

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

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### ABSTRACT

Indonesian coal consumption is dominated by a low-grade coal quality, and supplied from local coals mining which was composed of lignite. A technological breakthrough has to be main objective to convert low grade coal into upper-class coal. This paper reports on improving the quality of lignite coal by washing with biosurfactant. Di-alkyl carbohydrates were tested on coal sizes of 80, 64, 16 and 6 mesh. The optimum biosurfactant applied to increase the calorific value derived from brown algae, namely isopropyl stearate alginate (ISA) 0.5%. This was able to improve a calorific value of lignite coal up to 27722.74% or increased by 11%. The size of the coal also affects the calorific value of lignite coal. Four coal sizes applied in the study (80, 64, 16, and 6 mesh), indicates coal size 80 mesh has given the best calorific value improvement. Conversely, the smaller of the coal size, increase biosurfactant absorption. Thus, improve the washing capability of biosurfactants.

Keywords: biosurfactant, coal, dialkyl carbohydrate, lignite, calorific value

### INTRODUCTION

Coal is a fossil fuel that is the second mainstay after petroleum. According to Sukandarrumidi (1995) [1], 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. Indonesia is one of the second largest coal producing countries after China, with energy reserves of 462.6 trillion tons. 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% [2]. While in terms of combustion, lignite coal produces a lot of ash in which the ash contains sulfur, clay,  $K_2O$ ,  $Al_2O_3$ ,  $SiO_2$ . 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.

Upgrading the quality is not only in terms of increasing the calorific value of coal, but how to make the coal environmentally friendly when burned by reducing sulfur and ash levels. Coal washing technology is the solution of these problems because it can reduce impurities from organic groups such as organic and inorganic sulfur (ash). Washing

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technologies applied until now include desulphurization and de-ashing with flotation systems using chemicals and agglomeration using water and oil. The washing technology apparently does not have a positive impact on the environment because it produces liquid waste that has a high toxicity, so it is necessary to do a waste reductor unit.

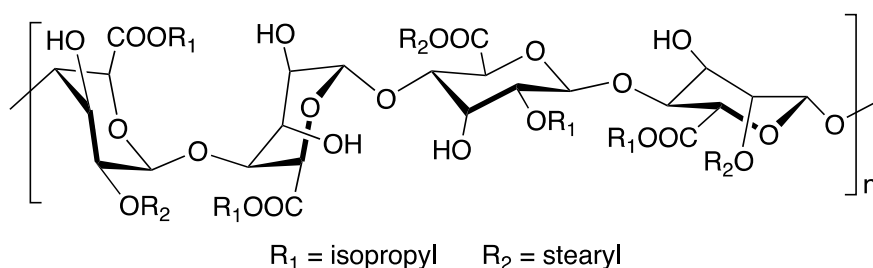
The chemical elements in coal are divided into two. The first is the organic elements containing carbon (C) (as aromatic/aliphatic), hydrogen (H) (contained in the methyl group (-CH<sub>3</sub>), and methylene group (CH<sub>2</sub>-), oxygen (O) (contained in the hydroxyl group (-OH), carboxyl (-COOH), carbonyl (=C=O), and ether (-O-), nitrogen (N), sulfur (S) (contained in thiolic groups (R-SH), aliphatic groups sulfide (RSR), and phosphorous (P) [2-3]. Meanwhile, the inorganic elements are metals from polluters such as silica (Si), aluminium (Al), iron (Fe), calcium (Ca), and magnesium (Mg) [4-5].

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) [6].

Sulfur in coal consists of organic sulfur and inorganic sulfur (pyrite/headquarters (FeS<sub>2</sub>)/sulfate (SO<sub>4</sub>)). Sulfur levels in coal also vary, ranging from very small quantities to more than 4% [7]. 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 [8], which is formed from the primary sulfur reduction reaction by desulfovibrio or desulfotomaculum bacteria, and ground water containing Fe<sup>2+</sup> 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 (H<sub>2</sub>S) 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) [3].

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 [7,9,10,11]. 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 SO<sub>2</sub> gas. Addition of sulfuric acid serves to dissolve inorganic sulfur so that it will come into the washing water. The addition of chemicals will increase or decrease the pH of both the coal's pH or the pH of the washing water. The risk of washing using active and hard chemicals can cause damage to the equipment.

Mahreni and Reningtua [12] reported how to make biosurfactants of dialkyl carbohydrate (Figure 1) from microalgae that were applied to the crude oil mixture. The manufacture of dialkyl carbohydrate biosurfactants came from brown algae (*Sargassum sp*), war algae (*Eucheuma cottonii*), and green algae. Furthermore, it was also explained that the result of biosurfactant from brown algae (*Sargassum sp*) was isopropyl stearyl alginate (ISA) and from war algae (*Eucheuma cottonii*) was isopropyl oleyl carrageenan (IOK). Whereas the biosurfactant from green algae was isopropyl oleyl agarose (IOA). ISA with a concentration of 0.25% produced the highest emulsion power than the other biosurfactants. Another natural based surfactant was also been reviewed for coal washing [13], not only for organic element cleaning or recovery but also for removing of inorganic heavy metal toxic from mining sources.



**Figure 1.** The chemical structure of isopropyl-stearyl alginate) surfactant [12].

Surfactant has hydrophilic (OH) group and hydrophobic group, namely compounds of alkyl  $R_1$  (isopropyl) and  $R_2$  (stearyl) [12]. The function of the hydrophilic group binds the compound in coal that are hydrophilic such as inorganic sulfur. While the function of hydrophobic groups ( $R_1$  and  $R_2$ ) binds or interacts with the compound in coal that are hydrophobic such as inorganic sulfur. The interaction of group bound to the surfactant with the group presented in coal makes it easy for the sulfur polluter compound to escape from the coal.

The surfactant can be classified as non-ionic surfactants with hydrophilic-lipophilic balance (HLB) ranging from 13-15. 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 [12].

This paper reports improvement the quality of lignite coal by using environmentally friendly materials. Lignite coal was washed with a biosurfactant solution of dialkyl carbohydrates from brown algae (ISA) and war algae (IOK) to increase its calorific value. Carbohydrate dialkyl biosurfactant was tested on coal sizes of 80, 64, 16 and 6 mesh.

## EXPERIMENT

### Chemicals and instrumentation

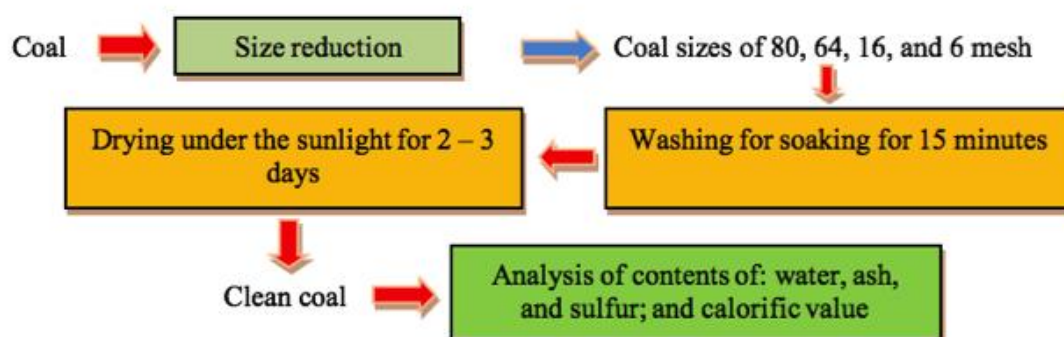
The main material in this research was the lignite coal taken from the River of Progo, Yogyakarta. The coal was uniformed in sizes into four: 80, 60, 16, and 6 mesh. The next ingredient was the UPNVY biosurfactant which was proven to be able to increase the calorific value. The dialkyl carbohydrate biosurfactant used was a biosurfactant from the previous research [12]. The biosurfactant came from macroalgae. Types of macroalgae used were brown algae and war 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 oleyl carrageenan (IOK).

### Procedure of the reaction

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.

The second experiment, 25 grams of coal were weighed. A 80 mesh coal was soaked with a solution of isopropyl oleyl carrageenan (IOK) biosurfactant with a concentration of 0.5% and 1%. Furthermore, coal with a size of 60 mesh was also soaked with biosurfactant war 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 were carried out for five hours. After the immersion with isopropyl stearate alginate (ISA) and isopropyl oleyl carrageenan (IOK) biosurfactants, the coal was dried for 2-3 days using sufficient sunlight. The coal test was analyzed for its calorific value. Flowchart describes the research process can be seen in Figure 2.



**Figure 2.** The flowchart of the coal washing process

## RESULT AND DISCUSSION

The calorific value of the initial coal was tested using the bomb method. The results can be seen in Table 1. From the test, the calorific value of the coal were relatively low, so that the coal was indeed the lignite coal.

**Table 1.** The analysis result of raw materials

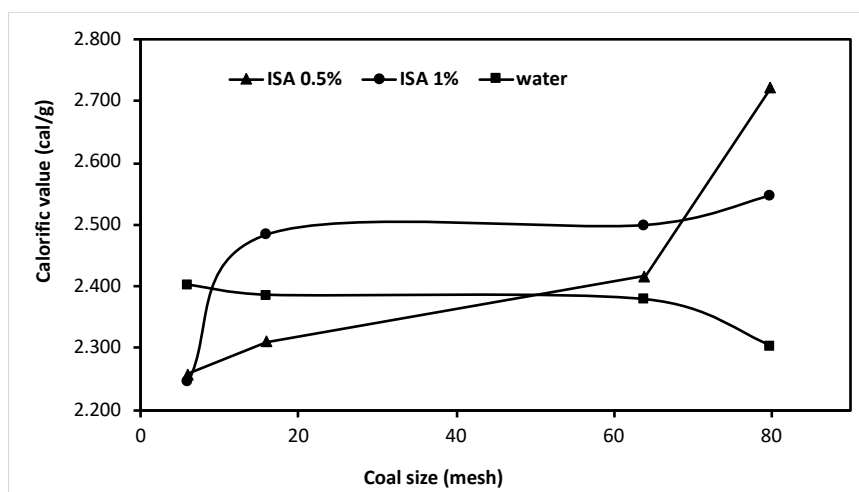
Test Parameter	Result	Unit
Ash content	49.90 %	%
Carbon	33.16	%
Water content	8.45	%
Calorific Value	2459.99	Cal/gr
Total Sulfur	4985.32	mg/kg

The application of dialkyl carbohydrate biosurfactant from brown algae, war algae for coal washing was compared to water processing. The result 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 the coal washing 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 washed with 0.5% ISA at 4 mesh size, actually decreased its heating value.

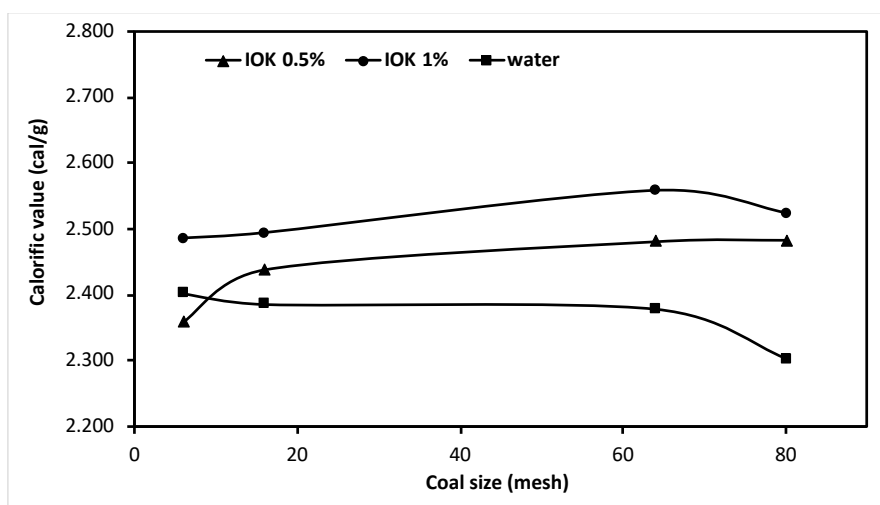
This also happened to the ISA 1% biosurfactant, 0.5% IOK, and 1% IOK. This was due to the size of the coal which was still too large so that the surface area of coal absorption was less than the maximum.

**Table 2.** Total analysis of calorific value on lignite coal in various sizes

No	Surfactant	Calorific value (Cal/gr) of coal in variation size (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 oleyl carrageenan (IOK) 0.5%	2483.702	2481.505	2438.767	2359.356
4	Isopropyl oleyl carrageenan (IOK) 1%	2523.915	2557.686	2493.86	2485.805
5	Water	2303.028	2378.453	2385.77	2402.392



**Figure 3.** The results of coal analysis using ISA biosurfactants



**Figure 4.** The results of coal analysis using IOK biosurfactants

Figure 3. shows a comparison of the results of lignite coal washing in various sizes using ISA 0.5% and 1% biosurfactants, and water. The washing results using 0.5% ISA biosurfactant at the largest size, 4 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.

The ISA biosurfactant with a concentration of 0.5% was the most optimal 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 optimal way to increase the calorific value is 80 mesh size. This is because the smaller the coal, the more surface area of the biosurfactant absorption, so that the ISA biosurfactant can be absorbed more by the coal. The absorption of surfactants can be optimal in the small coal sizes because biosurfactants are able to bind the pollutants 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.

Figure 4. shows a comparison of the results of lignite coal washing at various sizes using biosurfactants of 0.5% IOK, 1% IOK, and water. The results of washing using 0.5% IOK biosurfactant at the largest size, 4 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.

## CONCLUSION

The most optimal 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%, 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 absorption of the surfactants in the pores of the coal, making it easier for the biosurfactants to bind the pollutants in the lignite coal.

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## CONFLICT OF INTEREST

Author declare no competing interest.

## REFERENCES

- [1] Sukandarrumidi, Batubara dan Gambut, **1995**, Gajah Mada University Press: Yogyakarta.
- [2] Kirk-Othmer, Encyclopedia of Chemical Processing, 4<sup>th</sup> and 5<sup>th</sup> edition, **2001**, John Wiley & Sons Inc., Canada.
- [3] Sukandarrumidi, *Batubara dan Pemanfaatannya: Pengantar Teknologi Batubara Menuju Lingkungan Bersih*, 2<sup>nd</sup> Edition, **2009**, Gajah Mada University Press, Yogyakarta.



- [4] Briesemeister, L., Geißler, A., Halama, S., Herrmann, S., Kleinhans, U., Steibel, M., Ulbrich, M., Scaroni, A.W., Khan, M.R., Eser, S. and Radovic, L.R., *Coal Pyrolysis*, in Ullmann's Encyclopedia of Industrial Chemistry, **2016**, Wiley-VCH Verlag GmbH & Co. KGaA, Germany.
- [5] Khosdat, H., Sam, A., Vali, H. and Noghabi, K. A., *Int. Biodeterior. Biodegradation*, **2011**, 65(8), 1238-1243.
- [6] Al Baaqy, L., Arias, G., and Rachimoellah, M, *Jurnal Teknik ITS*, **2013**, 2(2), F228-F233.
- [7] Nukman, N., and Poertadji, S, *Jurnal Sains Materi Indonesia*, **2018**, 7(3), 31-36.
- [8] Speight, G, J., *Handbook of Coal Analysis*, **2015**, vol. 66, John Willey & Sons, Inc., Canada.
- [9] Aladin, A., *Jurnal Rekayasa Proses*, **2009**, 3(2), 50-56.
- [10] Siswati, N. D. and Festiani, A, *Desulfurisasi batubara menggunakan udara dan air*, UPN Veteran, **2010**, ISSN 1978-0427.
- [11] Yin, S., Tao, X., and Shi, K, *Fuel Process. Technol.*, **2011**, 92(8), 1554-1559.
- [12] Mahreni, M. and Reningtyas, R., *Pembuatan Surfaktan Dialkil Karbohidrat dari Alga*, in *Prosiding Seminar Nasional Teknik Kimia "Kejuangan" Pengembangan Teknologi Kimia untuk Pengolahan Sumber Daya Alam Indonesia*. **2015**. 18-1
- [13] Banat, I. M., Makkar, R. S. and Cameotra, S.S. *Appl. Microbiol. Biotechnol.*, **2000**, 53, 495-508.