

8-2-2016

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Recommended Citation

Mahidin, Mahidin; Gani, Asri; Hani, M. Reza; Syukur, Muhammad; Hamdani, Hamdani; Khairil, Khairil; Rizal, Samsul; Hadi, Abdul; and Mahlia, T.M.I. (2016) "Use of Green Mussel Shell as a Desulfurizer in the Blending of Low Rank Coal-Biomass Briquette Combustion," *Makara Journal of Technology*. Vol. 20 : No. 2 , Article 7.

DOI: 10.7454/mst.v20i2.3062

Available at: <https://scholarhub.ui.ac.id/mjt/vol20/iss2/7>

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Abstract

Calcium oxide-based material is available abundantly and naturally. A potential resource of that material comes from marine mollusk shell such as clams, scallops, mussels, oysters, winkles and nerites. The CaO-based material has exhibited a good performance as the desulfurizer or adsorbent in coal combustion in order to reduce SO₂ emission. In this study, pulverized green mussel shell, without calcination, was utilized as the desulfurizer in the briquette produced from a mixture of low rank coal and palm kernel shell (PKS), also known as bio-briquette. The ratio of coal to PKS in the briquette was 90:10 (wt/wt). The influence of green mussel shell contents and combustion temperature were examined to prove the possible use of that material as a desulfurizer. The ratio of Ca to S (Ca = calcium content in desulfurizer; S = sulfur content in briquette) were fixed at 1:1, 1.25:1, 1.5:1, 1.75:1, and 2:1 (mole/mole). The burning (or desulfurization) temperature range was 300-500 °C; the reaction time was 720 seconds and the air flow rate was 1.2 L/min. The results showed that green mussel shell can be introduced as a desulfurizer in coal briquette or bio-briquette combustions. The desulfurization process using that desulfurizer exhibited the first order reaction and the highest average efficiency of 84.5%.

Abstrak

Pemanfaatan Cangkang Kerang Hijau sebagai Desulfurizer dalam Pembakaran Briket Campuran Batubara Peringkat Rendah-Biomassa. Bahan alam berbasis kalsium oksida (CaO) tersedia secara melimpah. Salah satu sumberdaya yang potensial dari bahan alam tersebut berasal dari cangkang moluska laut antara lain kerang, simping (kerang kampak), remis, tiram, keong dan siput (siput terompet). Bahan berbasis CaO tersebut memperlihatkan unjuk kerja yang baik sebagai desulfurizer atau adsorben dalam pembakaran batubara untuk mereduksi emisi SO₂. Dalam kajian ini, serbuk cangkang kerang hijau, tanpa kalsinasi, digunakan sebagai desulfurizer dalam produksi briket dari campuran batubara peringkat rendah dan cangkang kelapa sawit (CKS), yang juga dikenal dengan bio-briket. Rasio batubara terhadap CKS dalam briket adalah 90:10 (dalam berat). Pengaruh kandungan cangkang kerang hijau dan temperatur pembakaran dikaji dalam rangka untuk membuktikan kemungkinan pemanfaatan bahan tersebut sebagai desulfurizer. Perbandingan Ca terhadap S (Ca = kandungan kalsium dalam desulfurizer; S = kandungan sulfur dalam briket) ditetapkan sebesar 1:1, 1.25:1, 1.5:1, 1.75:1, dan 2:1 (dalam mol). Temperatur pembakaran (atau desulfurisasi) berkisar antara 300-500 °C; waktu reaksi adalah 720 detik dan laju alir udara ditetapkan pada 1,2 L/menit. Hasil penelitian menunjukkan bahwa cangkang kerang hijau dapat ditambahkan dalam pembakaran briket batubara atau bio-briket sebagai desulfurizer. Proses desulfurisasi menggunakan desulfurizer tersebut memperlihatkan reaksi order pertama dan efisiensi penyerapan SO₂ rata-rata tertinggi adalah 84,5%.

Keywords: desulfurizer, biomass, briquette, combustion, green mussel shell, low rank coal

1. Introduction

Only a few studies on the utilization of of marine mollusk shells as a catalyst, adsorbent or desulfurizer can be

found [1-8]. All the studies used the calcined mollusk shell with a treatment temperature higher than 600 °C and most of them used it as a catalyst in biodiesel production. Only Lu *et al.* and Naruse *et al.* applied it as

a desulfurizer in bio-briquette combustion in 1998 [1,2]. High temperature application consequently implies high energy consumption or high cost. In order to lower the energy consumption in implementation, our proposed idea was to utilize green mussel shell as the desulfurizer without calcination and applied at low temperature desulfurization process [9-11].

The above mentioned idea was proved by the past studies on the self-desulfurization process [12]. In their observation, self-desulfurization was led by some alkaline components contained in the coal ash itself such as CaO, MgO, Al₂O₃, Fe₂O₃, K₂O, and Na₂O. Of course there was obviously no calcination in those content alkalines before they were put in the burning chamber. The alkaline sulfates should not be dominant at lower temperature under oxidizing conditions, while most of them are sulfides under reduction conditions. Those phenomena strongly brought us to a new concept in applying green mussel shell (a kind of Ca-based material) as a desulfurizer in the bio-briquette combustion without calcination, by means that Ca in the desulfurizer might act like alkaline in the coal ash as well.

Based on the literature study, Boro *et al.* [4] have pointed out that mollusk shells are a natural ceramic composite with excellent fracture strength and fracture toughness, which are attributed to their unique microstructures. The shell material is composed of 95-99% crystalline calcite or aragonite (form of calcium carbonate, CaCO₃) and a protein film which is used as the binder in varying amounts from 0.1% to 5% by weight [13]. The highest content of CaCO₃ in those materials give an advantage in the adsorption of sulfur even by using small amounts of adsorbent/desulfurizer.

Actually, calcium carbonate (CaCO₃) from limestone or seashells will decompose to form calcium oxide (CaO) and carbon dioxide (CO₂) at a temperature of 825 °C. The reaction is endotherm with the standard heat of reaction of 178.3 kJ per mole, which means the energy needed to run the reaction. Based on the several works mentioned above, CaCO₃ in the mollusk shells presented almost the same calcination temperature, i.e. ≥700 °C [1-8]. Only Lu *et al.* and Naruse *et al.* observed that the calcination temperature for oyster shells was 627 °C [1,2].

However, the study conducted by Yang *et al.* [14] has brought us to a conclusion that the calcination process occurred at a low temperature. They worked at temperature intervals of 250-450 °C. Furthermore, an additional effort to enhance the calcination at low temperature has been done in this study; this was the reduction of material particle sizes. Particle sizes of coal, PKS, jatropha seeds (as a binder) and desulfurizer were -60/+pan mesh, so that the mass transfer limitation in the solid phase transformation was minimalized by increasing the transfer surface area.

Figure 1 describes the solid phase transformations on limestone when exposed to alternating oxidizing and reducing conditions proposed by Hansen *et al.* [15]. The consumption of oxygen and reducing decomposition of CaSO₄ has great effects on the sulfation efficiency. The CaS produced in a reduced condition is further converted to CaSO₄ or SO₂ in an oxidizing situation. Those all reactions might take place since the oxidizing and reducing agents (O₂ and CO) are available in the combustion chamber. It is assumed that the CaCO₃ in green mussel shell has a similarity in physical and chemical characteristics with limestone. Thus the same phenomena is expected to appear for CaCO₃ of green mussel shell.

On the other hand, it was found that the sulfur retention efficiency of coal ash is promoted by an increase in the molar ratio of Ca/S, up to 96% at Ca/S = 8. Even though there was some scattering against the Ca/S molar ratio, resulting from the calcium amount involved in the sulfur capture, the reaction is different as different kinds of coal ash and other alkaline elements in coal may also have made contributions to sulfur retention [16].

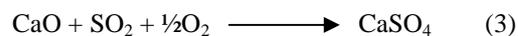
As in the previous study, we consider only the three following reactions. At first, sulphur in the bio-briquette is oxidized by oxygen to form sulphur dioxide (SO₂) [9]:



On the other hand, CaCO₃ in the green mussel shell will be decomposed to produce calcium oxide (CaO) and carbon dioxide (CO₂):



Finally, CaO chemically captures and bonds the SO₂ gas with the following reactions:



In terms of the reaction (3), the equation of reaction rate is $r = kC_{\text{CaO}}^a C_{\text{SO}_2}^b C_{\text{O}_2}^c$; where r is rate of the reaction; k is rate constant; C_{CaO} , C_{SO_2} , and C_{O_2} are concentrations of CaO, SO₂ and O₂, respectively; and a , b , and c are reaction orders for CaO, SO₂, and O₂, respectively. Since the concentrations of CaO and O₂ almost remained constant (because it is a catalyst and it is in great excess with respect to the SO₂), their concentrations can be included in the rate constant, obtaining a pseudo-first-order rate equation, $r = k_{\text{obs}} C_{\text{SO}_2}^b$; where $k_{\text{obs}} = kC_{\text{CaO}}^a C_{\text{O}_2}^c$. This new constant is called k_{obs} because this was the rate constant that was observed in the experiment. If the reaction rate is independent of the concentration of a reactant, changing its concentration would have no effect on the rate of the reaction, so that $r = k_{\text{obs}}$. This model is known as a pseudo-zero-order approximation.

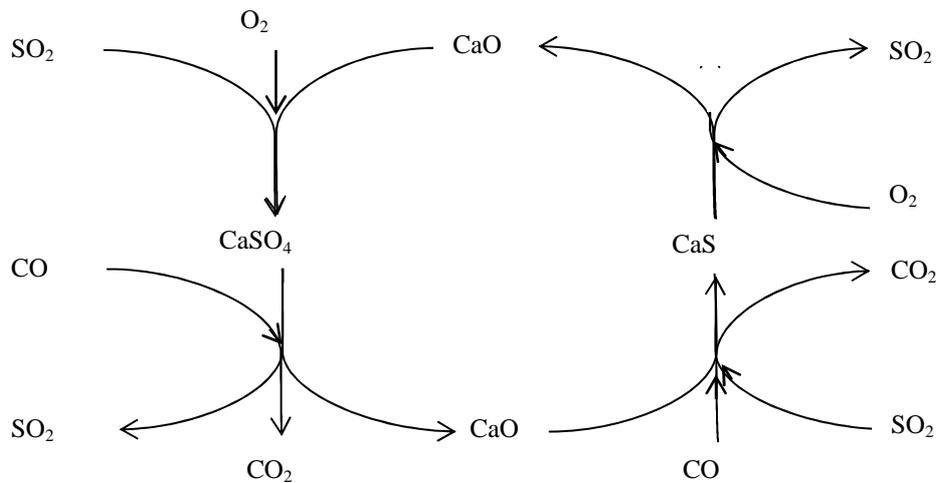


Figure 1. Solid Phase Transformations on Limestone

The objective of the paper is to investigate the possibility of using green mussel shell as a desulfurizer in the blending of low rank coal-biomass (PKS) briquette combustion, the effect of burning temperature and desulfurizer content (or Ca/S ratio) on the efficiency of desulfurization and the reaction order of desulfurization by using that material.

2. Methods

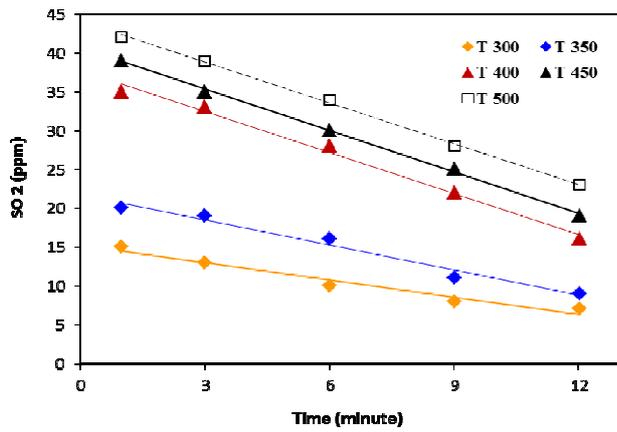
The detailed methodology has been described elsewhere [9,11]. The same materials, equipment, experimental procedures and conditions, and calculation methods were adopted here. Only the type of desulfurizer used here was different from previous studies. Green mussel shell examined here has Ca content of about 27.6% by weight [10,17]. The methodology is briefly summarized as follows: the ratio of coal to PKS (biomass) was 90:10 (weight to weight), and ratio of Ca to S (Ca = calcium content in the desulfurizer; S = sulfur content in the briquette) were fixed at 1:1, 1.25:1, 1.5:1, 1.75:1, and 2:1 (mole/mole). Briquetting pressure and hold pressing time were 6 ton/cm² and 300 seconds, respectively. The content of starch and jatropha seeds mixture (as a binder) was 10% (by weight). Desulfurization temperatures were 300, 350, 400, 450, and 500 °C, air flow rate was 1.2 L/min, and the reaction time was 720 seconds.

Based on the past study, there are two possibilities of kinetics that could appear, i.e. zero order and first order [2]. Since the attention was particularly paid to the pseudo-zero-order and pseudo-first-order approximations, the sorption rate of SO₂ can be defined as $r = k_{\text{obs}}$ (or $dC_{\text{SO}_2}/dt = k_{\text{obs}}$) and $r = k_{\text{obs}}C_{\text{SO}_2}^b$ (or $dC_{\text{SO}_2}/dt = k_{\text{obs}}C_{\text{SO}_2}^b$). Further, kinetics parameters were predicted by taking integration on the rate equation, both for zero and first orders.

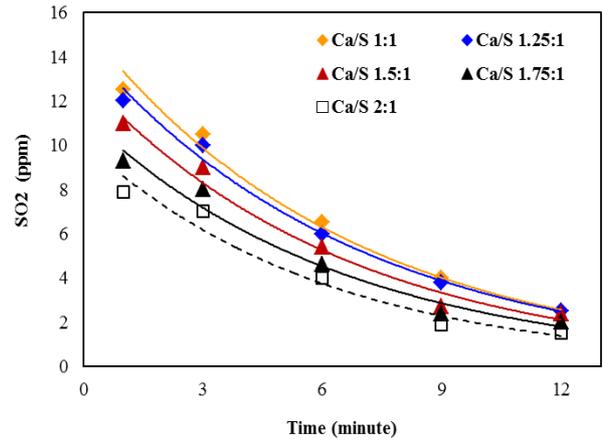
3. Results and Discussion

Figure 2 below presents the profile of SO₂ as function of temperature (for the combustion without the desulfurizer) and ratio of Ca/S during the bio-briquette burning. From the figure it is seen that the desulfurizer applied in this study can reduce the SO₂ content in the flue gas to a considerably low level, especially at the higher temperature and Ca/S ratio. The highest SO₂ without desulfurizer was up to 42 ppm (appeared at 500 °C), whereas the highest SO₂ after adding the desulfurizer only stood at 14 ppm (found at 300 °C and Ca/S ratio of 1:1).

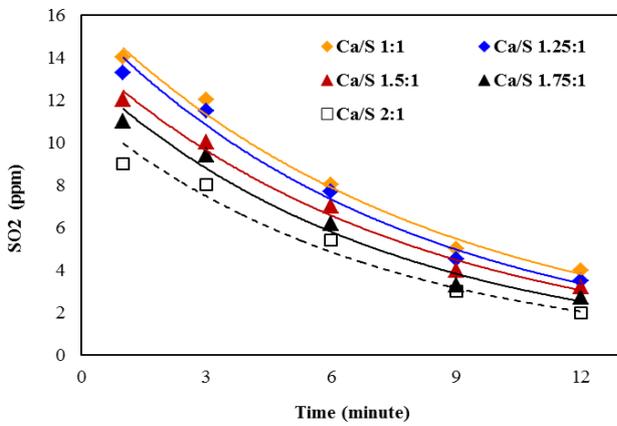
Furthermore, the smallest SO₂ was 0.8 ppm, observed at 500 °C and Ca/S ratio of 2:1. In the range of investigation conditions it was evident that the SO₂ concentration tended to decrease with an increase in temperature and Ca/S ratio. As was obtained in the previous researches, the mollusk shells-CaCO₃ effectively decomposed at temperatures ≥ 700 °C, therefore, this is the reason why the SO₂ still declined in regard to an increase of combustion temperature. A similar argument also satisfied for parameter Ca/S, but introduced higher desulfurizer in coal burning which will affect the specific energy content in the fuel. Then, the Ca/S ratio ≤ 2 is recommended. It was recorded in the past investigations that the greatest SO₂ suppression in the bio-briquettes combustion appeared at the Ca/S ratio of 2 [9,11]. Similar behaviors were also revealed in coal combustion, both for briquetted and pulverized coals, wherein the better Ca/S ratio was 2 [17-20]. In addition, at a temperature range of 400-500 °C, the SO₂ concentrations at 720 minutes were almost leveled off and converged. These facts proved that to finish the reaction after 720 seconds was acceptable.



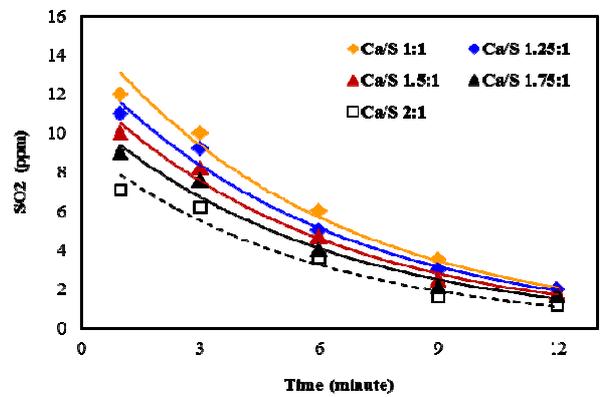
(a)



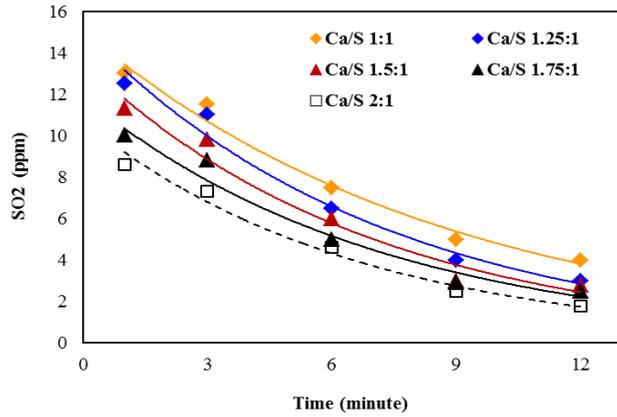
(d)



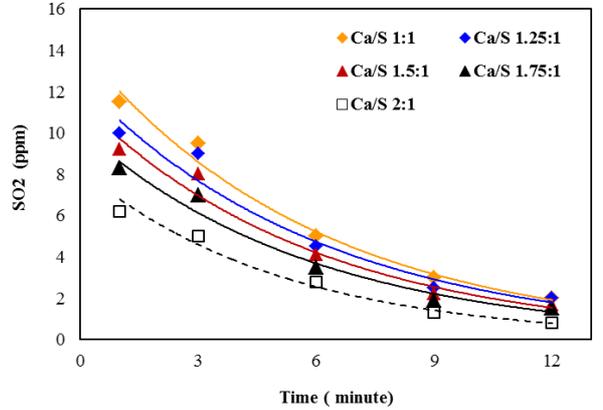
(b)



(e)



(c)



(f)

Figure 2. Profile of SO₂ Concentration in the Flue Gas; (a) without desulfurizer; (b) 300 °C; (c) 350 °C; (d) 400 °C; (e) 450 °C; (f) 500 °C

Since the entire bio-briquette was prepared under lower molding pressure (i.e. 6 ton/cm²) and smaller materials particle size (i.e. -60/+pan mesh or $d_p \leq 0.25$ mm), a higher desulfurization capability could be achieved. It was observed that smaller sorbent particles give higher SO₂ reduction and CaO conversion; it even appeared in

the pulverized coal combustion [21]. Reducing the desulfurizer diameter from 10 to 1 μ m promotes the SO₂ capture from 40 to 50% at Ca/S of 2 [22]. In contrast, for coal briquette burning, a large-sized briquette was recommended in order to provide longer residence time of the SO₂ in the particles and more chance for SO₂

capture by the adsorbent [23]. The same condition might occur in the bio-briquettes because both those briquettes were physically and chemically similar. In this examination, the briquette had a cylindrical form with a diameter of 1.6 cm and height of 2 cm, which can be considered as a medium sized briquette.

Thereafter, Figure 3 shows the average efficiency and reaction order evaluations. Figure 3(a) clearly shows that the efficiency of desulfurization rises by improving the temperature of combustion and the Ca/S ratio. The effect of temperature was more evident than the Ca/S ratio. The highest efficiency reached a level of 84.5%, reflected certainly in the same conditions to the lowest SO₂ content in the flue gas (i.e. at 500 °C and Ca/S ratio of 2:1). This level of efficiency is considerably greater than that reported by Guoqing et al. which was up to 67% only [1] and slightly higher compared to Naruse *et al.* i.e. 80% [2]. In this work, the desulfurization efficiency was estimated using the same procedure as the ones used by Guoqing et al. and Naruse et al. The largest efficiency at higher temperature was promised by decomposition of CaCO₃ and improvement in its value at higher Ca/S was due to the sulfur retention phenomena as discussed above.

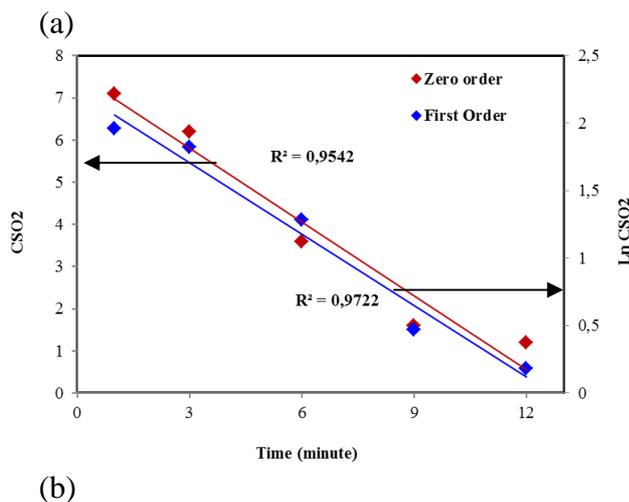
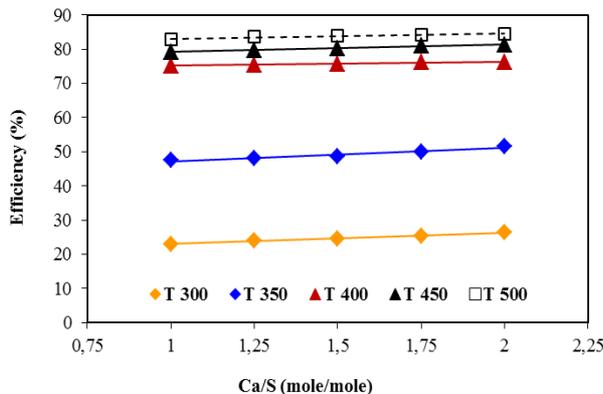


Figure 3. Desulfurization Efficiency (a) and Reaction Order (b)

It is evident that the greatest efficiency provided by the green mussels shell desulfurizer was comparable to the slaked lime one as reported by Wang et al. [24,25]; that SO₂ emissions were reduced by 75-95% during the combustion of bio-briquettes as compared to low rank coal. Their bio-briquettes were prepared under high pressure by blending the low rank coal (70-85 wt%) and biomass (15-30 wt%) at Ca/S ratio 1.5-2.0.

Moreover, the desulfurization reaction in this study closely followed the first order reaction as can be seen in Figure 3(b). This finding is in good agreement with the past similar work applying another kind of desulfurizers [11]. The sulfation reaction rate of ultrafine CaO particles ($d_p < 0.1 \mu\text{m}$) was found to be 5.10^2 – 5.10^3 times higher than that of the conventional CaO particles ($d_p > 1 \mu\text{m}$); however, the case was exhibited by dry injection processes in the coal burning [26]. Since the d_p in this experiment was around $0.01 \mu\text{m} - 0.25 \text{mm}$, the sulfation reaction rate predicted was moderate; there is no accurate estimation on the matter yet.

The sulfation reaction kinetics mentioned above only considered the overall chemical reaction from the view point of SO₂ gas concentration release to the atmosphere. Actually, the reaction between solid and gaseous reactants is not a simple process. As the reaction during the product layer diffusion is a rate-determining step, it is important to understand how and where the solid and gaseous reactants interact. The first opinion is that SO₂ and O₂ penetrate inwards through the product layer by gaseous or solid state diffusion, meeting CaO at the interface between CaO and CaSO₄ where sulfation takes place. That reaction has been assumed to happen whenever the untreated core model or the grain model is applied. The second opinion is that the solid reactant moves outwards through the product layer by ionic diffusion, reach SO₂ and O₂ at the outer surface of the CaSO₄ product layer where reaction occurs [21].

A combination of the two mechanisms is also possible, that is chemical reactions may occur at both locations. Accepting the assumption that chemical reactions take place at the interface of the reactant and product layer, the crystallization and fracture model is developed based on free energy-work analysis. It was found that the product 'layer' formed in the early stage of the reaction was not a true layer, but isolated nuclei and crystals. The 'continuous' product layer formed in the later stage was a monolayer of individual crystals with pore size of 2-3 nm along the boundaries [27-29]. In fact, the sulfation reactions were affected by many operational factors, such as the burning temperature, residence time, SO₂ partial pressure and molar ratio Ca/S. Also, the adsorbent from different sources had different calcination and sulfation performances [21]. In this examination, two of those parameters (i.e. temperature and Ca/S ratio) have at least been precisely proved.

4. Conclusions

Green mussel shell without any calcination can be used as the desulfurizer in the blending of low rank coal-biomass briquette combustion, therefore also recommended for the coal combustion. Burning temperature and desulfurizer content (defined as Ca/S ratio) significantly influenced the efficiency of desulfurization. The highest efficiency of desulfurization in this study was 84.5%. Desulfurization of the low rank coal-PKS briquette by using the green mussel shell desulfurizer mostly followed the first order reaction with the coefficient of determination (R^2) about 0.97.

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