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Utilization of Black Liquor as Urease Inhibitor for Ammonia Reduction

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ABSTRACT

Urea fertilizers in agricultural operations usually tend to produce large amounts of ammonia due to hydrolysis, therefore contribute to the air pollution. The purpose of this study was to study the potential black liquor from pulp industry as urease inhibitor. Characterization of the black liquor was carried out by Spectrophotometer Fourier Transform Infra-Red (FTIR) and Thermal Gravimetric Analyzer (TGA) instruments. Meanwhile, the determination of ammonia levels was carried out using UV-spectrophotometer. The black liquor used in this process contains OH stretching, C=O stretching, an aromatic ring vibration, ring vibration, and guaiacil ring vibration indicating the presence of lignin. TGA primary weight loss in black liquor occurs above 200 °C. The addition of urease enzymes to urea tends to increase the release of ammonia. Meanwhile, the results showed that black liquor could prevent the nitrogen loss of urea.

Keywords: black liquor, urea, ammonia, lignin, urease inhibitor

INTRODUCTION

Fertilizer is one of the vital ingredients in plant growth and nitrogen is the main nutrient in the agroecosystems (Abalos et al., 2019; Gogoi et al., 2018; Ichihashi et al., 2020; Umar et al., 2020). Wastewater produced by urea fertilizer factories has characteristics, namely the presence of high urea and ammonia content (Machdar et al., 2018). According to Swaminathan (Swaminathan et al., 1984), for every ton of urea produced, about 12 m^3 of water is needed and 2.3 m^3 of wastewater is produced. In the wastewater stream, the concentration of urea is between 1500–10 000 ppm and ammonia is between 400–3000 ppm (Darmadi, 2014; Prasetyo et al., 2019). This wastewater containing high concentrations of urea and ammonia will trigger eutrophication which is very detrimental to aquatic organisms (Afifah et al., 2020; Suryawan et al., 2021; Suryawan I.W.K. et al., 2021). Ammonia content usually increases when contaminated with domestic and agricultural waste because ammonia is found in urea fertilizers and detergents. However, the ammonia content can decrease when a body of water contains a high content of dissolved oxygen (DO).

Black liquor is a residual cooking solution from a pulp mill with a chemical process. In the sulfite process, the chemical commonly used is sodium bisulfite ($NaHSO_3$) (Apriani et al., 2020; Singh & Chandra, 2019). In pulp mills with alkaline processes (soda process and kraft process), the black liquor content is not lignosulfonates but lignin insoluble in water and other compounds (Reyes et al., 2020). Black liquor has the main component of water, inorganic compounds derived from the chemical residue of wood chip cooking, the reaction products during the cooking process, and organic compounds derived from the wood chips. In the pulp and paper industry, lignin must be separated from cellulose to obtain whiter fibers because lignin turns paper to yellow (Reddy et al., 2007). The content of inorganic components in black liquor reaches ~ 45% (Magdeldin & Järvinen, 2020). Besides cellulose, many important polymer organic substances in the plant world are lignin. Lignin is found in the cell wall and partly in the middle lamella (in the intercellular area). The structure of lignin is very diverse depending on the type of plant. In general, lignin polymers are composed of phenyl propane units, namely p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol, which are the parent compounds (pre-substance) of lignin (Davin & Lewis, 2005). The purpose of this study was to determine the effect of using isolated lignin from black liquor as urease inhibitor.

MATERIAL AND METHOD

Black liquor-based inhibitor

Two solutions were prepared to study the inhibition of urease by black liquor. To hydrolyse the urea, solution of urease enzyme was added to the mixture of urea, ethylenediaminetetraacetic acid (EDTA) and buffer solution. To study the inhibition, urease was mixed with isolated lignin from black liquor as inhibitor and the mixture was then added to the mixture of urea, EDTA and buffer solution.

FTIR Analysis

FTIR Thermo NicoletTM iSTM 5 was performed to determine functional group of the samples. Dried isolated lignin from black liquor as inhibitor was mixed with solid potassium bromide (KBr) (0.2–1%), then ground and pressed to form pellet. Each FTIR spectrum was recorded with a blank KBr pellet as background. The samples were then run under transmittance mode in the wavelength range of 500 cm^{-1} to 4000 cm^{-1}.

Thermal gravimetric analyzer

Thermogravimetry is the process of determining the weight of the material in response to changes in temperature and time. Thermal gravimetric analyzer (TGA) is a commonly used instrument based on a thermogravimetric process to investigate the thermal characteristics under a heating environment (Porshnov et al., 2018). In this study, the lignin-based inhibitor was subjected to TGA analyses to study the degradation of the sample. The sample was heated from room temperature to 800 °C at a heating rate of 10 °C/min with nitrogen flow was 20 mL/min (Jawaid et al., 2018).

Ammonia measurement

Beer's law equation was applied in this experiment to analyze absorbance data of ammonium obtained from the UV-VIS spectrophotometer. Standard calibration curves using ammonium stock solution were prepared before inhibition, and data were recorded at 640 nm.

RESULT AND DISCUSSION

Characterization of black liquor

Infrared radiation, which is essential in determining the structure or analysis of functional groups and is most widely used for practical purposes, is the medium infrared region with a wavenumber between 4000–500 cm^{-1} (Silverstein & Bassler, 1963). The FTIR spectrum of lignin shows several prominent absorption bands that can be assigned empirically to the groups present in the lignin molecule. Several bonds or extensions that should exist in lignin are OH stretching, C=O stretching, aromatic ring vibration, guaiacil ring vibration, and ring vibration (Kim et al., 2017; Nada et al., 1998). The lignin-based inhibitor shows several peaks subjected to FTIR (Figure 1). Some are OH stretching at wavelength 3343, C=O stretching at wavelength 1635, aromatic ring vibration at wavelength 1558, cylindrical ring vibration at wavelength 1370, and guaiacil ring vibration at wavelength 1111. These results indicate that lignin was successfully recovered from black liquor. This is because the syringyl and guaiacil rings are the main parameters of a lignin-containing material, these bonds

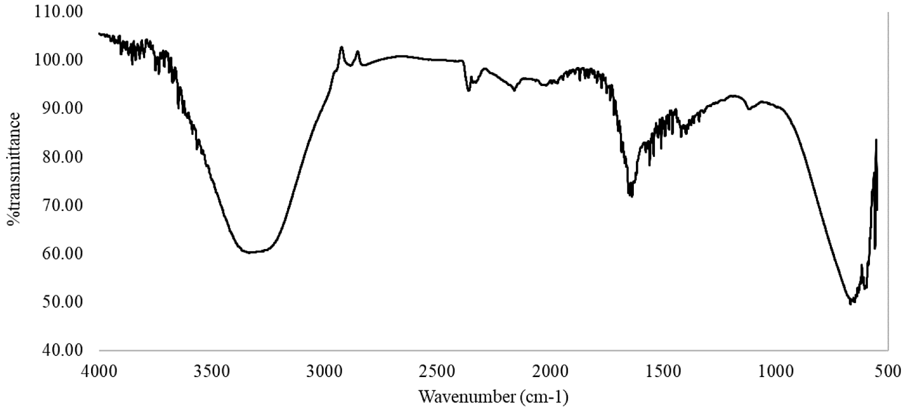

Figure 1. Characterization of FTIR in the lignin based inhibitor used in this research

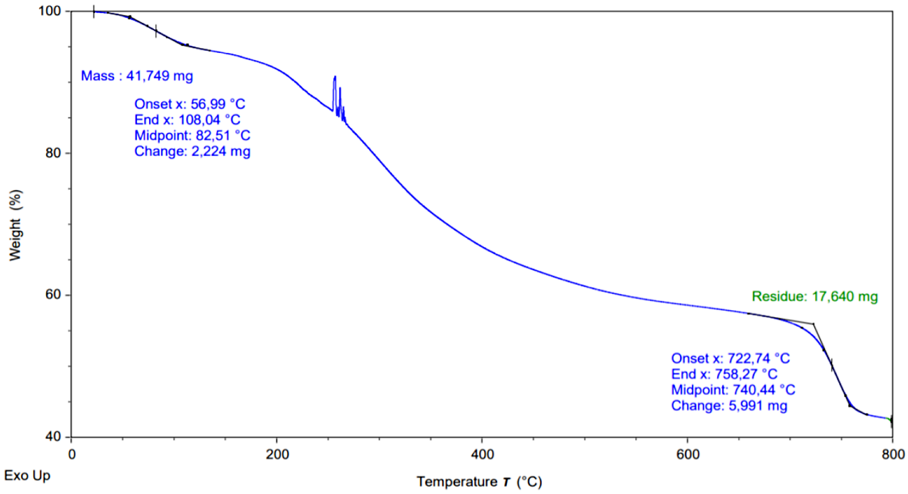

Figure 2. Characterization of TGA in the lignin based inhibitor used in this research

are obtained from the hardwood part of the plant (Kim et al., 2017).

The TGA curve for waste-based lignin, i.e., black liquor after isolation, can be seen in Figure 2. An initial weight loss of about 10% occurs near 10 °C due to moisture loss remaining in the extracted lignin (Kim et al., 2017). Primary weight loss occurs after about 200 °C. This can be explained that around 250 °C, lignin can soften, melt and then unite the lignin particles (Baliga et al., 2003). At this thermal stage which is about 250 °C to 500 °C, the guaiacyl or syringyl components of the lignin and their chemical structure begin to change, resulting in some weight loss. Due to phenol degradation further weight loss occurring above 500 °C is possible (Haykiri-Acma et al., 2010).

Ammonia release

After testing the urease enzyme inhibition with waste-based lignin, the results are as shown in Figure 3. In this inhibition test, two tests were carried out. The first treatment was the urea and urease enzyme, which was to assess the performance of the urease enzyme when mixed with urea without any inhibitors or lignin. The second test performed urea and urease enzymes mixed with lignin-based waste, which determines the performance of lignin-based waste inhibition on ammonia concentrations.

The ammonia change is plotted against time as lignin starts in contact with the urease enzyme. Changes in ammonia concentration were significant differences by addition of lignin-based inhibitor. The addition of lignin-based inhibitor can prevent hydrolysis of urea to ammonia. The effect of waste-based lignin on ammonia concentration can be seen significantly in each experiment (Table 1).

The result in Figure 3 shows that lignin based waste effectively inhibits the urease enzyme, which usually accelerates the urea hydrolysis reaction (Ramli et al., 2014). The parent compounds

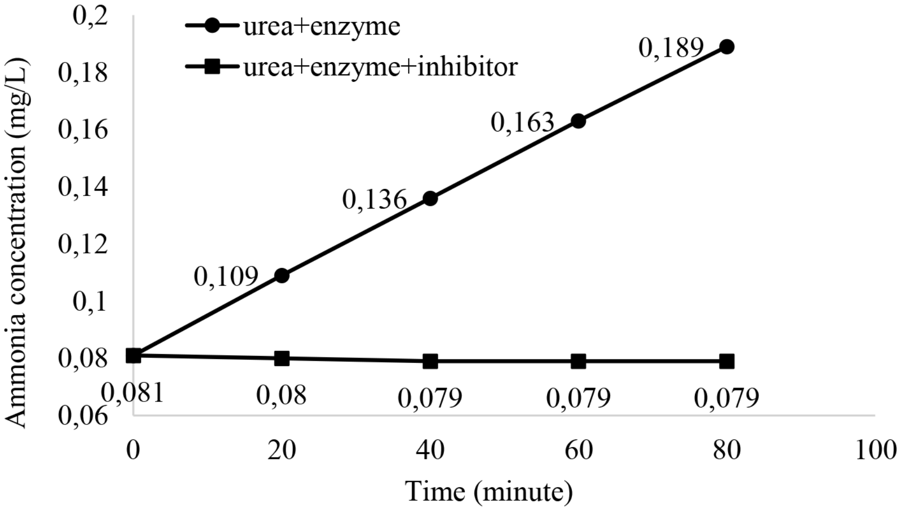

Figure 3. Effect of lignin-based inhibitor on ammonia change

Table 1. ANOVA analysis of differences by addition of lignin-based inhibitor

Source	Type III sum of squares	df	Mean square	F	Sig.
Corrected model	0.008[a]	1	0.008	9.066	0.017
Intercept	0.114	1	0.114	123.581	0
Inhibitor	0.008	1	0.008	9.066	0.017
Error	0.007	8	0.001		
Total	0.13	10			
Corrected total	0.016	9			
[a] R squared = .531 (Adjusted R squared = .473)					

in lignin such as p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol can inhibit the hydrolysis reaction, thereby inhibiting the response between urea-urease (Davin & Lewis, 2005; Ramli et al., 2014). Meanwhile, the highest ammonia concentration was found at 80-minute treatment, 0.189 mg/L. In this treatment, the urease enzyme accelerates the formation of ammonia. This is because urease enzyme plays an essential role as a catalyst for the hydrolysis of urea into ammonia and carbamic acid, which takes place spontaneously (Sujoy & Aparna, 2012).

CONCLUSION

The use of urea is associated with adverse environmental impacts and is a key source of greenhouse and harmful gas emissions. FTIR data revealed the presence of lignin in isolated black liquor. The addition of enzymes to urea tends to increase the release of ammonia. On the other hand, the use of black liquor can inhibit the release of ammonia.

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