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# Preparation and evaluation of lignosulfonates as a dispersant for gypsum paste from acid hydrolysis lignin

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**Abstract**

In order to effectively utilize a by-product of the acid saccharification process of woody materials, the chemical conversion of guaiacyl sulfuric acid lignin (SAL), one of the acid hydrolysis lignins, into water-soluble sulfonated products with high dispersibitity was investigated. At first, SAL was phenolated (P-SAL) to enhance the solubility and reactivity. Lignosulfonates were prepared from P-SAL by three methods of hydroxymethylation followed by neutral sulfonation (two-step method), sulfomethylation (one-step method) and arylsulfonation. Surprisingly, all prepared lignosulfonates possessed 30 to 70% higher dispersibility for gypsum paste than the commercial lignosulfonate. Evaluation of the preparations for gypsum paste suggested that the higher molecular weights and sulfur contents of the preparations increased their dispersibility.

*Keywords:* Lignosulfonate; Saccharification; Acid hydrolysis lignin; Sulfuric acid lignin; Gypsum; Dispersibility

## 1. Introduction

Recent statistics (Anonymous, 2002) reported that the reserves for crude oil are estimated to be approximately $1.0 \times 10^{12}$ bbl, however, these reserves will be depleted in approximately 40 years if the consumption of fossil energy continues at the present rate. Moreover, use of fossil resources releases abundant greenhouse gases, such as carbon dioxide, leading to global warming. If nothing is done to reduce these emissions, climatologists predict global warming of about 1.4 to 5.8 °C between 1990 and 2100 (Wigley and Raper, 2002). To maintain our present way of life, a reduction of fossil energy consumption is necessary and great interest has been devoted to exploring other energy alternatives (Wheals et al., 1999). Therefore, much attention has been focused on ways to utilized biomass energy which has the potential to take the place of the fossil energy because of its abundance and renewability. The saccharification of the biomass is one of the more effective methods of producing an alternative energy source.

The National Renewable Energy Laboratory (NREL) has researched and developed the technology to convert the lignocellulosic biomass of agricultural waste materials into fuel ethanol in order to reduce emissions of carbon dioxide derived from fossil resources and to use the ethanol instead of methyl *tert*-butyl ether (MTBE), which is alleged to have carcinogenic properties (Nguyen et al., 1996; Mielenz et al., 1996; Bailey and Colucci, 1997). NREL has also started a program to help industrial partners with their business plans to produce the ethanol from the lignocellulosic biomass (Cuzens and Miller, 1997). Some of the plans consist of an acid hydrolysis process which has the drawback of producing a large amount of less reactive acid hydrolysis lignin as a by-product, although with superior high conversion efficiency of sugar from the lignocellulosic biomass.

The ethanol production cost from the lignocellulosic biomass is relatively high compared to fossil fuels. To achieve production cost reductions and further develop this acid saccharification process, the effective utilization of a large amount of the acid hydrolysis lignin is important.

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Recently, Yasuda et al. (Yasuda et al., 1981; Yasuda and Terashima, 1982) investigated the structure of guaiacyl sulfuric acid lignin (SAL), one of the acid hydrolysis lignins from gymnosperm, suggesting the formation of condensed structures obtained by intermolecular dehydrations between the benzylic carbons and the six positions of the guaiacyl nuclei. Thus, SAL has extremely low reactivity because of the disappearance of the reactive benzylic hydroxyl and/or ether groups. In the course of basic studies on the chemical structures and reactivity of SAL, they (1989) also found that the condensed aromatic nuclei of SAL formed during concentrated sulfuric acid treatment and having a diarylmethane structure, are selectively exchanged with phenol in the presence of a sulfuric acid catalyst. As a result, phenolized sulfuric acid lignin (P-SAL), which is soluble in a dilute alkaline solution and in organic solvents, is enhanced in reactivity because a reactive *p*-hydroxyphenyl moiety is introduced at the side chain α-position instead of the condensed-type aromatic nuclei (Fig. 1).

Among lignin chemical products, lignosulfonate obtained from spent sulfite pulping liquors are the most available. Lignosulfonate has excellent dispersing properties, and is utilized as a superplasticizer in concrete or gypsum to maintain adequate fluidity. Worldwide production of lignosulfonate is approximately $9.8\times10^5$ tons/year (Gargulak and Lebo, 2000). Thus, the conversion of acid hydrolysis lignin into lignosulfonate is an effective way to utilize it in industrial materials.

In our previous papers, we have reported various procedures to introduce the sulfonate group in P-SAL (Fig. 1) (Yasuda et al., 1997, 1999). In this paper, some lignosulfonates were prepared from guaiacyl acid hydrolysis lignin according to the methods described in our previous papers and we estimate the dispersibility for gypsum paste.

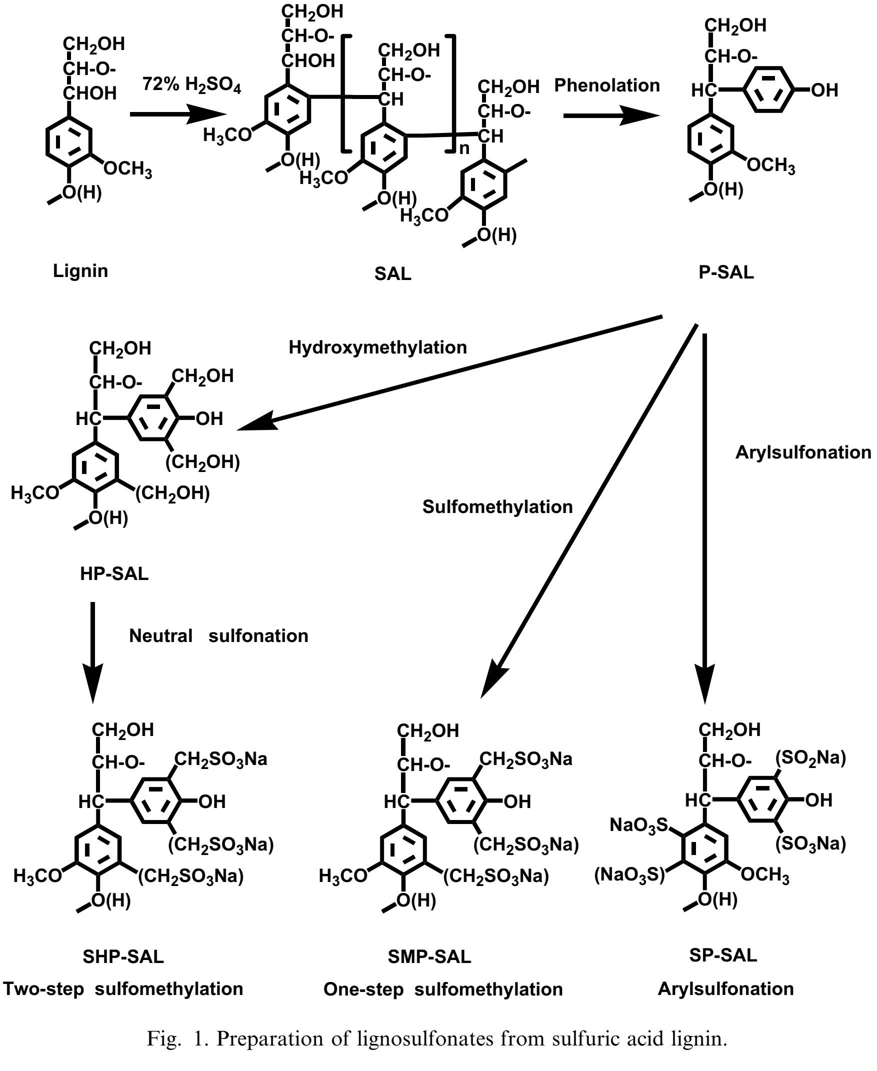

Fig. 1. Preparation of lignosulfonates from sulfuric acid lignin.