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by Mahreni Mahreni

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Preliminary Study of Calorific Value Increase on Lignite Coal Using Dialkyl Carbohydrate Biosurfactant

Mahreni dan Mitha Puspitasari*

[1,2] Department of Chemical Engineering, Faculty of Industrial Engineering, Universitas Pembangunan Nasioanal "Veteran" Yogyakarta

*e-mail: mitha.puspitasari@upnyk.ac.id

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ABSTRACT

Coal is a fossil fuel that is the second mainstay after petroleum. The use of coal in Indonesia is dominated by types of low or medium grade coal because of the abundant amount, such as lignite. A new technological breakthrough is needed to upgrade the quality of low-grade coal to middle and upper class coal. Upgrading the quality is not only in terms of increasing the calorific value of coal but also how the waste produced by the process is environmentally friendly. Therefore, coal washing using dialkyl carbohydrate biosurfactant can be used alternatively in the process of upgrading coal quality.

This research aims to improve the quality of lignite coal with environmentally friendly materials. Lignite coal was washed with a biosurfactant solution of dialkyl carbohydrates from brown algae (*Sargasum sp)* and red algae (*Euchema cottonii*) to increase its heating value. Dialkyl carbohydrates were tested on coal sizes of 80, 64, 16 and 6 mesh.

The most biosurfactant to increasing the calorific value was the biosurfactant from brown algae, namely Isopropyl Stearate Alginate (ISA) 0.5%, which was able to increase the calorific value of lignite coal up to 2722.74 cal/g, or increased by 11%. The size of the coal also influenced the calorific value of lignite coal. Of the four coal sizes of 80, 64, 16, and 6 mesh, the size of 80 mesh had the highest increase in calorific value. The smaller the coal size, the greater the adsorption of surfactants in the coal pores, making it easier for biosurfactants to bind impurities in lignite coal.

Key word: biosurfactant,coal,dialkyl carbohydrate,lignite,calorific value

INTRODUCTION

Coal is a fossil fuel that is the second mainstay after petroleum. Coal is a sedimentary rock (solid) and can be burned, derived from plants, blackish brown, and rich in carbon, which is caused by physical and chemical processes in its formation process[14]. Indonesia has 60% lignite type coal reserves, which is 93,4 billion tons[5]. With this large amount of reserves, it is expected to be able to meet the needs of the domestic industry around the next 100 years.

The use of coal in Indonesia is dominated by types of low or medium grade coal because of the abundant amount, such as lignite. Such coal is the coal with less economic value, because in terms of the calorific value, it is under 5200 kcal/kg, and contains a high-water content of 35-70% [9]. While in terms of combustion, lignite coal produces a lot of ash in which the ash contains sulfur, clay, K2O, Al2O3, SiO2, and so on. The ash will directly affect the calorific value of the coal and will pollute the environment. Due to this, a new technological breakthrough is needed to upgrade the quality of low-grade coal to middle and upper-class coal.

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Upgrading the quality is not only in terms of increasing the calorific value of coal but also how to make the coal environmentally friendly when burned by reducing sulfur and ash levels. Coal adsorption using biosurfactants is the solution to these problems because it can reduce impurities from organic groups such as organic and inorganic sulfur (ash). Adsorption is sticking the material on the surface of a solid adsorbent[3]. Materials or particles that are adsorped are called adsorbates and those that adsorps are called adsorbents. Most adsorbents are highly porous materials and adsorption takes place mainly in the pore walls or in certain locations within the particle [4].

The chemical elements in coal are divided into two. The first is the organic elements containing carbon (C) (as aromatic/aliphatic), Hydrogen (H) (contained in the methyl group (-CH3), and methylene group (CH2-), oxygen (O) (contained in the hydroxyl group (-OH), carboxyl (-COOH), carbonyl (=C=O), and ether (-O-)), Nitrogen (N), Sulfur (S) (contained in thiolic groups (R-SH), and aliphatic groups sulfide (RSR)), and Phosphorous (P) [15,9]. Meanwhile,the inorganic elements are metals from polluters such as Silica (Si), Aluminum (Al), Iron (Fe), Calcium (Ca), and Magnesium (Mg) [16,12].

The water content in coal will affect the amount of air used for the coal drying process because it can directly disrupt ignition. Water content in coal consists of surface moisture (water on the surface), capillarity water (water in coal microspores), mixture decomposition (water in decomposed organic compounds), and mineral moisture (water making up the crystal structure of silica hydrate compounds) [2].

Sulfur in coal consists of organic sulfur and inorganic sulfur (pyrite/headquarters (FeS2)/sulfate (SO4)). S levels in coal also vary, ranging from very small quantities to more than 4% [11]. The S element easily reacts with the H or O elements to form an acid compound (pH <5) whereas the acid compound is a trigger for pollution. The inorganic sulfur in coal can be reduced by the washing process [13] which is formed from the primary sulfur reduction reaction by desulfovibrio/desulfotomaculum bacteria, and groundwater containing Fe^{2+} ions. The organic sulfur binds to the hydrocarbon compounds in coal, which are formed from sulfate reduction by organic material, assisted with bacteria, to become hydrogen sulfide (H2S) in a dry environment and minimal Fe content, so it cannot be reduced by the cleaning process. Whereas sulfur sulfate is commonly found in the form of iron sulfate, barium sulfate, and calcium sulfate, and is not involved in the formation of SOX (sulfur oxide) [12].

Desulfurization of coal can be done in various ways including using water, sulfur-eating microorganisms, water mixed with CPO, surfactants, peroxide oxidizing agents, sulfuric acid, and Sodium hypochlorite [1,7,11,17]. The principle of desulfurization using chemicals is to oxidize organic sulfur (R-SH, RSSR) so that the alkyl and sulfur will split, and the sulfur is released, reacting with oxygen to produce SO2 gas.

Mahreni and Renung [10] began to make biosurfactants of dialkyl carbohydrate from microalgae that were applied to the crude oil mixture. In that research, the manufacture of dialkyl carbohydrate biosurfactants came from brown algae, red algae, and green algae. Mahreni and Renung [10] also explained that the result of making biosurfactant from brown algae was isopropyl stearate alginate (ISA). Biosurfactant that resulted from red algae was isopropyl oleil carrageenan (IOK). Whereas the biosurfactant from green algae was isopropyl oleil agarose (IOA). ISA with a concentration of 0.25% produced the highest emulsion power than the other three biosurfactants. Researchers Edwin and Bomantara [8] applied isopropyl stearyl alginate (ISA) biosurfactant on lignite coal. The result was that the calorific value of coal, which had a size of 4 mesh,was higher than the coal with a size of 1 mesh.

Surfactant has hydrophilic (OH) group and hydrophobic group, namely compounds of alkyl R1 (Isopropyl) and R2 (Stearyl). The function of the hydrophilic group binds the compound in coal that are hydropilic such as organic sulfur. While the function of hydrophobic groups (R1 and R2) binds or interacts with the compound in coal that is hydrophobic such as inorganic sulfur. The interaction of the group bound to the surfactant with the group presented in coal makes it easy for the sulfur polluter compound to escape from the coal.

From the results of the research by Mahreni A. and Renung R. [10], the surfactant was classified as non-ionic surfactants with Hydrophilr-Lipophile Balance (HLB) ranging from 13-15; Critical Micelle Concentration (CMC) that occurred, ranged from (10-5 - 10-4 M), and was easily degraded biologically. This surfactant was able to emulsify in a water-in-oil (W/O) system, and was able to reduce the interface voltage to 0.8 dyne/cm, using only a surfactant concentration of 2000 ppm. Different from surfactant that was produced from chemical synthesis of petroleum which was difficult to degrade. The strength and usefulness of surfactant were largely determined by the HLB value. Surfactant which had a more dominant hydrophobic group, had a low scale, making it more soluble in the oil phase. Conversely, if the surfactant was dominated by hydrophilic groups which had a high scale, making it easy to dissolve in water. The solubility of a surfactant in water/oil was influenced by the number of atoms C and H. The normal HLB value in the range 1-20 was included in the type of non-ionic surfactant, while the HLB value> 20 was included in the ionic surfactant type [10].

This research aims to improve the quality of lignite coal with environmentally friendly materials. Lignite coal was adsorped with a biosurfactant solution of dialkyl carbohydrates from brown algae (ISA) and red algae (IOK) to increase its calorific value. Carbohydrate dialkyl biosurfactant was tested on coal sizes of 80, 64, 16 and 6 mesh.

EXPERIMENT

Materials

The main material in this research was the lignite coal taken from the River of Progo, Yogyakarta. The coal were uniformed in sizes into four: 80, 60, 16, and 6 mesh. The next ingredient was the UPNVY biosurfactant which was proven to be able to increase the calorific value. The dialkyl carbohydrate biosurfactant used was a biosurfactant from the previous research[10]. The biosurfactant came from macroalgae. Types of macroalgae used were brown algae and red algae. This biosurfactant was in the form of a solution, each made in a concentration of 0.5% and 1%. Coal, of various sizes, was starting to be immersed with biosurfactant Isopropyl Stearate Alginate (ISA) and Isopropyl Oleil Carrageenan (IOK).

Procedure

In the first experiment, the coal with 80 mesh size was weighed at 25 grams. Then the coal was immersed using Isopropyl Stearate Alginate (ISA) biosurfactant solution with a concentration of 0.5%. Furthermore, the second coal size was 60 mesh and soaked with 0.5% Isopropyl Stearate Alginate (ISA) biosurfactant solution. This experiment was carried out up to 6 mesh size coal, and repeated for 1% Isopropyl Stearate Alginate (ISA) concentration.

In the second experiment, 25 grams of coal were weighed. 80 mesh coal was soaked with a solution of Isopropyl Oleil Carrageenan (IOK) biosurfactant with a concentration of 0.5% and 1%. Furthermore, coal with a size of 60 mesh was also soaked with biosurfactant red algae with a concentration of 0.5%. And so on, up to sizes 16 and 6 mesh. The immersion in the first and second experiments was carried out for five hours.

After the immersion with Isopropyl Stearate Alginate (ISA) and Isopropyl Oleil Carrageenan (IOK) biosurfactants, the coal was dried for 2-3 days using sufficient sunlight. The coal test was analyzed for its calorific value. For the research in the laboratory, it can be seen in Figure 1.

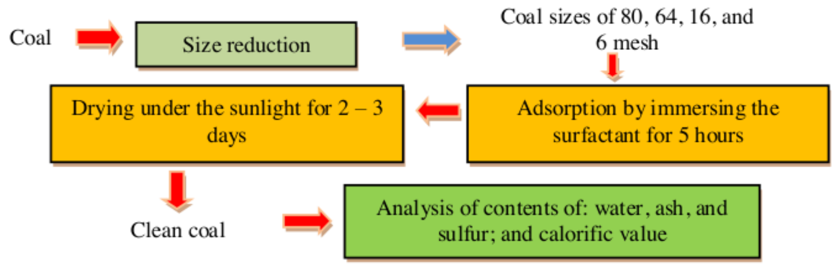

Figure 1. The flowchart of the coal adsorption process

RESULT AND DISCUSSION

The calorific value of the initial coal was tested using the bomb calorimeter. Ash content, carbon and water content were analyzed using gravimetry. Whereas total sulfur was analyzed by Spevtrometry uv-vis. The results can be seen in Table 1. From the test, the results of the calorific value of the coal were relatively low, so that the coal was indeed the lignite coal. Liginite has heating value <5250 cal/g [9].

Table 1. The Analysis Result of the Raw Materials

Test Parameter	Result	Unit	Methods
Ash content	49.90 %	%	Gravimetry
Carbon	33.16	%	Gravimetry
Water content	8.45	%	Gravimetry
Calorific Value	2459.99	Cal/g	Bomb Calorimeter
Total Sulfur	4985.32	Mg/kg	Spectrophometry Uv-Vis

Table 2. Total Analysis of Calorific Value on Lignite Coal in Various Sizes

No	Type and Concentrate of Surfactant	Coal calorific value (cal/g) with size in mesh			
		80	64	16	6
1	*Isopropyl Stearate Alginate* (ISA) 0,5%	2722.744	2416.254	2309.891	2258.611
2	*Isopropyl Stearate Alginate* (ISA) 1%	2547.011	2499.18	2483.635	2245.991
3	*Isopropyl oleil carrageenan* (IOK) 0,5%	2483.702	2481.505	2438.767	2359.356
4	*Isopropyl oleil carrageenan* (IOK) 1%	2523.915	2557.686	2493.86	2485.805
5	Water	2303.028	2378.453	2385.77	2402.392

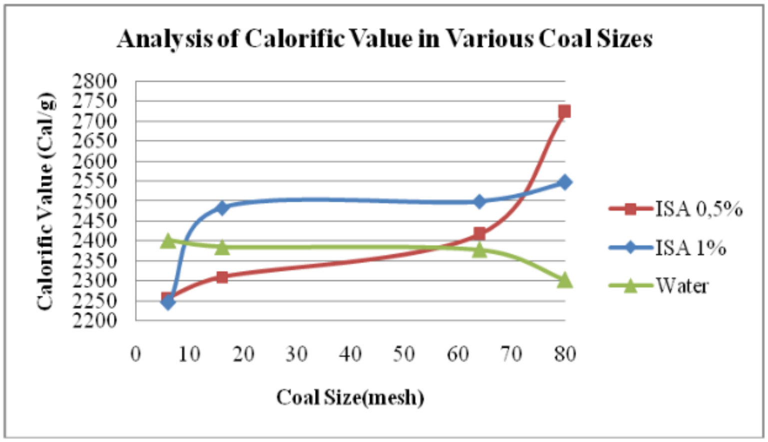

Figure 2. The Results of Coal Analysis Using ISA Biosurfactants

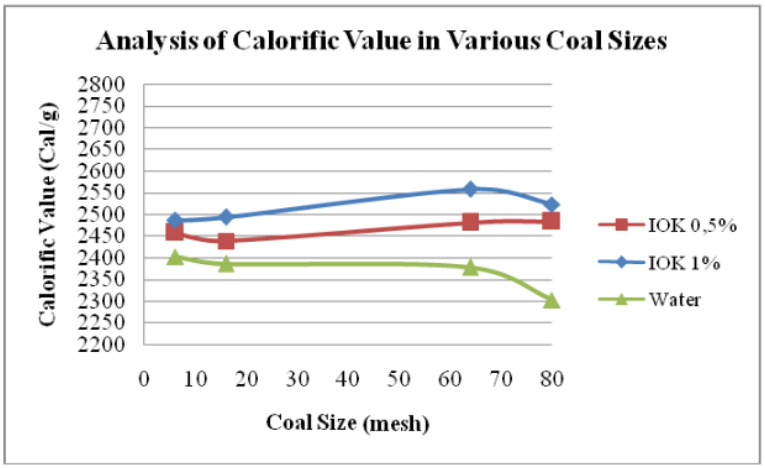

Figure 3. The Results of Coal Analysis Using IOK Biosurfactants

Table 3. Analysis of Water Content on Lignite Coal in Various Sizes

No	Type and Concentrate of Surfactant	Water Content (%) in various size of coal			
		80 mesh	64 mesh	16 mesh	6 mesh
1	*Isopropyl Stearate Alginate* (ISA) 0,5%	4.741	4.752	4.594	4.894
2	*Isopropyl Stearate Alginate* (ISA) 1%	4.753	5.185	4.771	4.953
3	*Isopropyl oleil carrageenan* (IOK) 0,5%	4.708	3.929	4.251	4.066
4	*Isopropyl oleil carrageenan* (IOK) 1%	4.700	4.318	4.083	4.128
5	Water	5.262	5.253	5.414	5.742

The application of dialkyl carbohydrate biosurfactant from brown algae, red algae, and water as a comparison, is presented in **Table 2**. The biosurfactants used are isopropyl stearate alginate (ISA) and isopropyl oleil carrageenan (IOK). These biosurfactants come from abundant biomass in the Indonesian sea. In addition, the use of biosurfactant is environmentally friendly, because after adsorption process, the material can be directly discharged into the environment. In this research, an initial study was carried out on the application of biosurfactants in various sizes of lignite coal. As a result, the coal adsorpted with 0.5% ISA at 6 mesh size, actually decreased its heating value. This also happened to the ISA 1% biosurfactant, 0.5% IOK, and 1% IOK. This was due to the size of the coal which was still too large so that the surface area of coal adsorption was less than the maximum.

Figure 2. shows a comparison of the results of lignite coal adsorption in various sizes using ISA 0.5% and 1% biosurfactants, and water. The adsorption results using 0.5% ISA biosurfactant at the largest size, 6 mesh, have not shown an increase in the calorific value. Likewise, in the size of 16 mesh and 64 mesh, the calorific value of the coal has not experienced an increase. While at the smallest size, 80 mesh, the calorific value significantly increased by 11%. Compared to being submerged with water alone, the lignite coal has a smaller calorific value.

Figure 3. shows a comparison of the results of lignite coal adsorption at various sizes using biosurfactants of 0.5% IOK, 1% IOK, and water. The results of adsorption using 1% IOK biosurfactant at the largest size, 6 mesh, have not shown an increase in the calorific value. Likewise, in the size of 16 mesh and 64 mesh, the calorific value of the coal has not experienced an increase. While at the smallest size, 80 mesh, the calorific value increased by 3%. Compared to being submerged with water alone, the lignite coal has a smaller calorific value.

The ISA biosurfactant with a concentration of 0.5% was the most biosurfactant in increasing the calorific value of coal. The value of coal increased from 2459.99 cal/gr to 2722.74 cal/gr. The coal increased by 11%. **Table 2** also shows that of the four coal sizes (80, 64, 16, and 6 mesh), the most way to increase the calorific value is 80 mesh size. This is because the smaller the coal, the more surface area of the biosurfactant adsorption so that the ISA biosurfactant can be adsorped more by the coal. **Table 3** shows water content of coal also decrease after adsorption using ISA and IOK. Adsorption of biosurfactant succeeded in reducing water content of coal . Biosurfactants are able to bind the polluters presenting in the coal, so that the coal is clean from its volatile matter. This causes an increase in the calorific value of the coal.

CONCLUSION

The most biosurfactant in increasing the calorific value was the biosurfactant from brown algae, namely the 0.5% isopropyl stearate alginate (ISA) which was able to increase the calorific value of the lignite coal, up to 2722.74 cal/g, or increased by 11%. The size of the coal also influenced the calorific value of the lignite coal. Of the four coal sizes of 80, 64, 16, and 6 mesh, the size of 80 mesh had the highest increase in the calorific value. The smaller the size of the coal, the greater the adsorption of the surfactants in the pores of the coal, making it easier for the biosurfactants to bind the polluters in the lignite coal.

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