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Seiichi Yasuda · Kyoko Asano

Preparation of strongly acidic cation-exchange resins from gymnosperm acid hydrolysis lignin

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Abstract The chemical preparation of strongly acidic cation-exchange resin from sulfuric acid lignin (Klason lignin) (SAL), a typical acid hydrolysis lignin, was investigated. Sulfonation of resinified SAL itself gave a resin with an ion-exchange capacity of 2.3 mEq/g. After resinification with formaldehyde, the phenolized SAL with a reactive *p*-hydroxyphenyl group yielded a resin with an ion-exchange capacity of 3.2 mEq/g. The latter capacity is superior to that of the corresponding commercial phenol-type resins (2–3 mEq/g), but did not reach the level of the corresponding commercial styrene-type resins (4–5 mEq/g).

Key words Lignin · Sulfonation · Cation-exchange resin · Hydrolysis lignin · Klason lignin

Introduction

Acid saccharification is an effective way to utilize woody biomasses as an organic industrial raw material in place of petroleum. The effective utilization of acid lignin is an important key to the success of the acid hydrolysis industry.

Acid hydrolysis lignin, readily obtainable through a concentrated-acid method, has a highly condensed and nonreactive structure^{1,2} due to the replacement of benzylic hydroxyl and oxygen-containing functional groups by aromatic nuclei (i.e., the formation of condensed-type aromatic nuclei). It has also been found that a condensed lignin can be quantitatively converted to an activated lignin by sulfuric acid-catalyzed phenolation,³ which is accompanied by the

cleavage of secondarily formed carbon–carbon linkages and introduction of a *p*-hydroxyphenyl group.

Furthermore, sulfonation⁴ of phenolized sulfuric acid lignin (P-SAL) from red pine was found to yield water-soluble lignoarylsulfonate derivatives with two sulfonic acid groups per C₉-C₆ unit. One sulfonic acid group was introduced on a guaiacyl nucleus and another on a *p*-hydroxyphenyl group. These findings suggest that it is possible to prepare a strongly acidic cation-exchange resin with a high ion-exchange capacity. Various attempts^{5,6} to prepare ion-exchange resins from acid hydrolysis lignin have been carried out, but the attempts have met with limited success. The preparation of a strongly acidic cation-exchange resin was investigated in this study.

Materials and methods

Phenolation of red pine sulfuric acid lignin

Phenolized SAL (P-SAL)⁷ was prepared from red pine (*Pinus densiflora* Sieb. et Zucc) Klason lignin (sulfuric acid lignin; SAL) and phenol by treating with 72% sulfuric acid (Fig. 1).

Resinification of P-SAL and SAL

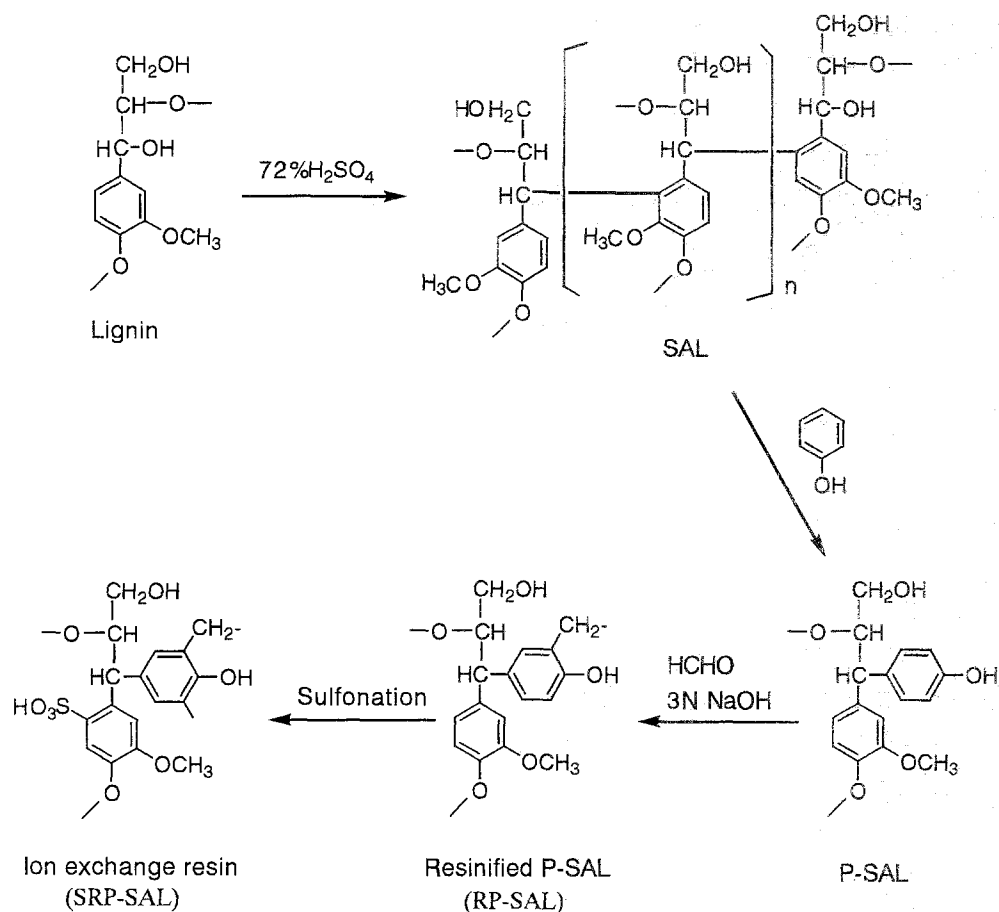
To a solution of 100 mg P-SAL in 1 ml 3 M NaOH was added 0.5 ml of 37% formalin. After heating at 60°C for 1 h and then 180°C for 1 h in a small stainless steel pressure tube, the solid contents were filtered off with a glass filter, washed with water, and then dried to give 102 mg resinified P-SAL (RP-SAL) (Fig. 1). Resinification of SAL itself under the above conditions gave resinified SAL (R-SAL).

Sulfonation of RP-SAL and R-SAL

To a suspension of 100 mg RP-SAL in 2 ml tetrachloroethane was added 250 mg chlorosulfonic acid. After stirring at

S. Yasuda (✉) · K. Asano
Division of Biological Material Sciences, Department of Biosphere Resources Science, Graduate School of Bioagricultural Sciences, Nagoya University, Nagoya 464-8601, Japan
Tel. +81-52-789-4159; Fax +81-52-789-4163
e-mail: syasuda@agr.nagoya-u.ac.jp

Fig. 1. Preparation of ion-exchange resin from acid hydrolysis lignin (SAL). SAL, sulfuric acid lignin; P-SAL, phenolized-SAL



50°C for 0.5 h and then at 100°C for 1 h, the suspension was made basic by carefully adding 20 ml 2 M NaOH, after which it was refluxed for 1 h. The contents were filtered off with a glass filter, washed with distilled water, and dried in vacuo to give 152 mg of dark-brown sulfonated resin (SRP-SAL) (Na⁺ form). Sulfonation of R-SAL under the above conditions yielded dark-brown sulfonated resin (SR-SAL).

Determination of sulfur content

The sulfur content of the prepared resins was determined quantitatively by a combustion method.⁷

Ion-exchange capacity of SRP-SAL and SR-SAL

The H⁺ form of SRP-SAL (Na⁺ form) was regenerated by washing the Na form with 1 M HCl and then with distilled water. A suspension of 100 mg SRP-SAL (H⁺ form) in 5 ml 0.05 M NaCl was allowed to stand for 2 h at room temperature with stirring at intervals. After filtering out the resin with a glass filter, 1 drop of methyl orange was added to a combined solution of the filtrate and the washings as an indicator and then titrated with 0.05 M NaOH. The ion-exchange capacity of SR-SAL (Na⁺ form) was measured using the same procedure.⁸

Results and discussion

Because treatment of protolignin occurring naturally in wood with 72% sulfuric acid causes extensive intermolecular condensation, SAL may be expected to be a polymeric material similar to polymeric resins. Therefore, SAL itself was first reacted with chlorosulfonic acid at 100°C. After alkali hydrolysis, a suspension of the products was dark brown, indicating considerable dissolution of the prepared arylsulfonate, a strongly acidic cation-exchange resin, into the alkaline solution and insufficient polymerization of SAL.

Despite resinification of SAL with formaldehyde in 3 M sodium hydroxide at 180°C, the prepared arylsulfonate (sulfonation material of R-SAL) SR-SAL was slightly dissolved into both 3 M sodium hydroxide and 1 M hydrochloric acid, probably indicating that the polymerization of resinified SAL (R-SAL) was again insufficient. During resinification under alkaline conditions, the *ortho* position of a phenolic hydroxyl group is responsible for condensation. Resinification of SAL does not proceed successfully because of the low solubility of SAL to the alkali medium, steric hindrance of an adjacent benzyl group at the C6 position of the guaiacyl nucleus (*para* position of aromatic methoxyl group) formed during treatment 72% sulfuric acid, and

Table 1. Preparation of strongly acidic cation-exchange resin from SAL and P-SAL

Sample	Resin (yield) ^a	Sulfonated (yield) ^b	resin (S%)	Degree ^c of sulfonation	Ion-exchange capacity (mEq/g)	
					Calculated ^d	Found
P-SAL	102	152	10.2	1.37	3.2	3.2
SAL	98	127	7.8	0.60	2.4	2.3

^a Based on sample^b Based on resin^c Number of introduced sulfonate group per C₉-C₆-C₁ for phenolized sulfuric acid lignin (P-SAL) and C₉ for sulfuric acid lignin (SAL)^d Calculated value, based on sulfur content

small portions of a vacant *ortho* position. The sulfur content of SR-SAL, determined by a volumetric method⁷ after combustion of the sample, was 7.8%, as shown in Table 1. On the assumption that the molecular weight per C₉ unit of SAL is 186³ and little crosslinking by methylene groups occurred, the sulfur content suggests that SR-SAL possesses 0.60 sulfonic acid groups per C₉ unit. The calculated ion-exchange capacity of 2.4 mEq/g was nearly equal to the determined ion-exchange capacity (2.3 mEq/g). This value means that SR-SAL is equivalent to the commercial phenol type (ion-exchange capacity 2–3 mEq/g) strongly acidic cation-exchange resin. In addition to the C6 of guaiacyl nuclei, sulfonic acid groups must be introduced on other aromatic carbons (i.e., *ortho* positions of a phenolic hydroxyl group in the introduced *p*-hydroxyphenyl unit). The value 2.3 mEq/g is higher than expected because in SAL nearly all of the guaiacyl nuclei were blocked at C6.

P-SAL, with a reactive *p*-hydroxyphenyl unit, was selected to introduce many more sulfonic acid groups. P-SAL was sulfonated after resinification (RP-SAL) with formaldehyde to yield the product SRP-SAL. The prepared SRP-SAL was not dissolved at all into either 3 M sodium hydroxide or 2 M hydrochloric acid, suggesting sufficient resinification. The weight yields of resinification and sulfonation were 102% and 152%, respectively. The sulfur content of SRP-SAL was 10.2%.

On the assumption that the molecular weight of P-SAL per C₉-C₆ unit is 275³ and that all C₉-C₆ units of RP-SAL are crosslinked with methylene bonds, this sulfur content means that SRP-SAL possesses 1.37 sulfonic acid groups per C₉-C₆-C₁ unit. During sulfonation⁴ of P-SAL under the same conditions, two sulfonic acid groups were introduced on aromatic carbons (i.e., at C6 of the guaiacyl nucleus and the *ortho* carbon of a phenolic hydroxyl group of the *p*-hydroxyphenyl unit. Considering the vacant aromatic C6 of RP-SAL, C6 must possess one sulfonic acid group; and about one-fourth portion of two *ortho* carbons of a

phenolic hydroxyl group in the *p*-hydroxyphenyl unit is used for sulfonation. The determined ion-exchange capacity of SRP-SAL was 3.2 mEq/g and lies between the values for commercial phenol and styrene types of strongly acidic cation-exchange resins (2–3 and 4–5 mEq/g, respectively).

The present preparation of the strongly acidic cation-exchange resin SRP-SAL from acid hydrolysis lignin holds promise as a useful method for utilizing this lignin.

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