Reduction of SO$_2$ Emission Using CuO/γ-Al$_2$O$_3$ Adsorbent: Case Study on Combustion of Algae Biomass Having High Sulfur Content

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(Received November 15, 2016)

Preparation, characteristic, and activity of CuO/γ-Al$_2$O$_3$ as re-generable SO$_2$ adsorbent have been studied. The model gas containing SO$_2$ of about 2,500 mg/m$^3$ (700 mmHg, and 27°C) was made to simulate the flue gas from combustion of algae biomass: Enteromorpha and Chlorella. Experiments were carried out in a tubular reactor electrically heated to maintain adsorption temperature of 300, 350, 400 or 450°C. Amount of adsorbent was 1, 2, 4, or 8 g, and the gas flow rate was set at 1.21 L/min (700 mmHg, and 27°C). Adsorbent with CuO content of about 7.5%-mass could adsorb SO$_2$ successfully and release the outlet gas with a SO$_2$ concentration to meet the national standard of SO$_2$ emission of 750 mg/Nm$^3$. Naturally, the more amount of adsorbent in the reactor, the more complete conversion of SO$_2$ and the lower utilization of CuO.

Key Words

Combustion of biomass, SO$_2$ conversion, CuO/γ-Al$_2$O$_3$ adsorbent, Dry impregnation

1. Introduction

Indonesia is an archipelago country with numerous rural areas that does not have access to electricity. Meanwhile, bioenergy should contribute up to 5% of the national mixed energy resources in 2025$^1)$. Biomass is an alternative fuel for electricity production in Indonesia. Types of biomass that may be found in remote area are grass, roots wood, coconut shell, coconut husk and algae.

Algae may grow rapidly in the watery areas that contain plenty of nutrition from farming activities, the changing of seasons and the movement of ocean currents in coastal areas. Direct combustion of algae biomass is among the most viable, technologically mature and effective options for thermo-chemical conversion$^2)$. The use of algae biomass (waste of production of raw material of medicine and food) as a fuel for the boiler or mini power plant presents an opportunity for the increase in utilization of this type of biomass.

Algae biomass may also be mixed with coconut shell as fuel for power generation in remote coastal area. Examples of proximate and the ultimate analysis of algae biomass, Enteromorpha (En) and Chlorella (Ch), and coconut shell are presented in Table 1. Combustion of these algae biomass may produce flue gas with SO$_2$ concentrations (see Table 2) higher than National Standard of SO$_2$ emission (750 mg/Nm$^3$; Regulation, Ministry of Environment Indonesia: No. 07/2007).

Application of a commercial flue desulfurization

| No | Component | En | Ch | Coconut Shell |
|----|-----------|----|----|---------------|
| 1  | Moisture  | 5.19 | 6.64 | 6.51 |
| 2  | Ash       | 28.12 | 5.99 | 7.56 |
| 3  | Volatile matter | 57.77 | 74.21 | 68.82 |
| 4  | Fixed Carbon | 8.92 | 13.16 | 17.11 |

HHV* (MJ/dry.kg) | 11.44 | 21.99 | 17.42 |

*Calculation using eq. HHV = 0.4571 (%C dry) -2.70$^6)
(FGD) similar to that in a coal fired power plant may be not economically feasible. Therefore, development of re-generable adsorbent such as CuO/γ-Al2O3 has been considered to have an attractive application in mini power plants. The use of the CuO/γ-Al2O3 adsorbent is expected to have some advantages, such as being re-generable without a significant decrease of adsorption capacity, and no significant change in physical and chemical properties 5) ~ 8). Reaction occurring in the adsorption is as follows:

\[
\text{CuO} + \text{SO}_2 + 1/2\text{O}_2 \rightarrow \text{CuSO}_4
\]  

and a side reaction is:

\[
\text{Al}_2\text{O}_3 + 3\text{SO}_2 + 3/2 \text{O}_2 \rightarrow \text{Al}_2\text{(SO}_4\text{)}_3
\]  

Reaction in the desorption or regeneration is:

\[
\text{CuSO}_4 \rightarrow \text{CuO} + \text{SO}_3
\]  

SO2 produced in this regeneration is then converted to H2SO4 similar to the sulfuric acid conventional process. Sulfuric acid has a wide range industrial application.

CuO/γ-Al2O3 can be made using several techniques. The dry impregnation has been chosen since it has advantages compared to the wet impregnation, such as a possibility for large production with even CuO distribution over the surface of support.

Effectiveness of CuO/γ-Al2O3 in SO2 adsorption depends on adsorption temperature, copper content in adsorbent, SO2 concentration in gas and other factors. Our previous study was carried out to evaluate the effects of copper content in adsorbent and adsorption temperature on the adsorption capacity, the conversion of CuO to CuSO4 in adsorbent 9). The model gas was prepared at high SO2 concentration with a concentration of about 48,320 mg/Nm3, to simulate the flue gas composition from the combustion of a high sulfur coal.

In our experimental study presented in this paper, the model gas was made at a SO2 concentration similar to that from the combustion of algae biomass (as presented in Table 2). Furthermore, this study has been focused on the effects of adsorption temperature and amount of adsorbent in the reactor on the adsorption capacity of CuO/γ-Al2O3, SO2 conversion, and CuO conversion. The SO2 concentrations at the outlet of reactor (adsorber) were observed from time to time to evaluate the breakthrough time, i.e. when the adsorbent attained saturation.

2. Experimental

2.1 Adsorbent Preparation

The 8Cu adsorbent (with Cu content of about 8%) was chosen instead of the 5Cu type. Although the 5Cu adsorbent had a better adsorption capacity, it was found that SO2 also reacted with Al2O3 according to reaction (2) 9).

In this study, the 8Cu adsorbent was prepared using the impregnating solution of Cu(NO3)2.3H2O on γ-Al2O3 support 9). As support, γ-Al2O3 was available in our laboratory as already used in previous study. In this research, adsorbent was prepared twice, i.e. 65 and 106 g.

The impregnated support (raw adsorbent) was dried in two steps: in an oven of 50°C for 8 h, then at 120°C for 5 h. Finally, the dry impregnated support was calcined at 400°C for 8 h to the readily adsorbent.

Table 2 SO2 concentration in flue gas from combustion of algae biomass and coconut shell, single and dual fuel at various amount of excess air

| No | Type of Biomass (mass ratio) | SO2 concentration in flue gas (dry basis, mg/Nm3) |
|----|-----------------------------|--------------------------------------------------|
| 1  | En 100%                     | 13,217 11,316 9,993                              |
| 2  | Ch 100%                      | 4,596 3,923 3,422                               |
| 3  | Coconut shell 100%           | 192 164 144                                     |
| 4  | En 75% + coconut shell 25%   | 9,355 8,011 7,004                               |
| 5  | Ch 75% + coconut shell 25%   | 3,802 3,248 28,34                               |
| 6  | En 50% + coconut shell 50%   | 5,944 5,091 4,452                               |
| 7  | Ch 50% + coconut shell 50%   | 2,846 2,432 2,124                               |

*theoretical calculation

2.2 SO2 Preparation

The model gas was a mixture of SO2 and air, with SO2 concentration of about 2500 mg/Nm3. Gas SO2 was obtained from the following reaction (procedure may be found in standard textbook of chemistry):

\[
\text{Na}_2\text{S}_2\text{O}_5 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + 2\text{SO}_2
\]  

The SO2 produced from above reaction was then injected into a storage tank and mixed with air. The SO2 concentration in the mixing tank and in the gas line during experiments were measured using the flue gas analyzer (Bacharach PCA-3).

2.3 Adsorption Test

Adsorptions of SO2 on 8Cu adsorbent were conducted at 300, 350, 400 and 450°C, for 90 min each. To avoid decomposition of CuSO4, (equation 3), the adsorption temperature were kept below 500°C 8). The 8Cu adsorbent was placed in a fixed bed reactor with varying bed weight of 1.0, 2.0, 4.0 and 8.0 g (see Fig. 1).

The gas flow rate was adjusted using a micro needle valve to get a desired flow of about 1.21 mL/min (measured at 700 mmHg and 27-30°C). The SO2 concentrations were measured at outlet of the reactor every minute while SO2 concentrations at the inlet of reactor were measured
at the beginning and at the end of experiment. These measurements were used for calculating the conversions of SO₂ and CuO. The SO₂ concentrations in the gas storage tank were also measured before and after each experiment.

2.4 Analyses

Copper content of the 8Cu adsorbent were analyzed using Atomic Absorption Spectroscopy (Varian Spectra AA 220). The pore properties of the adsorbent, i.e. surface area, volume and average diameter were analyzed using Nitrogen Adsorption-Desorption, BET method (Nova 3200e Quanta Chrome). Types of crystals in the 8Cu adsorbent were analyzed using X-Ray Diffraction (Bruker D8 Advance).

The adsorption capacity is defined as the cumulative amount of adsorbed SO₂ (in mg or mol) per gram of the 8Cu adsorbent. The amounts of adsorbed SO₂ were calculated from the measured concentration of SO₂ (every minute along the experiment of about 90 min). For every interval time of two successive measurements (At), the amount of adsorbed SO₂ was calculated using the trapezoidal method as follows:

\[
N_{SO_2,At} = \frac{Q_{gas} \cdot At \cdot [(C_{SO_2,i} - C_{SO_2,o})_t + (C_{SO_2,i} - C_{SO_2,o})_{t+At}]/2}{(4)}
\]

with:

- \(N_{SO_2,At}\) = amount of SO₂ adsorbed during a time interval from t to t+At
- \(Q_{gas}\) = gas flow rate (L/min)
- \(C_{SO_2,i}\) = SO₂ conc. at reactor inlet, (mol/L)
- \(C_{SO_2,o}\) = SO₂ conc. at reactor outlet, (mol/L)
- \(t\) = period of adsorption process (min)

The above calculation was then extended for the amount of absorbed SO₂ in the whole experiment. The measurements were taken with an equal period of 1 min.

\[N_{SO_2} = \sum N_{SO_2,At} ; \text{sum of all 1 min intervals between 0-90 min}\]

Conversions of SO₂ (\(X_{SO_2}\)) were calculated using the following equations:

\[X_{SO_2} = \frac{N_{SO_2}}{(Q_{gas} \cdot t \cdot C_{SO_2,i})} ; t = 90 \text{ min}\]

The molar amount of reacted CuO (RCuO) was the same as the adsorbed SO₂ in the whole experiment (see equation (I)):

\[R_{CuO} = N_{SO_2}\]

The conversion of CuO is:

\[X_{CuO} = \frac{R_{CuO}}{N_{CuO,0}}\]

with

\[N_{CuO,0}\] = initial amount of CuO (mol) in the bed of adsorbent.

3. Results and Discussion

3.1 Characteristic of 8Cu Adsorbent

The 8Cu adsorbent obtained from the two preparations with Cu contents of 7.54 and 755%-mass. The appearances of adsorbents are shown in Fig. 2.

The pore properties of mixed fresh adsorbent (see Table 3) might indicate that the original supports of adsorbent were homogeneous with our previous research. Furthermore the XRD analysis indicated similar patterns of the fresh adsorbents. Thus the dry impregnation for preparation of Cu/γ-Al₂O₃ adsorbent was repeatable with consistent result.

![Fig. 2 Photograph of adsorbents: (a) γ-Al₂O₃ original support, (b) 8Cu adsorbent after impregnation, (c) 8Cu adsorbent after drying & calcination](image_url)

### Table 3 Copper content and pore properties of fresh 8Cu adsorbent

| No | Adsorbent code | Production quantity (g) | Copper content (mass fraction) | Pore properties |
|----|----------------|-------------------------|--------------------------------|-----------------|
|    |                |                         |                                | Specific surface area (m²/g) | Volume (cm³/g) | Average diameter (Å) |
| 1  | 8Cu           | 10                      | 76.6%                          | 196.11           | 0.41          | 83.20          |
| 2  | 8Cu           | 10                      | 77.4%                          | 184.02           | 0.41          | 90.88          |
| 3  | 8Cu (this study) | 65                     | 75.5%                          | 192.30           | 0.44          | 90.09          |
| 4  | 8Cu (this study) | 106                    | 75.4%                          |                  |              |                |
3.2 Adsorption Test

It was found in every experiment that the concentrations of SO2 in the storage tank or at the inlet of reactor decreased noticeably (see Fig. 4). This was due probably to the reaction of SO2 with water vapor in the storage tank to form sulfurous acid. Therefore, average concentrations of those at the beginning and the end of experiments were used in the calculation of conversions of SO2 and CuO.

In general, the 8CuO adsorbent could adsorb SO2 to get the outlet SO2 concentration of less than the emission standard. Of course the adsorption capacity and rate depended on the amount of adsorbent and the adsorption temperature, as well as the gas flow rate and the inlet SO2.
The amount of adsorbed SO$_2$ clearly depended on the amount of adsorbent in the reactor as presented in Fig. 4 (a), (b), (c), and (d) for the amount of adsorbent of 1, 2, 4 and 8 g respectively. In the case of adsorption using small amount of adsorbent (1 and 2 g), the adsorptions approached saturation conditions quickly. Breakthrough curve like adsorption process could be seen in these cases with a saturation time of about 5 min.

In the adsorption using larger amount of adsorbent (4 and 8 g), the effect of temperature on the progress of adsorption could be seen more clearly than those with smaller amount of adsorbent. Anyhow, the higher temperature, the adsorptions were slower to attain saturation conditions. This phenomenon indicated that the reactive adsorption, equation (1), took place faster and utilized more available CuO at higher temperature.

In the adsorption using 8 g of adsorbent, the saturation condition was still far, and the SO$_2$ concentration at the reactor outlet met the standard emission up till the end of experiment.

Form data in Fig. 4 and using equation (4), the amount of adsorbed SO$_2$ could be calculated. With the increase in the amount of adsorbent in the reactor, the adsorbed SO$_2$ clearly increased (see Fig. 5). But as CuO was more available, more CuO was not utilized yet as represented as the increase in the distance between the measured adsorbed SO$_2$ and the stoichiometric one. This was in line with the observation, particularly presented in Fig. 4 (d). This was in line with the observation, particularly presented in Fig. 4 (d).

Presented in another way, SO$_2$ cumulative conversion increased with the increase in the amount of adsorbent (see Fig. 6). At the experiments using 8 g adsorbent, the SO$_2$ conversion attained almost 100%, as sufficient CuO were available. The more amount of adsorbent, the more space time for reaction, i.e.: 0.064 s (1 g adsorbent; bed height of 1.02 cm), 0.128 s (1 g; 2.04 cm), 0.257 s (4 g; 4.09 cm) and 0.514 (8 g; 8.17 cm), respectively.

Effect of temperature on the extent of SO$_2$ conversion could also be observed in Fig. 6 (see also Fig. 5). Calculation using stoichiometry in reaction (1), indicated that CuO conversion in 8Cu adsorbent increased with increasing adsorption temperature as shown in Fig. 7. The higher adsorption temperature, the more CuO conversion, which was in line with literature $^{10}$.

The effect of temperature on CuO conversion in the adsorption using different amount of adsorbent was presumably the same as presented in Fig. 6. But as seen in Fig. 7, the effect of temperature seemed more significant at experiments using small amount of adsorbent because almost all initial CuO had been utilized. On the other hand, more CuO was still available in the experiment using larger amount of adsorbent. This discussion might also explain the pattern of the change in the SO$_2$ concentration at the reactor outlet with time as presented in Fig. 4 (a), (b), (c) and (d).
4. Conclusions

The 8Cu adsorbent (containing 7.5%-mass of CuO) was made successfully using the dry impregnation method. Characteristics of adsorbents were more or less homogen from one preparation to the others.

Adsorption of SO\textsubscript{2} using the 8Cu adsorbent was considered satisfactory to reduce SO\textsubscript{2} concentration to meet the national standard of SO\textsubscript{2} emission. At a temperature in the range of 300 to 450\textdegree{}C, the increase in temperature could increase the SO\textsubscript{2} conversion, and accordingly could increase the CuO conversion.

The re-generable adsorbent CuO/\textgamma-Al\textsubscript{2}O\textsubscript{3} was considered to have a good prospect to be implemented in a mini power plant fueled with algae biomass having a high sulfur content.

Acknowledgment

This study is a part of doctoral research in Chemical Engineering Doctoral Program, ITB. Scholarship for doctoral program and research on re-generable adsorbent is financially supported by PT. Pupuk Sriwidjaja Palembang, and Faculty of Engineering, University of Sriwijaya, Palembang.

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