



Sulfur Removal in Bio-Briquette Combustion Using Seashell Waste Adsorbent at Low Temperature

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Abstract. Presently, biomass is mostly utilized as co-fuel in coal combustion in view of energy diversification and emission reduction. However, since the coal content of bio-briquettes is high (up to 80% in this study), gas emissions such as those of SO_x still occur. Therefore, the introduction of SO₂ adsorbent is common in coal briquette or bio-briquette combustion. A calcium-based material is usually used for this goal. The aim of this study was to observe the effects of desulfurization temperature and Ca/S ratio (Ca = calcium content in adsorbent; S = sulfur content in coal and biomass) on desulfurization efficiency and kinetics. The ratio of coal to biomass (palm kernel shell/PKS) was fixed at 90:10 (wt/wt) and the ratios of Ca to S were varied at 1:1, 1.25:1, 1.5:1, 1.75:1 and 2:1. The mixtures of coal, PKS and adsorbent were briquetted at a molding pressure of 6 ton/cm² with *Jatropha curcas* seeds and starch mixture as binding agents. Desulfurization was performed within a temperature range of 300 to 500°C for 720 seconds at an airflow rate of 1.2 L/min. The results showed that the highest desulfurization efficiency (90.6%) was associated with the Ca/S ratio of 2:1 and temperature of 400°C. Moreover, the highest reaction rate constant of desulfurization was 0.280 min⁻¹.

Keywords: *bio-briquette; calcium-based adsorbent; desulfurization kinetics; low temperature desulfurization; seashell waste.*

1 Introduction

Industrial desulfurization has mainly been performed at high temperatures of up to 1600°C for both pulverized and briquetted coal [1-4]. This is not appropriate for household application. The present study addressed bio-briquette desulfurization at lower temperatures using seashell waste as adsorbent in the absence of calcination. Applying this kind of adsorbent to bio-briquette production can greatly reduce its cost so that it is suitable for household consumption.

From an environmental point of view, the use of coal as a source of energy, particularly via combustion, has a serious effect on the ambient air quality. A

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number of efforts have been made to address the associated problems, for example: mixing the coal with co-fuel such as biomass [3-16], refuse-derived fuel [5,6], tire-derived fuel [5,6] and plastics [6]. These efforts involved both pulverized and briquetted coals.

The introduction of co-fuel, especially biomass, into coal combustion – which is known as co-combustion – has some advantages. Among them is the reduction of gas emissions of CO₂, N₂O and NO_x [10,11]. Biomass is known as a neutral cycle energy source. However, the problem of SO_x emissions is still associated with co-combustion, especially if low-rank coal is used as primary fuel. As is the case in coal combustion, it is necessary to adsorb and control SO_x emission during co-combustion. Many kinds of adsorbents have been adopted in the past, particularly calcium-based adsorbents [12-25]. The first generation of calcium-based scrubbers (a type of FGD) was made in Great Britain in 1920.

For calcium-based adsorbents, a number of studies on the desulfurization of coal briquettes have been conducted using both commercial-based and natural-based adsorbents. These studies were generally conducted using coal briquettes. There have been only a few studies on the desulfurization of bio-briquettes. In conventional combustion, when calcium-based adsorbents are injected directly into the flue gas, the sulfur removal efficiencies were only 40-60% [17]. Moreover, when the adsorbents were physically mixed with the coal, the desulfurization efficiencies were usually lower than 40% [17,18].

In recent years, a bio-briquette produced from a mixture of coal and biomass under high-compression pressure has been developed. It is possible to limit the dust emission to a level lower than that associated with pulverized coal combustion. The coal type was found to strongly influence the desulfurization efficiency of the bio-briquettes, which varied from 25-67% [12]. In addition, a number of investigators have observed very good SO₂ removal results of up to 80% in bio-briquette combustion [13]. In their studies Lu, *et al.* [12] and Naruse, *et al.* [13] added scallop shell, limestone and calcium hydroxide to the bio-briquettes as desulfurizer.

Limestone (in the form of CaO and Ca(OH)₂ in some cases) is commonly added as adsorbent to coal and coal/co-fuel blend combustions, both for pulverized and briquetted coal [19-25]. There is also a combined adsorbent of Ca(OH)₂/fly ash [21]. It has been found that Ca(OH)₂ shows better desulfurization capabilities than limestone because of its lower calcination temperature. Scallop shell did so too due to its larger porosity after calcination [13]. On the other hand, the application of seashell adsorbent for the desulfurization of coal or coal/co-fuel blends is still limited [12-15].

For the present investigation, the selected adsorbents were natural calcium-based adsorbents from seashell waste, i.e. scallop shell. This kind of adsorbent ranks below $\text{Ca}(\text{OH})_2$ in calcination temperature and surface area. However, scallop shell is a waste material that is abundantly available. Moreover, it consumes less energy in the drying step than $\text{Ca}(\text{OH})_2$ and performs better than limestone or CaO .

It is well known that desulfurization using a calcium-based desulfurizer or adsorbent in fossil fuel combustion involves some chemisorption reactions. First, the oxidation of the sulfur in the bio-briquette results in the formation of sulfur dioxide (SO_2) [14]:



During calcination, a desulfurizer in the form of CaCO_3 decomposes at a temperature above 840°C (in the case of limestone) to produce calcium oxide (CaO) and carbon dioxide (CO_2):



However, in this case, the calcination of the scallop shell adsorbent and the desulfurization processes were predicted to occur simultaneously during bio-briquette combustion at lower temperatures (only up to 500°C).

In the next step, the CaO compound chemically captures and adsorbs the SO_2 gas in the following reactions:



As has been outlined in ref. [16], if the rate of Reaction (3) is independent from the concentration of a reactant, changing its concentration has no effect on the reaction rate, so that $dC_{\text{CaSO}_4}/dt = k_{\text{obs}}$, where dC_{CaSO_4}/dt is the reaction rate (CaSO_4 production) and k_{obs} is the rate constant. This model is known as a pseudo-zero-order approximation. The new constant is called k_{obs} because this is the rate constant that was observed in our experiment. Since particular attention was paid to the sorption of SO_2 (the SO_2 consumption) by choosing SO_2 as a primary reactant, it was possible to define the rate of sorption (for a zero-order reaction, with $k_{\text{obs}} = k$) as:

$$\frac{dC_{\text{SO}_2}}{dt} = -k \tag{4}$$

Thereafter, if the reaction has a pseudo-first-order rate, the equation for the reaction rate is $dC_{\text{CaSO}_4}/dt = kC_{\text{CaO}}^m C_{\text{SO}_2}^n C_{\text{O}_2}^o$, where C_{CaO} , C_{SO_2} and C_{O_2} are the concentrations of CaO , SO_2 and O_2 , respectively; and m , n and o are the reaction orders for CaO , SO_2 and O_2 , respectively. It is assumed that the concentrations of CaO (a solid phase adsorbent) and O_2 (excess air condition) remain almost

constant; their concentrations can be included in the rate constant, a pseudo-first-order rate reaction, $dC_{\text{CaSO}_4}/dt = k_{\text{obs}}C_{\text{SO}_2}^n$, where $k_{\text{obs}} = kC_{\text{CaO}}^mC_{\text{O}_2}^o$ can be defined for the SO_2 consumption (with $k_{\text{obs}} = k$) as:

$$\frac{dC_{\text{SO}_2}}{dt} = -kC_{\text{SO}_2}^n \quad (5)$$

The objectives of this study were to examine the effects of the combustion temperature and the ratio of Ca/S (Ca = calcium content in adsorbent, S = sulfur content in coal and biomass) on the SO_2 profile, desulfurization efficiency and kinetics (rate constant). The proposed process diverged from previously developed processes in the application of low-temperature desulfurization and a low Ca/S ratio. The efforts were very valuable from an economic standpoint and useful in technical terms.

2 Experimental Procedure

The materials used were low-rank coal from West Aceh District and palm kernel shell (PKS) from a palm oil industry area in the District of Aceh Tamiang, Indonesia. Scallop shell was collected in Banda Aceh City (Indonesia), where it had been dumped in abundant amounts as restaurant waste. Starch (tapioca-based) and jatropha seeds (for use as a binding agent) were also found in Banda Aceh. The starch was available commercially. The study employed a crusher, a briquette molding machine, a furnace, a screen, a gas analyzer, a condenser, a compressor, BET (Brunauer-Emmett-Teller) and X-ray diffraction (XRD).

The procedures and conditions associated with the bio-briquette mold were the same as those from our previous studies [14] and [15]. The amount of binder added was also comparable to that from past studies [26-28]. It has been found that the best coal/PKS ratio for the bio-briquette is 90:10 (wt/wt); this results in maximum water resistance and durability [14,15]. Therefore, the bio-briquettes in this sequel study were produced solely at the coal/PKS ratio mentioned above.

The air-flow rate for desulfurization was 1.2 L/min (300% excess of stoichiometric air-to-fuel ratio) and the desulfurization time was 12 minutes (720 seconds). Moreover, the desulfurization temperature was varied at 300°C, 350°C, 400°C, 450°C and 500°C. Table 1 presents the proximate and ultimate analysis of the low-rank coal, PKS and jatropha seeds. The scallop shell (without calcination) had a Ca content of 27.8% (wt) [15], which was significantly lower than that of the limestone (53%) [13]. However, it was found that the scallop shell exhibited good desulfurization capabilities due to its CaO content and high porosity after calcination.

Table 1 Ultimate analysis data for low-rank coal, PKS and jatropha seeds.

	Unit (adb) ^{a)}	Low-rank coal	PKS	Jatropha seeds
Carbon	%	60.65	29.32	56.39
Hydrogen	%	5.75	5.88	7.99
Nitrogen	%	0.48	0.30	2.81
Total sulfur	%	0.38	0.13	0.21
Oxygen	%	27.34	61.74	28.44
Calorific Value	kcal/kg	5,904	4,865	5,864

^{a)}adb = air dried base

Jatropha seed was used as a binding agent because jatropha is a renewable energy source. Moreover, the seed contains a gum that was expected to play a role as a binder. It should be noted that jatropha shell and crude jatropha oil (CJO) have been observed to be suitable substitute fuels. Investigations into this property were conducted using direct combustion [29,30]. In the present examination, the jatropha used in the bio-briquette mixture included the seed and the shell. The use of jatropha seed as a binder in the briquetting of the coal and biomass mixture is a new idea, seeking to avoid smoke. Since the biomass (PKS and binder) content of the bio-briquettes was up to 20%, it was expected that their desulfurization behavior would differ from that of coal or biomass briquettes.

A desulfurization test was conducted using a vertical tube furnace to which were attached an electrical heater element, a thermocouple, an on-off controller, a compressor, a flow meter, a sample basket, a gas pipe, a condenser and a gas analyzer. The experiment was performed in a closed combustion chamber for all briquettes at all Ca/S ratios and oxidation temperatures. A bio-briquette sample was put in a sample basket. Air flowed through the basket and over the outer surface of the briquette and in the next step diffused to the pores of the briquette, reacting with the C, H, N and S in the briquette. There was no resistance for mass and heat transfers between the briquette and the air. The flue gas released was analyzed after 1 minute, 3 minutes, 6 minutes, 9 minutes and 12 minutes using Gas Analyzer Model E 4400-S. A schematic of the apparatus is shown in Figure 1. Desulfurization efficiency was predicted using the following equation [12,13]:

$$\eta_{SO_2} = 1 - \frac{SO_{2(Ca/S=n)}}{SO_{2(Ca/S=0)}} \tag{6}$$

where $SO_{2(Ca/S=0)}$ represents SO_2 emission in bio-briquette combustion without adsorbent or desulfurizer, and $SO_{2(Ca/S=n)}$ is SO_2 emission in bio-briquette combustion with adsorbent or desulfurizer.

The reaction order and rate constant were evaluated by taking the integration on Equations (4) and (5). These reaction orders and rates only represent the chemical reaction or chemical-sorption; they do not consider the diffusion. The reaction order is not affected by the adsorbent content and temperature; these two parameters only influence the reaction rate (i.e. rate constant).

3 Results and Discussion

3.1 Effect of Temperature on the SO₂ Profile without Adsorbent

This part of the experiment was conducted to determine the effect of temperature on bio-briquette combustion without adsorbent. The real concentration of SO₂ produced from combustion at temperatures of 300°C, 350°C, 400°C, 450°C and 500°C could have been determined by burning the bio-briquette in the absence of an adsorbent since the bottom ash resulting from the combustion adsorbed only a negligible amount of the SO₂ gas. The results were used as a reference in the prediction of the desulfurization efficiency of the bio-briquette combustion in the presence of adsorbent.

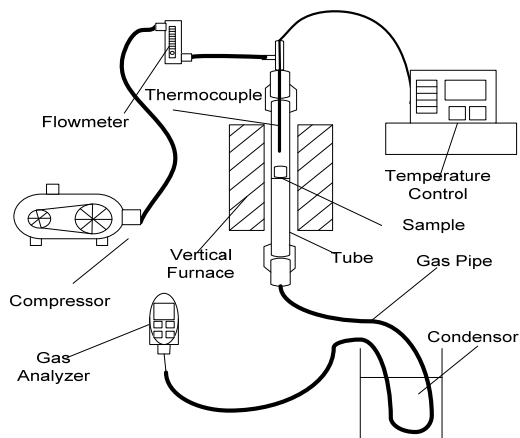


Figure 1 Schematic of experimental apparatus.

However, in the kinetics investigation discussed in Sections 3.4 and 3.5, the amount of sulfur (or SO₂) in the bottom ash and fly ash was taken into account in the sulfur's overall mass balance. The overall mass balance of the sulfur was determined by assuming that the air oxidized all the sulfur to form SO₂. Thus, the SO₂ adsorption rate of the adsorbent was based on the remaining SO₂ (theoretical SO₂ minus SO₂ released in the flue gas).

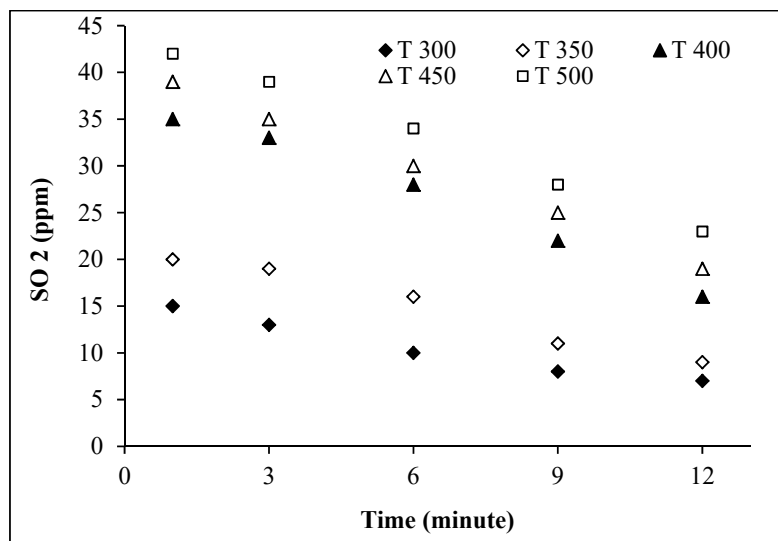


Figure 2 Concentration of SO₂ released without adsorbent.

Profiles of the SO₂ produced in bio-briquette combustion without adsorbents are presented in Figure 2. The figure shows that the highest concentration of SO₂ appeared at a combustion temperature of 500°C. It is clear that the combustion temperature affected the amount of SO₂ released in the flue gas and this trend was maintained at all temperature levels. The highest concentration of SO₂ at 500°C was 42 ppm and at 300°C it was 15 ppm after 1 minute of burning. Moreover, after 12 minutes of burning, the concentration of the released SO₂ dropped to 23 ppm and 7 ppm for the temperatures of 500°C and 300°C, respectively. As the figure shows, for the remaining temperatures, the SO₂ concentration lay between the aforementioned values.

3.2 Effect of Temperature and Ca/S Ratio on the SO₂ Profile with Adsorbent

A higher sulfur content in bio-briquettes may cause environmental issues during combustion. To solve this problem and reduce SO₂ emissions, it is necessary to add adsorbent. Calcium-based adsorbent reacts with SO₂ to form solid gypsum. In the second stage of our experiment, the aim was to determine how much SO₂ was captured by the adsorbent. The stoichiometric reaction between the calcium (Ca) in the adsorbent and the sulfur (S) in the bio-briquette was used to determine the total number of moles of adsorbent used. The profile of SO₂ released during the burning of bio-briquettes with adsorbent is shown in Figure 3.

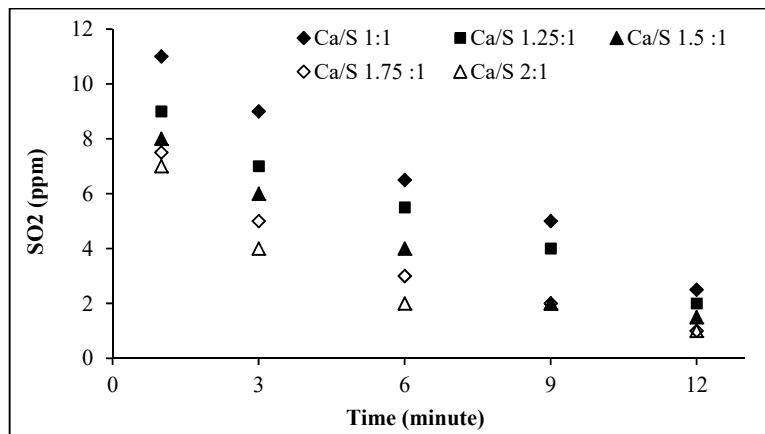


Figure 3 Concentration of SO₂ released at a temperature of 500°C.

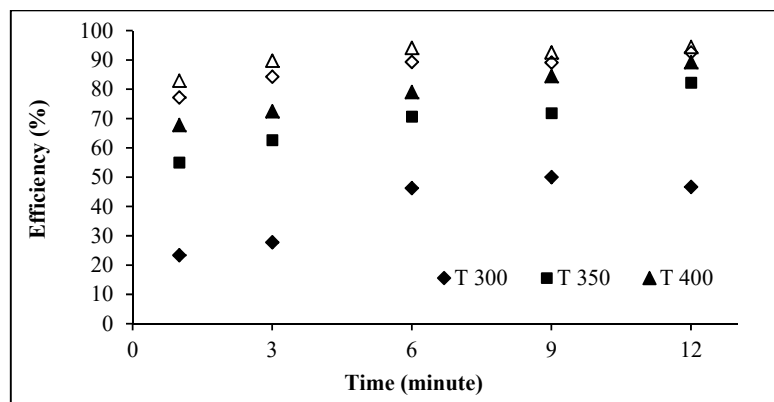


Figure 4 Desulfurization efficiency at Ca/S ratio of 2:1.

From Figure 3, it is apparent that the concentration of SO₂ decreased significantly as the adsorbent content increased (i.e., with an increase in Ca/S ratio). The concentration of SO₂ produced at 500°C was very low (11 ppm for a Ca/S ratio of 1:1 and 7 ppm for a Ca/S ratio of 2:1) after burning for 1 min. After the experiment had run for 12 minutes, the amount of SO₂ released declined sharply to 2.5 and 1 ppm for the aforementioned Ca/S ratios, respectively. The remaining temperatures, ranging from 300 to 450°C, exhibited similar phenomena. Therefore, can be stated that the adsorbent was good at shifting the SO₂ emissions.

In addition, a rise in temperature tended to lower the SO₂ production, however, the effect was not significant. This explains why the calcination of the scallop

shell improved at the higher temperature of 500°C, forming a much larger amount of CaO. The effect of temperature on SO₂ adsorption is presented in Figure 4 (for the Ca/S ratio of 2:1). Other Ca/S ratios exhibited similar trends.

It was predicted that desulfurization would mainly occur during the devolatilization and char burning, since the SO₂ would be captured even at a low temperature (300°C). In our previous studies, devolatilization occurred at a very low temperature (200°C) for low-rank coal drying. However, the drying process was done in a vacuum state of 160 Torr [31,32]. Since the lowest temperature observed in this investigation was 300°C, it is expected that devolatilization and char burning had partly taken place.

At atmospheric pressure, the oxidation of coal would also have occurred at a temperature $\leq 200^\circ\text{C}$ [33]. The establishment of these facts evidently proves that devolatilization and char combustion accompanied the oxidation of the coal. All the experimental studies cited here was performed using Indonesian low-rank coal (lignite).

Some of the physical properties of the adsorbent are discussed in greater detail here too. The surface area of the scallop shell adsorbent was 35.4 m²/g (measured using BET (SHIBATA APP.SA-1100) at a nitrogen flow rate of 150 ml/min). The particle size of the adsorbent was -60/+pan mesh (250 μm). The stated surface area was good enough compared to limestone that had been calcined at 1,100°C, giving 47 m²/g, and at 900°C, giving 27 m²/g, for a particle size of 91 μm [1].

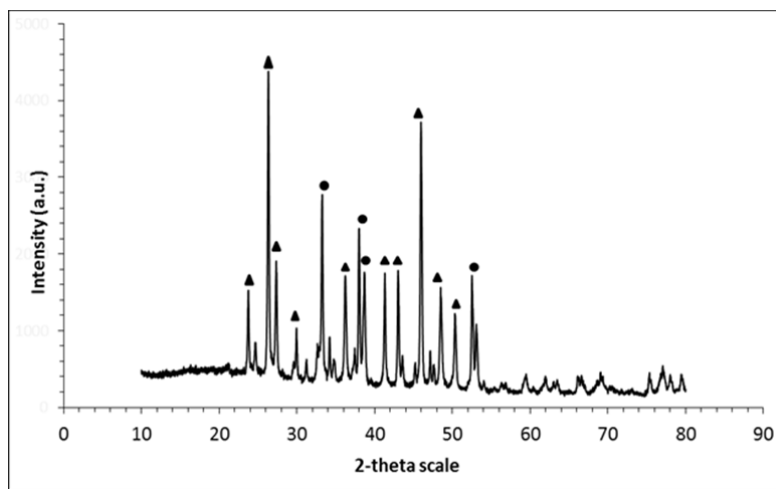


Figure 5 XRD pattern for natural scallop shell powder (▲ CaCO₃; ● CaO).

Figure 5 shows the XRD patterns of natural (non-calcined) adsorbent (taken using an XRD-6100 Shimadzu). Reference to previous observations reveals that the adsorbent was mainly composed of CaCO_3 . The diffraction peaks at 2θ around 23.7° , 26.3° , 27.3° , 30° , 36.2° , 41.3° , 43° , 46° , 48.5° and 50.3° are indicative of this. CaO also appeared at 33.2° , 38° , 38.1° and 52.5° [34-36]. It is expected that the CaCO_3 was decomposed in situ during the burning of the bio-briquettes to produce CaO . In that case, the CaO component will act as an adsorbent, capturing SO_2 in the presence of air in accordance with Reaction (3). The CaCO_3 content (comprising CaO) was more than 60% (wt); the MgCO_3 content followed at more than 18%.

3.3 Effect of Temperature and Ca/S Ratio on the Efficiency of Desulfurization in the Combustion of Bio-Briquettes

Figure 4 presented above shows the influence of temperature on the efficiency of desulfurization at a Ca/S ratio of 2:1. The efficiency was evaluated in relation to the difference between SO_2 concentrations release without and with adsorbent, not to the initial content of S in the bio-briquettes [12,13], and therefore is called relative efficiency. Consequently, the efficiency of desulfurization was not directly influenced by the bio-briquette mass loss during the combustion process. The concentrations of SO_2 in the absence of adsorbent for any temperature of investigation are plotted in Figure 2. These data were used as reference in the efficiency calculation. It can be seen that the effect of temperature was the most significant at the lowest experimental temperature (300°C). At temperatures in the range of 350 - 500°C , the temperature did not have a great impact on the efficiency.

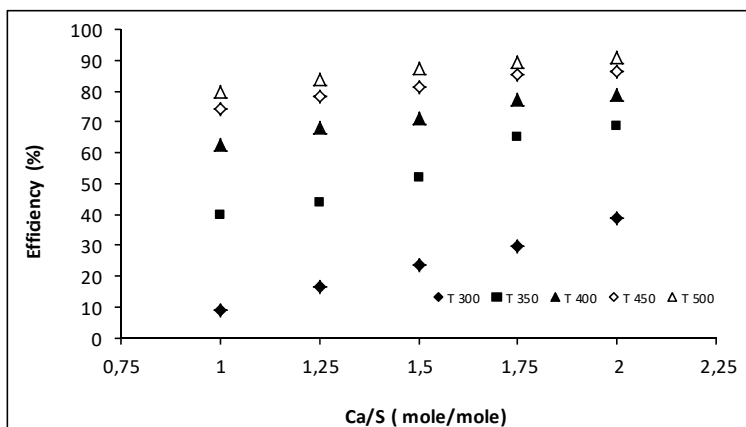


Figure 6 Desulfurization efficiency as a function of temperature and Ca/S ratio.

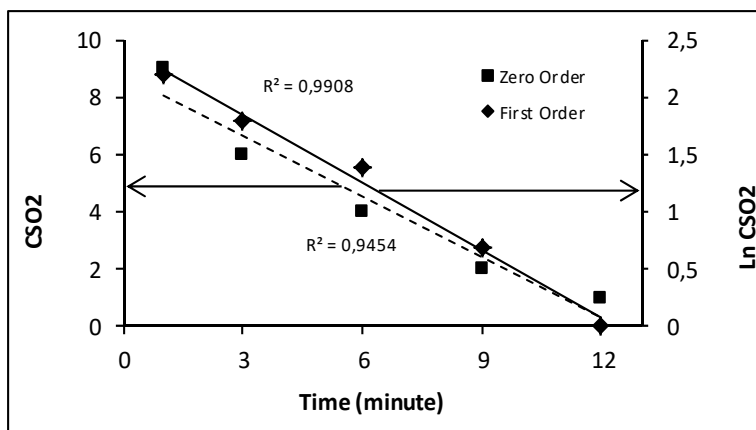


Figure 7 Plot of the C_{SO_2} and $\ln C_{SO_2}$ at the Ca/S 2:1 and a temperature of 300°C.

For a clearer discussion, Figure 6 shows the efficiency of the bio-briquette desulfurization as a function of temperature and the Ca/S ratio. The data in the figures indicates that the efficiency of desulfurization increased with the temperature and the Ca/S ratio, and the maximum values were achieved at a temperature of 500°C and a ratio of 2:1. The entire adsorbent gives the highest efficiency (as much as 90.6%). This indicates that the proposed desulfurization process had a better performance than previously proposed processes [12,13], even when the temperature and Ca/S ratio were low.

In their investigations, Lu, *et al.* and Naruse, *et al.* [12,13] applied a higher temperature range (700-900°C) as well as Ca/S ratios of up to 5. The highest efficiency was only 80%. It was claimed that scallop shell has a calcination temperature of about 627°C (900 K). However, it is possible that the calcination temperature of scallop shells is actually lower than 600°C since the efficiency of desulfurization obtained in the present study was greater than any observed in the past. As mentioned above, the present research was conducted at temperatures $\leq 500^\circ\text{C}$.

All the data obtained in the present study, especially those concerning the efficiency of desulfurization, accord well with facts observed in the past [12,13], namely those indicating that the desulfurization efficiency tends to increase with the Ca/S ratio. The temperature and Ca/S ratio significantly influence some data but do not have the same effect on other data. At higher temperatures, the effect of the Ca/S ratio is not strong enough.

As elaborated above, the bio-briquette combustion process occurred in two stages: volatile combustion and char burning. A volume reaction model was developed to describe the volatile combustion and a shrinking-core reaction model was developed to describe the char combustion. Since the desulfurization mainly occurs in the char combustion stage [12], the present study adopted the shrinking-core reaction model as the basis for predicting the kinetics of the desulfurization process. For the desulfurization process during char combustion it was assumed that: (1) sulfur and desulfurizer were uniformly distributed in the bio-briquettes; (2) only oxidation of carbon and sulfur, to form CO_2 and SO_2 , took place during char combustion; and (3) the diffusion rate of the flue gas exiting was equal to that of the oxygen entering. The adsorbent then captured the SO_2 produced at the flame sheet.

3.4 Determination of the Desulfurization Reaction Order

The bio-briquette desulfurization process is determined by the reaction kinetics when the associated combustion occurs. The mechanisms of desulfurization using calcium-based adsorbent have been established and applied elsewhere [37-40]. In this study, the desulfurization mechanism used a previously proposed model. There were two possibilities for the kinetics: zero order kinetics or first order kinetics. To prove them, then, the reaction order was estimated for all the experimental data collected at all the observation conditions. Different from the desulfurization efficiency evaluation, the kinetics were estimated using the integral method based on the material balance by considering the initial content of S in the bio-briquettes.

From the data presented in Figure 7, for a Ca/S ratio of 2:1 and a temperature of 300°C , the desulfurization of the bio-briquettes closely followed the first order reaction. The more linear the trend, the more accurate the data reflecting the reaction order. It was clear that the correlation coefficient for the first order was approximately 0.99 (99%). This value was higher than for the zero order, which was approximately 0.945 (94.5%). In general, the desulfurization of bio-briquettes using scallop shell adsorbent is a first order reaction. Naruse *et al.* elaborated on this in their work [13] using the shrinking-core reaction model, which fit the experimental data well. Because the characteristics and concentration profiles of SO_2 observed here were similar to those observed in the past, it was possible to apply the shrinking-core reaction model to the present study.

3.5 Effect of Temperature and Ca/S Ratio on Desulfurization Reaction Rate

To determine the value of the reaction rate constant (k) of the desulfurization, the experimental data were plotted in a straight line. The reaction had a first order rate as indicated by the slope, which is evident from Figure 7. In this case, $-k$ = the slope of the line. The k value at a Ca/S ratio of 1:1 and a temperature of 400°C was 0.280 min⁻¹ (or $-k = -0.2795$ min⁻¹). As Table 2 indicates, this was the highest k value for the scallop shell adsorbent.

It was determined that the best conditions for the k values occurred in a desulfurization temperature range of 400-450°C and at a Ca/S ratio of 1:1. In this case, the Ca/S ratio did not actually affect the reaction rate. The higher Ca/S ratio did not necessarily result in a higher reaction rate. The Ca/S ratio of 2:1 did not result in a higher reaction rate than the Ca/S ratio of 1:1. In addition, the reaction kinetics did not influence the efficiency of SO₂ adsorption. This was evident as the Ca/S ratio of 1:1 had the lowest efficiency but was associated with the highest reaction rate.

Table 2 Reaction rate constant (k , min⁻¹) Values for bio-briquette desulfurization.

Temperature (°C)	Ca/S ratio (mole/mole)				
	1:1	1.25:1	1.5:1	1.75:1	2:1
300	0.195	0.193	0.124	0.173	0.197
350	0.162	0.185	0.090	0.186	0.165
400	0.280	0.197	0.135	0.193	0.175
450	0.153	0.157	0.211	0.112	0.205
500	0.189	0.198	0.076	0.106	0.148

4 Conclusions

SO₂ emissions from bio-briquette combustion were successfully suppressed by introducing adsorbent or desulfurizer into bio-briquettes. Scallop shell adsorbent was proven to have self-desulfurization capabilities in bio-briquette combustion. Desulfurization mainly occurred during the devolatilization and char combustion stages as the SO₂ was even captured at lower temperature (300°C). Bio-briquette desulfurization with seashell (i.e. scallop shell) as the adsorbent or desulfurizer has first order reaction kinetics.

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