Study on functional group, oil adsorption process, and the effect of chemical wash on lignite and sub-bituminous coal

A Rahmadian¹, S Nikmatin¹,², H Hardhienata¹, and S Darmawan²

¹Physics Department, IPB University, Meranti Street, IPB Darmaga, Bogor 16680
²Forest Product Research and Development Center, Gunung Batu Street No.5, Bogor, 16119
³Surfactant and Bioenergy Research Center, IPB University, Bogor, Indonesia
Email: adhirahmadian@outlook.com

Abstract. This study was to determine the characteristics of Indonesia's low-grade coal, which was sub-bituminous taken from Samarinda coal mine and lignite taken from Palembang coal mine. Experiment was conducted using Fourier Transform Infrared (FTIR) spectroscopy to analyze the functional group of the coal. Inherent moisture was 2.16 g in 5 g lignite coal, and 1.42 g in 5 g sub-bituminous coal. Soaking coal with liquid smoke reduced the percentage of residual (volatile matter and ash content) combustion and increased fixed carbon. Adsorption of oil by coal was measured by the change of free fatty acid (FFA) in the oil, in which lignite coal was decreased about 0.1% and sub-bituminous coal was decreased about 0.07%. In contrast, by heating adsorption 100 °C, FFA change in the oil was increased about 0.28% for lignite coal and increased about 0.46% for sub-bituminous coal, by heating adsorption 125 °C, the increase was about 0.44% for lignite coal and was about 0.59% for sub-bituminous coal, and by heating adsorption 150 °C, FFA was increased about 0.41% for lignite coal and about 0.46% for sub-bituminous coal.

1. Introduction
Coal is still believed to be the world's energy source even though data from Ministry of Energy and Mineral Resources in mid-2010 showed that the potential for petroleum is still around 7.99 billion barrels for the 23-year reserve ratio. World coal consumption in 2006 ranged from 6.74 billion tons and is estimated to increase by an estimated 9.98 billion tons in 2030. With Indonesia's coal reserves reaching 124 billion tons (Data from Geological Agency of the Ministry of Energy and Mineral Resources 2014), opportunities to fill the coal market potential are wide open, both used directly as a source of community energy and exported abroad.

The coal rank can be sorted from the lowest, namely lignite, sub-bituminous, bituminous and anthracite. This ranking change was followed by an increase in carbon content, a decrease in the content of hydrogen, oxygen, volatile matter inherent moisture, increased calorific value, and also reflections from vitrinite. Coal rank classification can be determined based on American Standard Testing Material (ASTM), or British Standard (B.S.), namely by proximate analysis (water content, ash, cutting substance, and solid carbon) and heating value, ultimate analysis (carbon, hydrogen, sulfur, nitrogen and oxygen), and petrographic analysis (vitrinite, inertinite, liptinite / excinite and value of reflection) [1].
Coal in Indonesia itself has a fairly high water content in the range of 30-50%, so innovation is needed that can significantly reduce the amount of water content in coal so that the calorific value can be increased and can produce bituminous, clean and stable coal. Because without these innovations, 60% of all Indonesia’s coal reserves will be a natural resource reserve that is less useful or is likely to even be in vain [2]. The solution to the problem of water re-absorption in this coal is by coating using oil by adsorption process. In addition, the use of oil is also able to increase the heat of low-grade coal.

The worldwide production of vegetable oil in one year is about 60 million tons with majority of oil is used for frying [3], so the waste of oil either. This study investigated basic characteristics of Indonesia’s low-grade coal such as functional group, adsorption process by used cooking oil, and the effect of chemical wash to coal combustion output, so it be used in further research.

2. Materials and Methods

The coal used in this research were lignite and sub-bituminous which were obtained from PT. Anindya Wiraputra, Jakarta. The lignite coal was from Palembang coal mine and sub-bituminous was from Samarinda coal mine. Sample was labeled L for lignite coal and labeled SB for sub-bituminous coal, respectively. Coal was enumerated using the diskmill method using FOMAC 25000 rpm to obtain coal filtered microparticles to pass the size of 60 mesh size.

Used cooking oil was provided from private Bogor household which has been used for frying by 3-5 times. Lignite and sub-bituminous coal powder escaped 60 mesh each was treated by adsorption at room temperature and heating the oil and coal simultaneously at 100 °C, 125 °C, and 150 °C for 120 min while each was stirred using a 500 rpm using magneting stirrer with ratio between coal and oil by 1 : 20. Adsorption test was performed, and adsorbed coal sample was labeled L1 for lignite with room temperature adsorption, L2 for lignite with 100 °C heating, L3 for lignite with 125 °C heating, and L4 for lignite 150 °C heating, and SB1 for sub-bituminous with room temperature adsorption, SB2 for sub-bituminous with 100 °C heating, SB3 for sub-bituminous with 125 °C heating, SB4 for sub-bituminous with 150 °C heating. The adsorption process was conducted in open environment using titration method. Oil and ethanol 96% were titrated with NaOH 0.1 N. Difference volume of NaOH needed to neutralized the oil was calculated to determine %FFA in oil.

Before proximate analysis, lignite and sub-bituminous coal were soaked in Sodium Lauryl Sulfate (SLS) and liquid smoke non-food grade for a day. Soaked lignite coal samples were labeled LS for SLS-coal sample, and LL for liquid smoke-coal sample, and soaked subbituminous coal samples were labeled SS for SLS-coal sample, and SL for liquid smoke-coal sample. The proximate analysis conducted were inherent moisture, ash content, volatile matter, and fixed carbon. A coal-KBr mixture at 1:100 ratio was used to perform functional group test, which was analized using Fourier Transform Infrared (FTIR) Spectroscopy brand ABB MB3600 series.

3. Results and Discussion

3.1. Coal Functional Group

The chemical characteristics of coal can be evaluated by using FTIR spectra [5]. FTIR spectra region for coal can be analyzed by measuring the absorbed intensity of infrared on functional group. Selected functional group for coal is shown in Table 1. Functional group characteristic of Indonesia’s coal are shown in Figure 1 and Table 2. Sub-bituminous coal showed most different peak compared to lignite coal at 1580 to 1625 cm⁻¹ which was aromatic benzene and aliphatic -CH₃ groups in region 2800 to 3000 cm⁻¹, which was sub-bituminous coal have higher peak. Aromatic group make the coal unique and classified because the more benzene ring is constructed in the coal, make it more tough and more energy stored, but need more time to initiate the flame because the bond energy is high. In contrast,
aliphatic group make the coal easy to burn but it make the coal more brittle and have low output energy. In region of 1500 to 1800 cm\(^{-1}\), oxygen contain functional group which is carbonyl and carboxyl acid group. The more carboxyl group in the coal, it means the coal containing more inherent moisture because of its hydroxyl group. Hydroxyl bond in the coal is shown by comparing the carboxyl acid group to carbonyl acid group. Around 3000 cm\(^{-1}\) it was a hydroxyl function group which was the dominant functional group in this coal.

\[\text{Figure 1. Functional group of Indonesia’s a) lignite coal and b) sub-bituminous coal samples}\]

Inherent moisture was measured based on ASTM D3173 and the result showed that in this coals water content were 2.16 gram of 5 gram lignite coal, and 1.42 gram of 5 gram sub-bituminous coal which was about 30-50% as reported by Hartiniati [2]. It is explained why the hydroxyl bond is dominant in Figure 1.

| Peak (cm\(^{-1}\)) | Functional Groups | Intensity\(^a\) |
|-------------------|-------------------|-----------------|
|                   |                   | Standard [6]    | Lignite | Sub-bituminous |
| 1580–1625         | C=C               | vs              | s       | vs             |
| 1650–1690         | -C=O              | s               | m       | s              |
| 1700–1725         |                   | vs              | m       | s              |
| 2880–2890         | -CH               | w               | w       | w              |
| 2840–2870         | -CH\(_2\)         | m               | w       | w              |
| 2915–2940         |                   | m-s             | w       | m              |
| 2865–2885         | -CH\(_3\)         | m               | w       | w              |

\(^a\) Intensity: **s** (strong), **m** (medium), **w** (weak)
2950–2975 m-s w w
3010–3080 Ar-H m vs vs
Note: *w=weak; m=medium; s=strong; vs=very strong

3.2. Adsorption Process

Adsorption process of oil and coal can be varied, but the process is still the same, where the free fatty acid (FFA) is adsorbed to coal surface and bonding occurred, with the bond can be physical or chemical. The most FFA in cooking oil is palmitic acid (C_{16}H_{32}O_{2}) with 256 molecular weight [4]. % FFA adsorption by coal is shown in Table 2.

Table 2. % FFA adsorption by coal

| Sample     | FFA by adsorption (%) |
|------------|------------------------|
| Lignite    | 0.23 | 0.64 | 0.79 | 0.77 |
| Sub-bituminous | 0.28 | 0.82 | 0.95 | 0.82 |

Calculation of the %FFA of oil before and after adsorption process was performed to examine the difference. The %FFA before adsorption conducted was 0.36%, and after the adsorption process %FFA L1 was decreased about 0.13%, and SB1 was decreased about 0.08%. For the adsorption process with heating, %FFA L2 was increased about 0.28%, %FFA L3 was increased about 0.44%, and %FFA L4 was increased about 0.41%. %FFA SB2 was increased about 0.46%, %FFA SB3 was increased about 0.59%, and %FFA SB4 was increased about 0.46%. The data showed that adsorption processing with coal occurred with FFA adsorbed to its surface with the decrease of %FFA compared to sample control. However, with some heat, adsorption of FFA cannot be determined, vice versa it increased the %FFA with the maximum increase at 125 °C.

3.3. Proximate analysis

Proximate analysis was conducted to determine the change of residual combustion and fixed carbon by the process of chemical wash. The percentage of residual combustion (volatile matter and ash content) show the coal produced residual product in combustion, and the percentage of fixed carbon shows potential energy produce in combustion.

Table 3. Tabel of proximate analysis of treated coal

| Coal             | Treatment          | Volatile Matter (%) | Ash Content (%) | Fixed Carbon (%) |
|------------------|--------------------|---------------------|-----------------|-----------------|
| Lignite          | No Treatment       | 52.96               | 10.30           | 38.49           |
|                  | Soaked in Liquid Smoke | 49.75               | 6.20            | 43.32           |
|                  | Soaked in SLS      | 48.46               | 9.09            | 45.23           |
| Sub-bituminous   | No Treatment       | 52.30               | 8.78            | 39.05           |
|                  | Soaked in Liquid Smoke | 49.93               | 6.43            | 46.50           |
|                  | Soaked in SLS      | 45.57               | 12.13           | 36.45           |

Data in Table 3 show that for both coal (lignite and sub-bituminous), if it was soaked with liquid smoke, the percentage of residual combustion was reduced and fixed carbon of coal was increased compared to non treated coal. However, if it was soaked with SLS, it showed different results. For lignite coal soaked with SLS, the percentage of volatile matter was reduced, while the percentage of
ash content and fixed carbon was increased. For sub-bituminous coal soaked with SLS, the volatile matter and fixed carbon were reduced, and the ash content was increased.

4. Conclusions and Recommendations

Indonesia’s low-grade coal are below standard of usable coal, but it is potential to be an alternative energy after some treatments before the usage. It is recommended to reduce the inherent moisture before the treatments. Washing treatment on coal using liquid smoke can be applied before combustion to reduce the residual product and increase the potential output energy. Liquid smoke is affordable for public, so low-grade coal with washing treatment using liquid smoke can be a new alternative energy instead using petroleum and natural gas. The use of low-grade coal without treatments is not recommended. According to Huscher [7], the use of low-grade coal especially lignite, produces flying substances resulting from coal combustion which is very dangerous for human health which can cause chronic heart disease and respiratory diseases in living things, and it is also one of the main causes of climate change for producing high CO₂ emissions results in the greenhouse effect [7].

References

[1] Heri Heriyanto, Widya Ernayati K, Chaerul Umam, Nita Margareta. 2014. Pengaruh minyak jelantah pada proses ubc untuk meningkatkan kalori batubara bayah. Jurnal Integrasi Proses. 5 (1) : 56-60
[2] Hartiniati. 2010. Proses Peningkatan Mutu Batubara Muda (Lignite) Menjadi Exportable Coal atau Batubara Layak Ekspor/Jual. Jakarta (ID): Badan Pengkajian dan Penerapan Teknologi.
[3] Kajimoto G. 1994. Effective Utilization of Waste Edible Oil. J. Jpn. Oil Chem. 43 305-313.
[4] A Fuadi Ramdja, Lisa Febrina, Daniel Krisdianto. 2010. Pemurnian minyak jelantah menggunakan ampas tebu sebagai adsorben. Jurnal Teknik Kimia. 17 1
[5] Ibara J V. 1996. Vibrational Spectroscopy. 10 311-318
[6] Fuller E L, Smyrl N R, Howell R L, and Daw C S. 1984. Chemistry and structure of coals: evaluation of organic structure by computer aided diffuse reflectance infrared spectroscopy. American Chemical Society Division of Fuel Chemistry 29 (1): 1-9.
[7] Huscher Julia. 2012. Health impacts of lignite-fired power plants the German-Polish region Lusatia. Air Quality : Health and Enviroment Alliance (HEAL).