure and properties of technical lignins are dependent on reaction conditions. For example, lignin is depolymerized to fragments during Kraft pulping with large chemical changes. Lignosulfonate obtained by sulfite pulping includes sulfonate groups, which contribute to its properties as a polyelectrolyte [2]. Kubo et al. reported the solvolysis of wood meal using carbonate/ethylene glycol with H_2SO_4 at 150 °C. The polysaccharides are converted into water-soluble low-molecular-weight compounds, while high-molecular-weight glycol lignin was obtained by grafting glycols into lignin as water-insoluble solids [3]. Ethylene glycol chains were introduced on lignin at α and γ-positions.

With respect to molding and processing, fusibility is an essential property. However, several technical lignins lack thermal flow properties. The addition of plasticizers, such as poly(ethylene oxide), poly(ethylene terephthalate), and

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polypropylene, allows technical lignin to possess thermal fluidity [4–6]. An acidic solvolysis system using polyethylene glycol (PEG) was also developed [7–9]. In this system, PEG is introduced into lignin to yield polyethylene-modified lignin (glycol lignin), in which the glycol lignin exhibited a viscous thermal flow property [10]. Lin obtained thermally fusible lignin from softwood by cooking a mixture of PEG and sulfuric acid. The fusibility was caused by the PEG moiety introduced by solvolysis. Carbon fibers were prepared from this by melt-spinning followed by oxidative thermostabilization and carbonization procedures [8]. Flexible clay polymer films were prepared by combining glycol lignin and natural clays. The films exhibit a high moisture-barrier property and can be used for flexible electronic devices, such as tough sensors [11, 12].

The glycol lignin is separate from pulp by dissolving it in an alkali solution after acidic solvolysis. The acidity of the solution is adjusted with sulfuric acid to produce a precipitate, and this is centrifuged to obtain solid glycol lignin. In the precipitation process, the glycol lignin is generated as very small particles leading to dewatering difficulties in the centrifuging process. This leads to a reduction in productivity.

In this study, the addition of flocculant to improve dewatering efficiency was investigated. To simplify the system, the flocculant was synthesized from glycol lignin (Fig. 1). Additionally, the use of sulfuric acid and the amount of sodium sulfate as a by-product are reduced if solid glycol lignin is obtained at neutral pH at the precipitation stage using the flocculant, and this reduces the production cost. In the study, the flocculants were developed for achieving high flocculation efficiency at neutral pH.

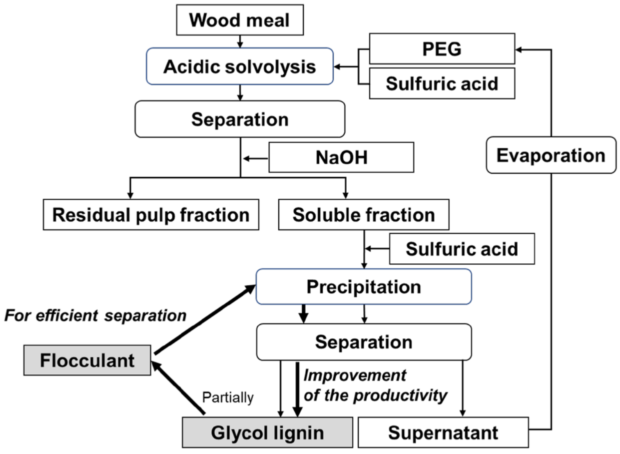


Fig. 1 Schematic illustration for preparation of flocculant with high performance from glycol lignin to improve the production efficiency of glycol lignin [9]

Materials and methods

Materials

The glycol lignin was supplied from the bench scale plant of Forestry and Forest Products Research Institute of Japan (FFPRI) which performed an acid catalyzed PEG solvolysis of Japanese cedar (*Cryptomeria japonica*). The basic process of the glycol lignin production was followed by the previous report [10] with the reaction conditions of 140 °C of the reaction temperature and 90 min of the reaction time with acidified PEG (0.3% (w/w) sulfuric acid of PEG). In this study, PEG200, PEG400 and PEG600 were used to prepare the glycol lignins (PEG200-lignin, PEG400-lignin and PEG600-lignin, respectively).

Fractionation of glycol lignin

Specifically, PEG200-lignin was fractionated by gradient acid precipitation [13]. Additionally, PEG200-lignin (20 g) was dissolved in 0.5 N NaOH (1.25 L). A part of glycol lignin was precipitated by adding 0.5 M H_2SO_4 dropwise to pH 10. The solution was centrifuged at 10,000 rpm for 10 min to obtain the precipitant (Fraction 1). The supernatant was submitted for a successive precipitation process at a gradient lower pH (pH 9.5, 7, and 2) by the same procedure as mentioned above. The precipitants were termed as Fraction 2, 3 and 4, respectively.

Molecular weight distribution

The molecular weight of glycol lignin was evaluated using gel permeation chromatography (GPC). The solid phase and elution solution were Sepharose CL-6B and 0.5 N NaOH, respectively. Polystyrene sulfonates were used as standard samples [14, 15].

FT-IR spectrometry

The FT-IR spectra were recorded on a Horiba FT-720 spectrophotometer by the KBr method.

Preparation of the flocculant from glycol lignin by cationization

Furthermore, glycol lignin was dissolved in 0.5 N NaOH, and glycidyltrimethylammonium chloride (GTA) was added to the solution. It was heated at 50 °C for 3 h. The reaction mixture was dialyzed using a cellulose tube (3500 MWCO) or neutralization with H_2SO_4 [16]. Nitrogen

Table 1 Reaction conditions for preparation of cationized glycol lignin and nitrogen content of the cationized glycol lignin

Cationized glycol lignin	Reaction conditions				Reaction product
	Raw material		GTA	Treatment	N content
	Glycol lignin	(g)	(mL)	after reaction	(%)
P200G1	PEG200-lignin	1.0	3.0	Dialysis	2.3
P200G2	PEG200-lignin	1.0	1.0	Dialysis	1.7
P200G3	PEG200-lignin	3.0	1.0	Dialysis	1.5
P200G4	PEG200-lignin	3.0	0.5	Dialysis	1.1
P200G5	PEG200-lignin	3.0	0.2	Dialysis	0.4
P200G6	PEG200-lignin	3.0	1.0	Neutralization	1.8
P400G	PEG400-lignin	3.0	1.0	Neutralization	2.0
P600G	PEG600-lignin	3.0	1.0	Neutralization	2.0
F1G[a]	Fraction 1[a]	0.2	0.2	Neutralization	3.5
F2G[a]	Fraction 2[a]	0.2	0.2	Neutralization	3.5
F3G[a]	Fraction 3[a]	0.2	0.2	Neutralization	3.5
F4G[a]	Fraction 4[a]	0.2	0.2	Neutralization	3.9

[a] PEG200-lignin was fractionated by gradient acid precipitation at pH 10 (Fraction 1), pH 9.5 (Fraction 2), pH 7 (Fraction 3) and pH 2 (Fraction 4). F1G, F2G, F3G and F4G were prepared from Fraction 1, 2, 3 and 4, respectively

content was determined by performing an elementary analysis. The reaction conditions are shown in Table 1.

Flocculation test

PEG400-lignin was used for the flocculation test as a suspension (pH 6.5) including small particles of glycol lignin. The required amount of the cationized glycol lignin (0.1, 0.5, and 1.0 wt% based on solid content of the suspension) was added to the suspension in a test tube, and the cap was closed. After turning it upside down immediately once, the volume of the precipitate was measured with respect to time as follows:

$$\text{Volume of the precipitate (\%)} = \frac{b}{a} \times 100,$$

where b denotes the height of flocculated glycol lignin in the test tube, and a denotes the height of the suspension solution in the test tube prior to adding the flocculant. Essentially, the tests were operated at 50 °C and pH 6.5. To investigate the effect on the temperature, the experiment was performed at 30 and 50 °C.

Table 2 Molecular weight and proportion of glycol lignins

	Proportion (%)	M_w ($\times 10^3$ g/mol)
PEG200-lignin	–	6.5
PEG400-lignin	–	8.1
PEG600-lignin	–	8.0
Fraction 1	86.9	9.7
Fraction 2	3.9	8.0
Fraction 3	5.4	6.2
Fraction 4	3.7	4.9

Results and discussion

Properties of glycol lignins

In this study, glycol lignins (PEG200-lignin, PEG400-lignin, and PEG-600-lignin) were used. Additionally, four fractionated PEG200-lignins that were separated by gradient acid precipitation were also submitted to prepare the flocculant. Table 2 shows the molecular weight and proportion of the fractions, and the GPC profiles are shown in Fig. S1 and Fig. S2. The molecular weight of PEG200-lignin was lower than that of PEG400-lignin and PEG600-lignin. There is a low difference in molecular weight between PEG400-lignin and PEG600-lignin. Given the characteristics of gel permeation chromatography, both the hydrodynamic radii may exhibit almost the same value.

There was a high difference in molecular weight between the four fractions, and this suggested that high molecular weight glycol lignin was precipitated at high pH. A potential reason is that the range of van der Waals attractive forces of large molecules exceeds that of small molecules [13]. The molecular weight of Fraction 1 was approximately twice higher than that of fraction 4. The proportion of Fraction 1 was 86.9%, and this suggested that it was a major part of PEG200-lignin.

Figure 2 shows the IR spectra of the glycol lignins. In all the glycol lignins, the peak at 2800–3000 cm^{-1} attributed to the stretching of the methylene group was observed. The highest intensity corresponded to the peak for PEG600-lignin due to the presence of a high amount of ethylene oxide unit. In the spectrum of PEG200-lignin, the band at 1716 cm^{-1} appears due to the stretching of the carbonyl group of carboxylic acid. The peak was not observed in the spectra of Fraction 1, 2 and 3. However, only Fraction 4 that was precipitated at pH 2 exhibited a carboxylic acid peak. This implied that the carboxylic acid group was contained in the small molecules of glycol lignin.

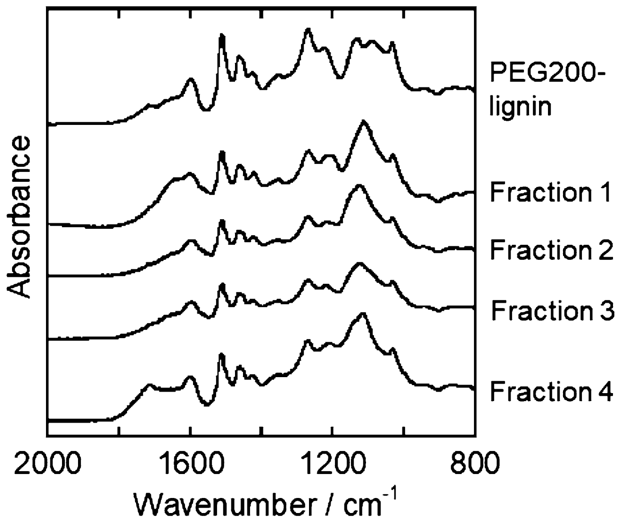


Fig. 2 FT-IR spectra of PEG-lignin and Fraction 1–4

Preparation of flocculant from glycol lignin

In the system, it is observed that the cationic polymer is adequate for the flocculant because glycol lignin includes a phenolic hydroxyl group. Specifically, lignosulfonate includes anionic groups although it is not efficient as a flocculant. In our study, a dimethylamino group was introduced into phenolated sulfuric acid lignin by the Mannich reaction [17–19].

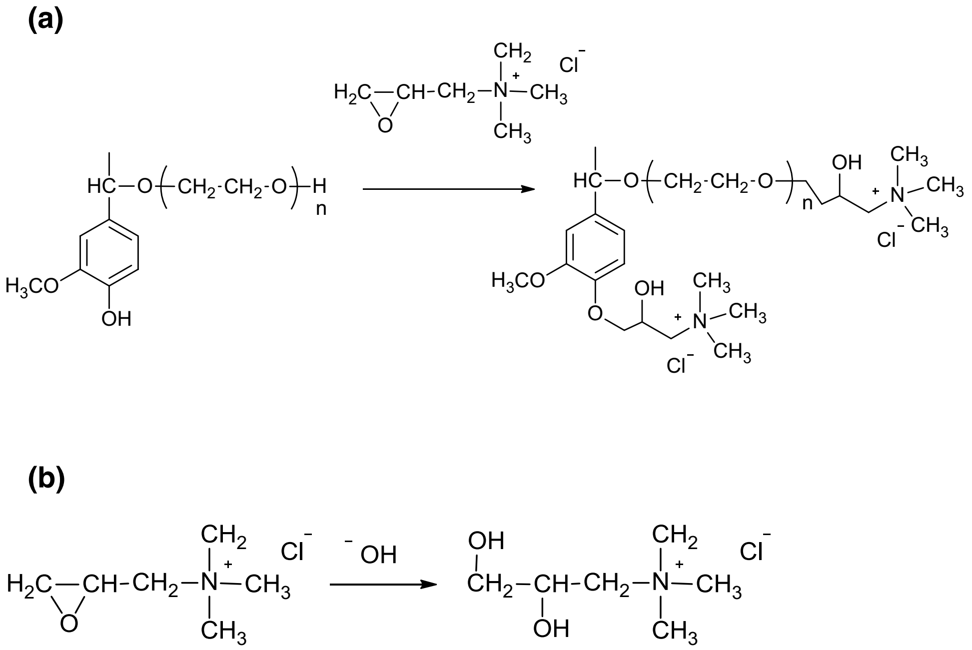
GTA was also used as a cationization reagent. Generally, cationic starch that is produced by a reaction between starch and GTA is routinely added to a wet-end process to improve the dry strength of paper [20]. Seong et al. synthesized chito-oligosaccharide using GTA as antimicrobial agent [21]. Wahlström et al. prepared cationic lignins from hardwood organosolv lignin and enzymatic hydrolysis lignin through a reaction with GTA and applied the same to water purification [22].

The quaternary ammonium derivatives steadily exhibit a cationic property in the aqueous solution independent of the pH. Thus, in this study, GTA was selected to introduce the cationic group on glycol lignin. The reaction mechanism is shown in Fig. 3. The phenolic hydroxyl group is reacted with GTA [23]. Additionally, PEG exhibits high values of the second virial coefficient and low values of the polymer–solvent interaction parameter (χ), and this suggests that PEG chain of glycol lignin exhibits high mobility and high excluded volume [24]. Thus, there is a possibility that the hydroxy group at the end of the long-chain PEG moiety can react with GTA because the moiety spreads widely in the solution and results in GTA readily participating in the reaction.

As a competitive reaction, GTA was reacted with hydroxy ions. The proportion of this side reaction increases when the concentration of hydroxyl ion is high. In the study, 0.5 N NaOH was selected based on a previous study [22].

Table 1 shows the reaction conditions and nitrogen contents of the reaction products. The nitrogen content in cationized PEG200-lignin was 2.3% when excess GTA was reacted (P200G-1 in Table 1). As expected, the nitrogen content decreased with decreases in the dosage proportion of GTA to PEG200-lignin (P200G1-P200G5 in Table 1). When an excessively low amount of GTA is added, it causes insolubility of the product in water at neutral pH (P200G4 and

Fig. 3 Proposed reaction mechanism for **a** cationization of glycol lignin and **b** side reaction using GTA



P200G5 in Table 1). The results indicate that the minimum amount of GTA required to dissolve the reaction product into water is 1 ml for 3 g of PEG200-lignin (P200G3, nitrogen content is 1.5%).

To shorten work hours and reduce the number of the operation processes for preparing the flocculant, neutralization was applied as opposed to dialysis. With respect to the nitrogen content of the reaction product in P200G3 and P200G6, both exhibited almost similar values. This suggested that the amount of the remaining side reaction products was low in the reaction conditions of P200G3 and P200G6, and thus they did not significantly affect the performance of the prepared flocculant.

Flocculation test

Effect of reaction conditions

In the suspension solution, the surface charge of glycol lignin exhibited a negative value due to the phenolic hydroxy group. Thus, the prepared cationized glycol lignin acts as a flocculant for the small particle glycol lignin through an electrostatic interaction. In the study, the flocculation efficiency was estimated by measuring the volume of the precipitate after the addition of the cationized glycol lignin.

To investigate the effect on the flocculation efficiency of temperature, P200G1 submitted the flocculation test at 30 and 50 °C (Fig. 4). The results suggested that the flocculation efficiency increased with increases in the temperature. This phenomenon could be related to the lower critical solution temperature (LCST) of glycol lignin. Generally, with respect to the LCST, the micelle of nonionic surfactants with a polyethylene glycol chain exhibits phase separation due to the cleavage of the hydrogen bond between polyethylene glycol chain and water, and this lead to a decrease in the solubility [25].

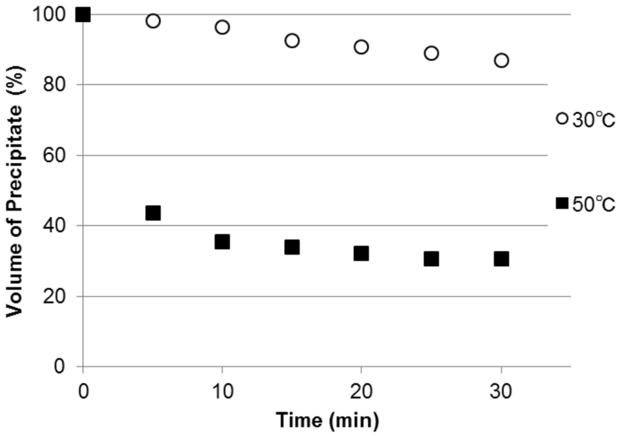


Fig. 4 Effect on flocculation efficiency of P200G1 at different temperature

In the study, when the prepared flocculant was added to the suspension of glycol lignin, the trimethylamino group of the prepared flocculant connected to the glycol lignin to generate a complex. The complex (glycol lignin-cationized glycol lignin) included long chain PEG regions at the surface that act as the nonionic surfactant. An increase in the temperature allowed the complex to easily agglomerate with each other due to the breakage of the hydrogen bonds between the complex and water.

Figure 5 shows the volume of the precipitate in P200G1–P200G3 and P200G6 at 50 °C and pH 6.5. All prepared flocculants exhibited the flocculation ability when the dosage was 1 wt%. At 0.5 wt% dosage, P200G1 exhibited flocculation performance given its high nitrogen content although the other flocculants did not exhibit the same. When the dosage was 0.1 wt%, all prepared flocculants did not exhibit flocculation performance for the flocculation.

The flocculant efficiency of P200G6 has higher than that of P200G2, even if the nitrogen contents of both are same (Fig. 5b, d; Table 1). The difference might be caused by the preparation procedure; however, it is difficult to show clearly why P200G2 was better.

According to Fig. 5c, d, neutralization was better than dialysis for the posttreatment of the preparation reaction. The cationized glycol lignin had high flocculation performance even if the posttreatment was neutralization. It leads the simplicity of the production process for the cationized glycol lignin, resulting in the increase of productivity for glycol lignin.

Effect of the length of PEG in glycol lignin

The hydrophilic PEG chains in glycol lignin were considered as spread widely in the solution, and this affected the flocculation efficiency of the cationized glycol lignin. Figure 6 shows the flocculation efficiency of the prepared cationized glycol lignin using PEG200-lignin, PEG400-lignin, and PEG600-lignin. The efficiencies of the cationized PEG200-lignin (P200G6) and PEG400-lignin (P400G) were equivalent to each other while the cationized PEG600-lignin (P600G) exhibited lower efficiency when compared with those of the others. This is also explained by the LCST theory. The amount of hydrogen bonds between the PEG chain of the coagulation complex (glycol lignin–cationized glycol lignin) and water increased with increases in the length of PEG chain, and thereby led to increases in the LCST. Thus, it was difficult for the complexes including cationic PEG600-lignin to agglomerate with each other. This phenomenon was also observed in the water-soluble polymer with PEG (co-polymer using *N*-isopropyl acryl amide and polyethylene glycol with primary amine). Hazer

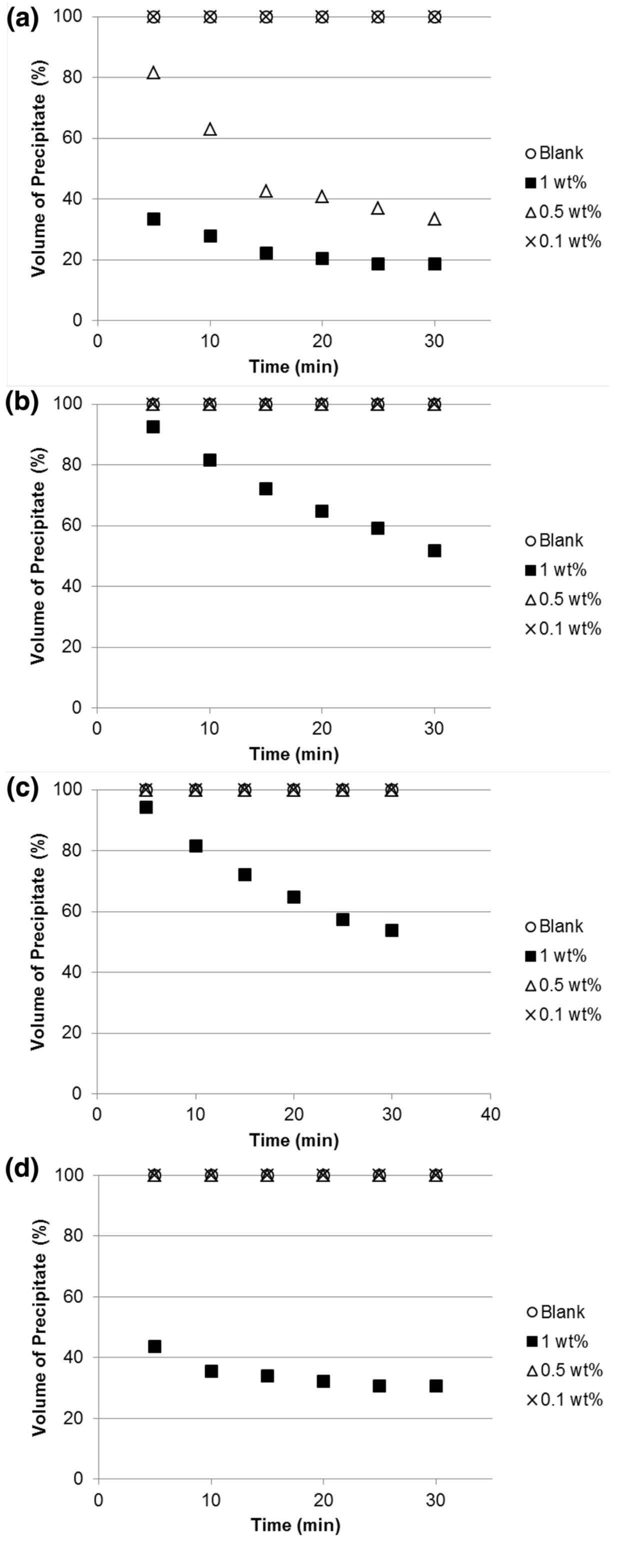


Fig. 5 Volume of precipitate flocculation test. **a** P200G1 **b** P200G2 **c** P200G3 **d** P200G6. Conditions: Dosage 0.1, 0.5 and 1 wt%, 50 °C, and pH 6.5

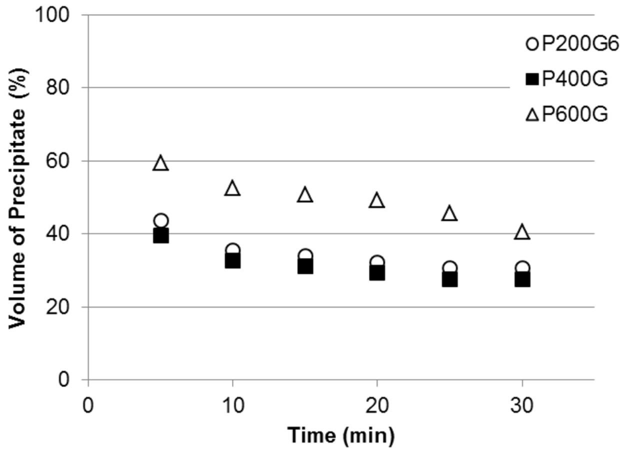


Fig. 6 Flocculation efficiency of P200G6, P400G and P600G. Conditions: Dosage 1 wt%, pH 6.5, 50 °C

et al. suggested that the LCST of the polymer increased with increases in the amount of PEG [26].

Effect of the fractionation of glycol lignin

To investigate the characteristics of the glycol lignin for cationization, fractionated PEG200-lignins (F1G, F2G, F3G, and F4G in Table 1) were subjected to a reaction with GTA, and the flocculation efficiency was estimated (Fig. 7). F1G–F3G shows the flocculation ability although F4G did not exhibit flocculation. Specifically, F4G included carboxylic acid (Fig. 2) that influenced the surface electrostatic charge of the F4G.

The flocculation efficiency of F2G was lower than that of F1G and F3G. The difference might be influenced by many factors, such as the ratio of nitrogen content to molecular

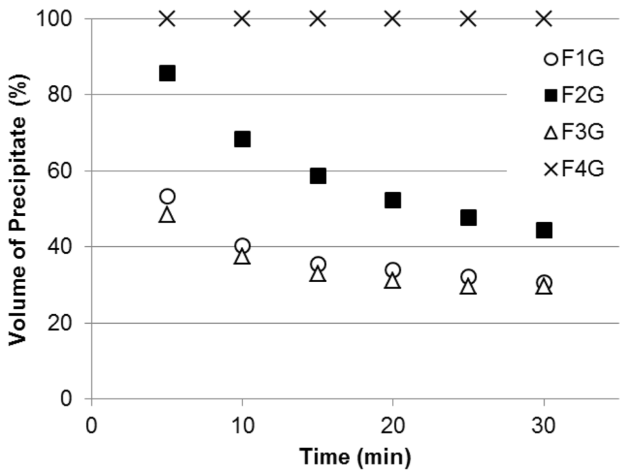


Fig. 7 Flocculation efficiency of F1G–F4G. Conditions: Dosage 1 wt%, pH 6.5 and 50 °C

weight and mass of lignin to PEG moiety. However, it is difficult to mention the reason. It requires further research to understand the flocculation efficiency clearly.

Conclusions

In this study, lignin-based flocculants were synthesized from glycol lignin through the simple reaction system. Their performance on the glycol lignin production system was examined in consideration of the structural parameter and reaction conditions. As a result, the optimally prepared flocculant showed high flocculation ability and improved the glycol lignin productivity by acceleration of the dewatering process. The improvement of glycol lignin production using glycol lignin-based flocculants should be a favorable self-cooperation approach to realize commercial mass production of the biorefinery platform material.

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