A NEW SYNTHESIS PROCESS OF LIGNOSULFONATE USING LIGNIN RECOVERED FROM BLACK LIQUOR OF PULP AND PAPER MILLS

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ABSTRACT

Lignosulfonate is an important deriver of lignin, which has many advantages as a surfactant in various fields, for example, in petroleum, printing, construction and agricultural industries. In this study, a new synthesis process of lignosulfonate by two steps were investigated. The results showed that lignosulfonates synthesized by two steps process have similar characteristics and functional groups with lignosulfonates synthesized by one step process. Process by two steps can be easier operated than that by one step, also reaction time and reaction temperature in two steps process were shorter and lower than in one step process.

Keywords: Lignin, lignosulfonate, methylsulfonation.

1. INTRODUCTION

Annually in Vietnam, the pulping and papermaking processes have created a large amount of black liquor, is a kind of difficult to treat industrial wastewater. Lignin, the main component and coloring material of black liquor, is a new organic resource that can be recovered and used in the production of value-added products.

However low solubility in water of lignin is its main challenges, hinder its applications. Therefore, modification of lignin is required to improve its potential application in industrials. Modification of lignin is a challenge as structure of lignin is complex [1]. Many modifications were studied, in which methyl sulfonation process had high efficiency to increase activity of lignin and create the lignosulfonates that have high water solubility.

Lignosulfonates function primarily as dispersants and binders in the construction, mining and agricultural industries. Concrete admixtures are the largest dispersant use of lignosulfonates, while copper mining, carbon black and coal represent the biggest binder applications. Overall economic performance will continue to be the best indicator of future demand for lignosulfonates. By 2016, Central and Eastern Europe is expected to increase its share of world
lignosulfonate consumption to 28 %, driven by demand in most applications including construction, oil drilling and mining. China is expected to become the second-largest consumer of lignosulfonates, accounting for 17 %, followed by the United States with 15% and Western Europe with 13 %. Lignosulfonates will enjoy strong demand in regions that are expected to invest in significant infrastructure building in the next few years [2].

In our previous study [3], methyl sulfonation process that produces lignosulfonate (LS), was conducted in one step, where methylation (through the addition of formaldehyde) and sulfonation (via using sulfite as the sulfonation agent) were implemented simultaneously. In this process, lignin was dissolved into water to form 20 % sludge, then formaldehyde and Na$_2$SO$_3$ solution were simultaneously added into this 20 % sludge for synthesis reaction. Reaction were conducted under under 105 ºC for 120 min with stirring constantly. Reaction can be briefly outlined as follow:

\[ \text{HCHO} + \text{Na}_2\text{SO}_3 + \text{Lignin} \rightarrow \text{Lignosulfonate} \]

However, it still remains several disadvantages such as long time reaction and high temperature required.

Mohan et al. [9], have reported that pH had significant influence on modification of lignin. The results indicated an increase in solubility from 1 % (unmodified lignin) to 89 % due to sulfomethylation using sodium sulfite and formaldehyde at pH 8.

If lignosulfonate was synthesized by one step process as previous study [3], alkali condition, to completely dissolve lignin for a successful reaction, lignosulfonate was not well produced. For this reason, this study proposed a new process to improve efficiency of lignosulfonate synthesis, in which reaction between sodium sulfite and formaldehyde was able to produce both of agent, that participated in methyl sulfonation, and alkali medium. Lignin tends to dissolve best in alkali condition, therefore lignosulfonate synthesis was more effective.

2. METHOD AND MATERIAL

2.1. Materials

+ Lignin: extracted from black liquor by the pulping and papermaking processes of Vietnam Paper Cooperation (Phu Ninh district, Phu Tho province). This black liquor was cooked by alkali method with Eucalyptus and Acacia melaleuca wood as feedstock. Chemical composition of this black liquor is shown in Table 1.

Table 1. Chemical composition of black liquor by the pulping and papermaking processes of Vietnam Paper Cooperation [3]

| No. | Property          | Percent in concentrated black liquor (%) |
|-----|-------------------|----------------------------------------|
| 1   | Total dried solid | 25.9                                   |
| 2   | Lignin            | 26.5                                   |
| 3   | Acetic Acid       | 3.32                                   |
| 4   | Isobutanoic Acid  | 2                                      |
| 5   | Resin             | 1.31                                   |
| 6   | Sugar             | 1.02                                   |
| 7   | NaOH              | 1.2                                    |
+ Sodium sulfite and formaldehyde: for the methyl sulfonation process.
+ Pure chemicals for separation of lignin and synthesis of LS was made in Vietnam and China.

2.2. Methods

2.2.1. Separation of lignin

Lignin was extracted from black liquor and purified by method described by Komarp [3,5,6], as mentioned in previous study [3].

2.2.2. Synthesis of lignosulfonat from lignin separated from black liquor

In this study, LS was synthesized by two steps methylsulfonation, concentration of chemicals and lignin for this reaction were the same for one step reaction, only time and temperature were changed. Lignin, used for methylsulfonation, was extracted from collected black liquor provided by Vietnam Paper Cooperation [3]. Methyl sulfonation was divided into two steps as Figure 1.

First of all, sodium sulfite (3.2 g) reacted with formaldehyde (0.8 g) to produce CH₂(OH)SO₃Na agent in liquid, at room temperature.

\[ \text{HCHO} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{HO-CH}_2\text{-SO}_3\text{Na} + \text{NaOH} \]
Then methyl sulfonation of lignin was performed by adding dried lignin (1 – 5 g) to produce liquid agent, at 85 ºC, for 90 min under constant stirring speed. After the reaction, solution was cooled to room temperature, then neutralized with H₂SO₄ 20 %, unreacted fraction and other contaminants were separated by filter (Φ 47 mm and nominal pore size 0.45 μm). Afterward, solution was concentrated and dried at 70 ºC – 80 ºC in an oven, so that dried modified lignin was obtained. Last, this product was grinded into fine powder. Flow diagram of synthesis was shown in Figure 1.

\[
\text{HO-CH}_2\text{-SO}_3\text{Na} + \text{Lignin} \rightarrow \text{Lignosulfonate}
\]

The results from one-step method of LS synthesis process in our previous study [3] were used for comparison to the two-step method. Characteristics of LS synthesized by one step process and two steps process were determined by the same analysis method.

2.2.3. Characterising of LS

+ Determination of solubility of LS in solutions at different pHs: to measure the solubility of lignin samples at different pHs, 1g of LS samples was suspended in 20 ml of deionized water at different pHs ranging from 5 to 12. The solubility of these samples was determined according to equation:

\[
\text{Water Solubility (wt.%) } = \frac{\text{Mass of dissolved LS}}{\text{Initial mass of LS}} \times 100
\]

+ Determination of surface tension of LS solution by ASTM D 1331-11 method (Standard Test Methods for Surface and Interfacial Tension of Solutions of Surface-Active Agents).

+ Measuring of IR spectrum to determine molecular structure of LS.

+ Determination of efficiency of reaction: content of residual lignin after reaction was used to calculated efficiency of lignosulfonate from following equation:

\[
\text{Efficiency of reaction (%) } = (1 - \frac{m_{ls}}{m_{lo}}) \times 100
\]

where: \(m_{ls}\): content of residual lignin after methylsulfonation (g); \(m_{lo}\): content of initial lignin (g).

2.2.4. Equipments

+ FT-IR/Raman Impact 410 System (Nicolet Inc. Madison, USA) was used for measuring FT-IR spectrum of products.

+ System of Kruss Optronic GmbH - Alsterdorfer Strasse 220 - 22297 Hamburg, Germany was used for measuring surface tension of LS.

3. RESULTS AND DISCUSSION

3.1. Characteristics of lignin

3.1.1. FT - IR Spectrum of lignin
In this study, FT-IR spectroscopy was used to confirm the chemical structure of lignin by means of conveniently determination of functional groups. Figure 2 presents FT-IR spectrum of lignin, while characteristic absorptions observed are listed in Table 2.

The strong and broad peak at around 3435 cm\(^{-1}\) characterise for OH or phenolic groups. The aromatic skeletal vibrations occur at around 1600 cm\(^{-1}\) and 1500 cm\(^{-1}\). At 1600 cm\(^{-1}\) wave numbers an absorption band of double bonds valence vibrations (C=C) is easily observed, that is explained by bond in aromatic ring of the lignin and aliphatic fragment containing C=C [7,8]. The increase in absorption peaks at around 1461 and 1424 cm\(^{-1}\) correspond to C-H bending and C-H stretching of methylene groups. Peak at 1384 cm\(^{-1}\) can be attributed to C-H stretch in methyl group. In the spectrum of lignin, absorption band observed at 830 cm\(^{-1}\) is related to deformation vibrations of the syringal ring, typical for hardwood lignin [9].

Thus, the spectrum shows that the lignin is composed of guaiacyl and syringal structures, are typical for lignin of hardwood pulp. Band intensity changes in the spectrum reflect the changes taking place during bleaching and lignin extraction.

The results revealed that spectrum of lignin obtained from our study is similar to spectrums reported by other authors [7,8,9]. It can be included that product obtained from extraction was exactly lignin.

### Table 2. Infrared absorption bands frequencies (cm\(^{-1}\)) of lignin [7,8,9]

| Wave number (cm\(^{-1}\)) | Structural group                                           |
|--------------------------|-----------------------------------------------------------|
| 3435.7                   | OH - groups valence vibration (involved in H-bond)       |
| 2938.6                   | C-H bond valence vibration (in methyl and methene groups |
| 2843.4                   | Aromatic skeletal vibrations                              |
| 1613.4                   | Skeletal vibration of aromatic ring                       |
| 1513.7                   | Deformation vibration of C-H bond                        |
| 1461.7                   | Skeletal vibration of aromatic ring                       |
| 1424.3                   | Aliphatic C-H stretch in methyl                           |
| 1383.8                   | Syringal ring vibration with valence vibration of CO-group|
3.1.2. Recovery efficiency of lignin

Recovery efficiency of lignin is calculated as equation:

\[ H = \frac{m_{TT}}{m_{LT}} \times 100\% \]

where:  
- \( m_{TT} \) - yield of recovered lignin, 0.18 kg;  
- \( m_{LT} \) - yield of black liquor, 1 kg.  

Therefore, recovery efficiency of lignin was 18%.

3.1.3. Solubility of lignin under different pH

Observation of the changes of solubility of lignin is shown in Table 3.

| pH | Solubility of lignin (%) |
|----|-------------------------|
| 5  | 0                       |
| 6  | 0                       |
| 7  | 3                       |
| 8  | 52                      |
| 9  | 65                      |
| 10 | 78                      |
| 11 | 85                      |
| 12 | 91                      |

The results in Table 3 show that lignin is not almost dissolved in water; solubility of lignin is increased with the increasing of alkalinity. This suggests that alkali condition in solution was more suitable to dissolve lignin than other.

3.2. Characteristics of lignosulfonate

3.2.1. Changes of pH of reaction between sodium sulfite and formaldehyde

Initial pH of Na₂SO₃ solutions were similar (3.2 g Na₂SO₃ was dissolved in water to form solutions with pH 7.8). The content of HCHO for reaction changes as follow: 0.1; 0.2; 0.4; 0.6 and 0.8 g. The variation of pH of reaction between sodium sulfite and formaldehyde are shown in Table 4.
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Table 4. Changes of pH of reaction between sodium sulfite and formaldehyde.

| $m_{HCHO} (g)$ | Initial pH of Na$_2$SO$_3$ solution | pH of reaction |
|----------------|----------------------------------|---------------|
| 0.1            | 7.8                              | 8.6           |
| 0.2            | 7.8                              | 10.4          |
| 0.4            | 7.8                              | 11.5          |
| 0.6            | 7.8                              | 12.6          |
| 0.8            | 7.8                              | 13.1          |

After reaction, a larger amount of NaOH was produced, resulted in the significant increasing in pH of system, as shown in Table 3. As stated earlier, alkali conditions allow better dissolution of lignin. This result indicated that reaction between Na$_2$SO$_3$ and HCHO was provided appropriate condition to dissolve lignin for producing agent in methylsulfonation of lignin.

3.2.2. Physical properties of lignosulfonate

LS 1 and LS 2 were products of one step and two steps methyl sulfonation of lignin, respectively. Comparison of physical properties of LS1 and LS2 was shown in Table 5.

Table 5. Physical properties of LS products.

| Properties                  | LS 1         | LS 2         |
|-----------------------------|--------------|--------------|
| Colour                      | Black-brown  | Black-brown  |
| Solubility in water (mg/L)  | 45           | 46           |
| Surface Tension (mN/m)      | 46           | 44           |

The results indicated that surface tension of LS solutions is lower than the one of water (72 mN/m. This reveals that obtained products possess properties of surfactant. As seen in Table 4, physical properties of LS2 is similar to LS1.

3.2.3. FT-IR spectrum of lignosulfonates

FT-IR spectroscopy was employed to characterize the raw material and to analyse the changes in the lignin structure during its modification reactions, mainly to observe the introduction of new functional groups or disappearances of existent ones. The FT-IR spectrum of modified lignins or lignosulfonates (LS1 and LS2) are presented in Figure 3 and 4.

In both of lignosulfonate samples, it can be seen that there exists a broad signal around 3400 cm$^{-1}$, which denotes to hydroxyl group. The aromatic skeletal vibrations are presented and located at 1400-1600 cm$^{-1}$. Peaks at 1370 cm$^{-1}$ in spectrum of lignin, which can be attributed to C-H stretch in methyl group is unobservable in lignosulfonates. The peak at 830 cm$^{-1}$ attributing to the aromatic C-H bending is not present in lignosulfonates.

More importantly, the introduction of new groups in lignin structure is usually indicated by presence of bands at 626.9 cm$^{-1}$ after methylsulfonation reaction. 626.9 cm$^{-1}$ peaks corresponds to (C=S) of the sulfonic acid group [7]. The IR peak at 626.9 cm$^{-1}$ is characteristic of the C=S
linkage, which was selected for normalizing each of the sulfonated copolymer spectrums [8]. This peaks, which associated with the sulfonate group attached to lignin, are clear in spectrum. This provides further indication that sulfur is incorporated in to sodium sulfite lignin samples.

Figure 3. FT-IR result of lignosulfonate obtained from one step methylsulfonation.

Figure 4. FT-IR result of lignosulfonate obtained from two steps methyl sulfonation.

3.2.4. Comparative assessment of two methyl sulfonation of lignin

Methylsulfonation of lignin was conducted in both one step and two steps process. Content of methylsulfonated agent were constantly kept, then lignin was added to agent with content of 1, 2, 3, 4, 5 g. Both of processes were performed under the temperature and reaction time as above.

Table 6 shows efficiencies of one step and two steps methylsulfonation reactions of lignin.

| No. | Na₂SO₃ (g) | HCHO (g) | Lignin (g) | Efficiency of reaction (%) |
|-----|------------|----------|------------|---------------------------|
|     |            |          |            | One step | two steps |
| 1   | 3.2        | 0.8      | 1          | 87.5  | 90.1    |
| 2   | 3.2        | 0.8      | 2          | 87.9  | 90.2    |
| 3   | 3.2        | 0.8      | 3          | 85.6  | 88.4    |
| 4   | 3.2        | 0.8      | 4          | 83.3  | 85.6    |
| 5   | 3.2        | 0.8      | 5          | 75.7  | 82.3    |

Lignosulphonate was synthesized with high efficiency. The yield increase with the decreasing of content of lignin. The efficiency of two steps methyl sulfonation is 90.2 %, higher than 87.9 % of one step methyl sulfonation.
In these reactions, formaldehyde provide methyl group and sodium sulfite provides sulfonated group for methyl sulfonation [7]. The reaction proceeds through electrophilic substitution. Under alkali condition, the phenolic groups in lignin are converted to active electrophiles and sodium sulfonate methyl derivative is formed by nucleophilic addition of sodium sulfite anion. For these reasons, the results could be explained as followed: the using of two steps process have more efficient than one step process in forming alkali medium, reaction occur as followed:

\[
\text{HCHO} + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{HO-CH}_2\text{-SO}_3\text{Na} + \text{NaOH}
\]

Lignin added into agent solution from two steps process could be mainly dissolved in alkali medium formed by above reaction. \(\text{H}^+\) in phenolic \(\text{OH}\) group of aromatic ring unit is substituted by \(\text{Na}^+\), to convert dried lignin powder into mobile ionic. Reaction system become homogeneous system, consequently SO_3^- group could be easily attached to subunits of aromatic ring.

![Figure 5. Mechanism of two steps methylsulfonation of lignin.](image)

In one step methyl sulfonation of lignin, adding of HCHO can introduce hydroxyl methyl groups to aromatic rings in lignin in alkali medium, which improve reactivity of lignin, so that sulfonic groups can be introduced to lignin during sufonation [10]. Low alkality medium will result in poor efficiency, adding of NaOH is required, also reversible reaction could be occured. These are disadvantages of one step methylsulfonation of lignin.

![Figure 6. Mechanism of one step methylsulfonation of lignin [9].](image)

In general, results demonstrated that two steps methylsulfonation of lignin is better compared to one step methylsulfonation of lignin. The main advantages of two steps methylsulfonation of lignin include shorter reaction time, lower reaction temperation and higher efficiency.

**4. CONCLUSION**

Lignosulfonate was successfully synthesized via formaldehyde and sodium sulfite. FT-IR spectrum of both of lignosulfonates appeared peak at 626.9 cm\(^{-1}\), corresponds to (C=S) linkage of the sulfonic acid group. Surface tension of LS solutions are 46 mN/m and 44 mN/m, respectively.
Two steps methyl sulfonation of lignin performed at 85 °C, for 90 min is better in comparison with one step process at 105 °C, for 120 min [3], which has high efficiency, smoothly reaction mode, shorter reaction time and lower reaction temperature. The best efficiency is up to 90 %.

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