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Increasing Added Value of Low Rank Coal through Humic Acid Extraction. Case study; Extraction of Humic acid from lignite coal of the Sajau Formation in North Kalimantan, Indonesia.

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Abstract
In this study, humic acid was extracted from low-rank lignite from the Sajau Formation, Berau Basin, Indonesia, through chemical pretreatment with HNO_3. The lignite samples were subjected to nitric acid oxidation followed by extraction using different concentrations of KOH. Raw lignite and nitric acid-treated coal were analyzed using proximate and ultimate analysis. The physicochemical characteristics of nitric acid-treated coal have shown a decrease in ash and fixed carbon, with low aromaticity and increased oxygenation bonds with more oxygen and nitrogen, hydrogen and sulfur, and lower C content. Different concentrations of KOH solution, namely 0.5%, 1.5%, 2.5%, 3.5%, and 4.5% were used as alkali treatments for humic acid production. According to the analysis results, it can be concluded that the concentration of KOH 4.5% in lignite causes an increase in the maximum yield of humic acid from 38.38% - 57.93% for treated lignite compared to raw lignite. Humic acid produced through oxidation of HNO_3 and 4.5 KOH concentrations showed more significant amount of humic material with increased efficiency compared to raw coal.

Keywords: lignite, humic acid, pre-treatment nitric acid, KOH, Berau Basin.

1.Introduction

Indonesia is one of the largest coal producers in the world. However, most of our coal reserves are still dominated by low rank coal with a calorific value below 5100 Kcal/kg (Fig 1). Coal with low calories in production and utilization can cause environmental problems; such as the use of coal as a material for Steam Power Plants; has the potential for air pollution with various gases produced such as CO, CO_2, SO_2, H_2S, CH_4, and other gases. One of the gases that can cause a greenhouse effect is CH_4, which has the potential to cause warming global (global warming). Apart from that, the selling value of low calories coal is very low.

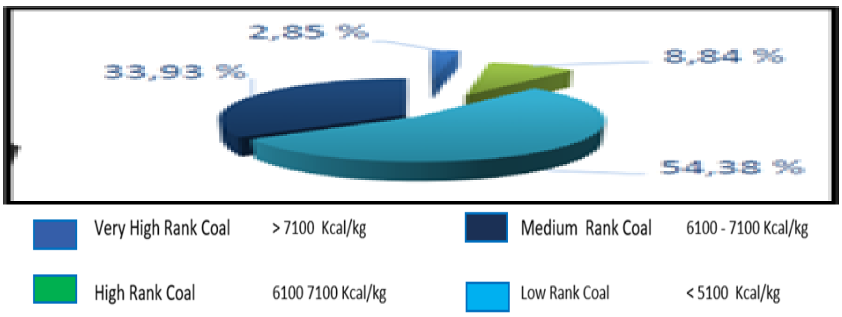

Fig.1: Indonesian's Coal Rank composition (Modified from Geological Board, 2021; Ministry of Energy and Mines)

Various studies have shown that biogenic elements and humic substances are necessary for the better growth and development of plants [1,2,3]. Humic acid is one of the three ingredients that make up humic substances, which are components that form humus. Humus is soil with a high fertility level, which is Humic acid obtained through a humus extraction process. Humic acid can improve soil's chemical, physical, and biological properties. Thus, applying humic acid can improve the condition of degraded soil and minimize the possibility of losing nutrients from organic fertilizer due to leaching or evaporation. Inorganic fertilizers in soil are not all absorbed optimally by plants because these nutrients experience leaching, evaporation, or are bound by the soil. It May cause low fertilization efficiency and potentially cause environmental pollution. The accumulation of fertilizer residue can result in a decline in soil quality, both physical, chemical, and biological. Apart from humic acid, it can help plants absorb plant nutrients (N, P, and K) and prevent leaching or detrimental changes in plants and the soil [4,5]. Humic acid is often found in lakes, swamps, soil, peat, lignite, oxidized bituminous coal, weathered coal, shale, and flora/fauna residues [6,7,8,9]. Humic acid sourced from lignite has proved to contain saturated long-chain alkanoic acids with a strong predominance of even-numbered homologs compared to soil humic acid [10].

Several studies have shown that lignite is found in large quantities in the stratigraphic succession of Tertiary sediments, which widely spread in the southeast-northwest direction of North Kalimantan Province. However, lignite has not been exploited commercially due to its low economic value. In addition, the large lignite reserves in North Kalimantan Province are a significant source of raw materials for the production of humus fertilizer [11,12,13,14].

Several studies have shown that coal contains a small amount of humic acid. Enrichment of humic acid in lignite can be done with acid oxidizing agents such as HNO_3, or enrichment can also use several oxidizing agents in a basal environment. (e.g., H_2O_2), $KMnO_4$) [1,2,15,16, 17,18].

Research on the lignite of the Berau basin in North Kalimantan Province (Figure 1), carried out to purpose of this paper is to study the characteristic oxidation process of lignite coal between nitric acid-treated coal by acid oxidation agent (HNO3) and by basal oxidation agent (KOH) related to humic acid extraction from lignite.

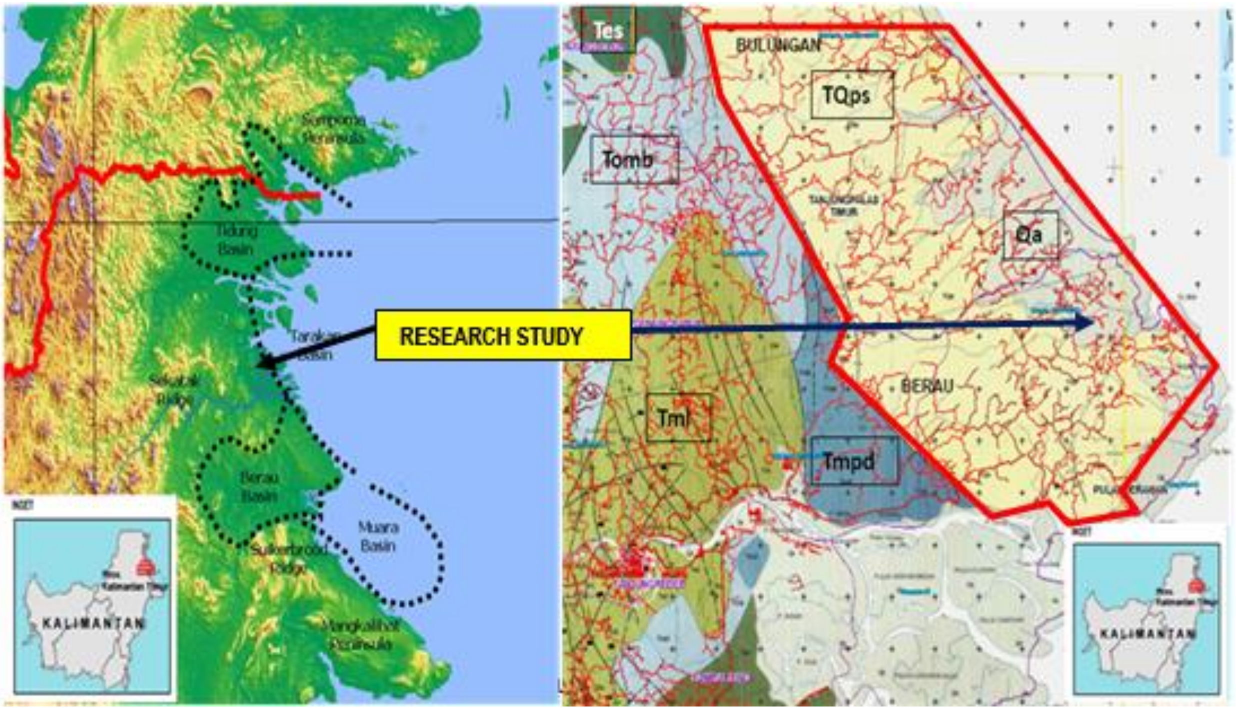

Fig.2: Research location in Berau Basin, Indonesia.

2. Materials and methods

2.1 Coal samples and sample location

Coal samples were taken from the Patriot Wiraperkasa and Delmar coal mines, North Kalimantan Province, with an average weight of 20 kg. The lignite used in the experiment was taken from the roof layer of the excavation. The experiment used around 2-3 kg for each sample to be analyzed.

2.2 Coal samples preparation

The samples have to be crushed into fine particles using mortar and pestle. Later on, the coal samples were sieved through sieved to a granulation size of 0-5 mm, and to achieve the best results, it was previously dried in an oven at a temperature of 105°C.

2.3 Proximate and Ultimate Analysis

To perform a proximate analysis using the standard ASTM method. A proximate analysis includes moisture content, ash, volatile matter, and fixed carbon. Total sulfur and calorific values were also measured. The ultimate analysis includes carbon (C), nitrogen (N), Sulfur (S), and hydrogen (H). All proximate and ultimate analyses were carried out at the Sucofindo Laboratory, Balikpapan, East Kalimantan

2.4 Pre-treatment using acidic oxidizing agents of HNO_3

To further enrich the humic acid in lignite, pre-treatment was carried out using acidic oxidizing agents (HNO_3)

2.5 Extraction of Humic Acid Using KOH.

The experiment was carried out by mixing lignite powder with 0.5%, 1.5%, 2.5%, and 3.5% KOH solutions for 24 hours, followed by continuous stirring. Each sample had a different concentration of KOH solution, which was filtered and stored in a tightly closed bottle.

3. Results & Discussion

3.1 Effect of Proximate and Ultimate Measurement due to HNO_3 Oxidation on Lignite

Proximate and ultimate analyses were conducted on coal samples before and after pre-treatment with nitric acid (HNO_3). Proximate analysis of pre-treatment coals (PT-C) shows reduced ash and fixed carbon, while volatile matter and moisture content show an increasing trend in concentration.

Figure 1 shows the proximate results of coal samples before (RC) and after pre-treatment with HNO_3 (PT-C). The proximate analysis of all coal samples before pre-treatment (Raw Coal/RC) showed total moisture (TM) content ranging between 46.11% - 49.12%, ash content 5.52% - 8.16%, while volatile matter (VM) content ranged between 23.27% -26.24%, fixed carbon (FC) content showed a range of 19.49% - 22.48%. The total moisture, ash, volatile matter, and fixed carbon content average is 47.13%, 6.92%, 2.46%, and 21.49%, respectively. Different proximate analysis results were found in coal samples pre-treated with HNO_3 (PT-C samples code); there was an increase in total moisture and volatile matter and a decrease in fixed carbon and ash content (Figure 3). Changes in proximate parameter values did not only occur for each parameter but were also observed from the distribution of their average values. The average value of the analysis results for the PT-C sample is as follows: average value of Total Moisture: 49.84%, Ash 3.99%, Volatile Matter: 26.82%, and Fixed Carbon: 19.33%.

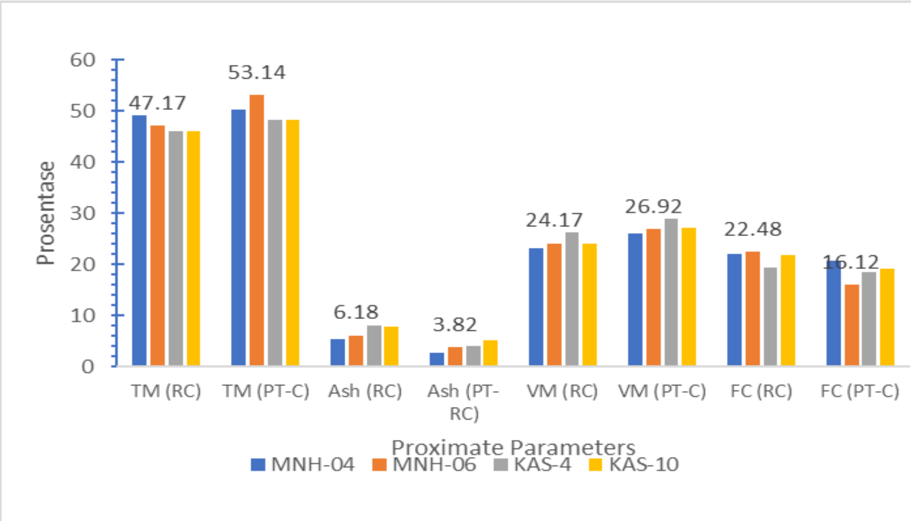

Fig. 3: Proximate Analysis of raw coal (RC) and pre-treatment coal (PT-C).

The ultimate analysis results indicated an increase in hydrogen (H), nitrogen (N), and oxygen (O). At the same time, Carbon (C) and sulfur (S) concentrations were decreased (Figure 4).

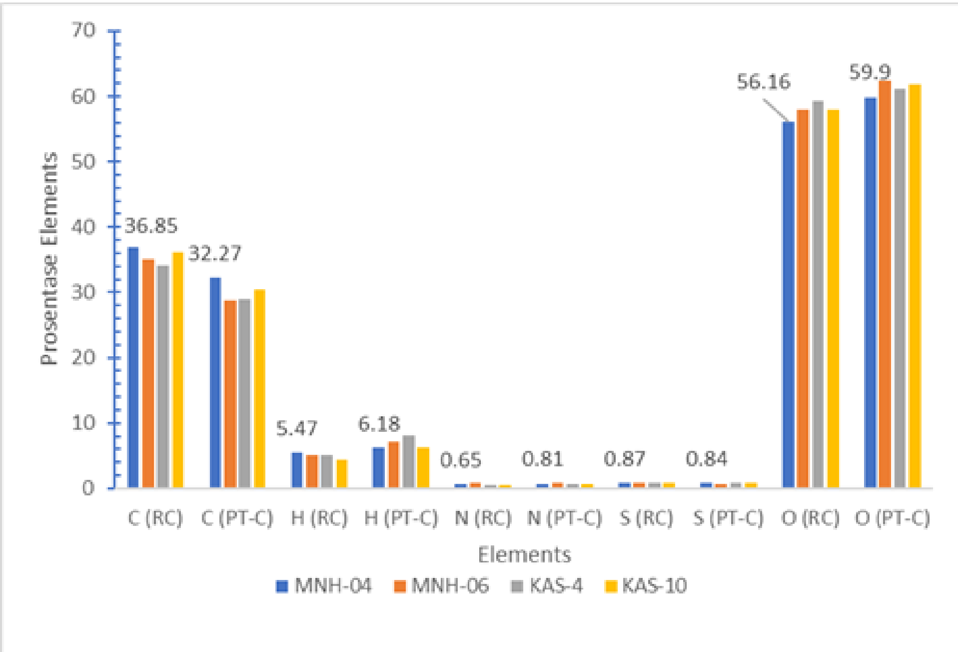

Fig. 4: Ultimate Analysis of raw coal (RC) and pre-treatment coal (PT-C).

Several studies have shown that the coal oxidation process using an oxidizing agent such as HNO_3, H_2O_2, and $KMnO_4$ (1,2,15, 17,18) has caused changes in the physical-chemical characteristics, molecular structure, and humic acid products produced.

The results of the proximate and ultimate analysis of acid-oxidized lignite using nitric acid indicate the presence of physio-chemical changes in lignite that are associated with HNO_3 pre-treatment. During the oxidation process with HNO_3, inorganic materials (ash) in lignite that react with HNO_3 will be dissolved. Inorganic substances identified in the Sajau Formation lignite, such as kaolinite, montmorillonite, and quartz, have low chemical reaction capabilities. Other inorganic elements, such as major oxides such as SiO_2, Al_2O_3, Fe_2O_3, K_2O, Na_2O, CaO and MgO can be identified. These inorganic substances can react with HNO_3. For example, solid K2O reacts with HNO3 to form soluble KNO_3. This reaction process explains why the ash concentration in pre-treated coal becomes smaller than in raw coal (Fig. 1; as shown in MNH-04, the ash content in raw coal is 6.15% compared to 3.82% from pre-treatment coal); total moisture also decreased. The HNO_3 oxidation process that occurs can also cause chemical leaching of inorganic elements such as minerals and ash and can also cause dissolved carbon elements so that the fixed carbon in lignite (RC) is more significant than in the pre-treatment of lignite (Fig. 3) [19,20].

The next reaction that occurs is the carboxylation process on the aromatic ring. The carboxylation process causes an increase in carboxyl and oxygen and a decrease in aromaticity[21]. In addition to the reaction on the aromatic ring, an oxidation reaction also occurs on the aromatic ring's side chain, which increases oxygen. Another reaction that occurs is the nitration reaction. During the nitration reaction, nitronium ions are formed when nitric acid reacts with sulfuric acid. Nitrobenzene is a product resulting from the nitration reaction. Therefore, there is an increase in nitrogen in the lignite pre-treatment [22]

3.2 The influence of different KOH Concentration on Humic Acid content

This study used different percentages of KOH concentrations, i.e., 0.5%, 1.5%, 2.5%, 3.5%, and 4.5%, to identify the maximum concentration of humic acid produced before and after treatment with HNO_3 in lignite coal (Figure 5). Measuring the percentage yield of humic acid shows that the maximum product yield is obtained from the extraction of Raw Lignite (RC) with a KOH concentration of 4.5%, ranging from 18.26% - 22.65%.; while in the pre-treatment of lignite (PT-C), there is an increase in the maximum product to 38.38% - 57.93%. Thus, there is an increase in humic acid production from 110% to 155%. Research conducted by Fatima et al.[2] from lignite samples in Pakistan shows that the maximum humic acid product produced from KOH extraction with a concentration of 4.5% is 42.6%. Similar research conducted by Benjamin et al.[15] shows that humic acid extracted from HNO_3 pre-treatment of lignite in Bosnia and Herzegovina shows an increase of 245% from 17.5% (untreated lignite) to 60.55% (HNO_3 treated coal). Although the enrichment of humic acid in lignite pre-treatment varies, several studies have concluded that using HNO_3 will provide optimal results.

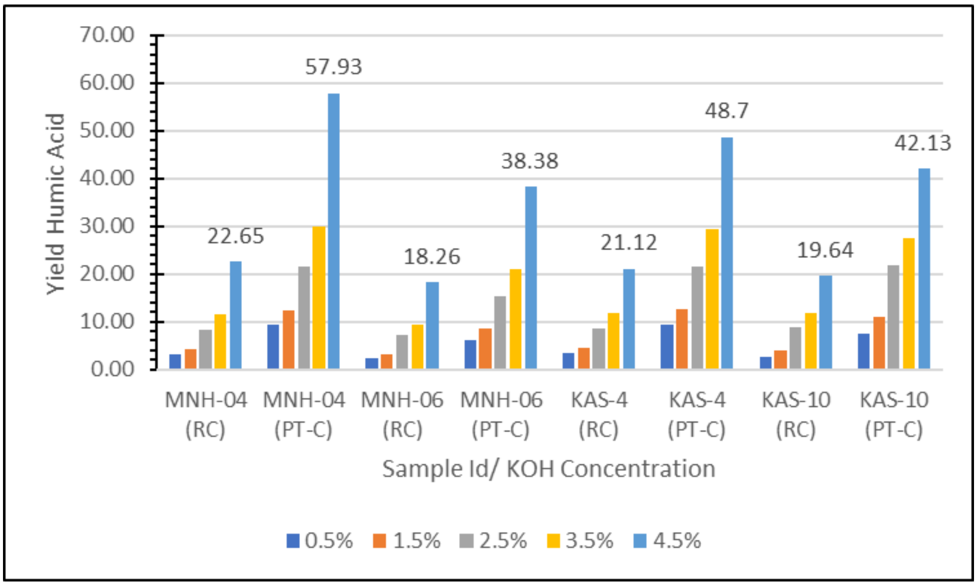

Fig.5: Yield Humic Acid production from Raw Coal Lignite (RC) and Pre-Treatment Lignite (PT-C) using different KOH Concentration.

Current research is conducted on raw coal lignite (RC) and pre-treatment lignite (PT-C) with KOH concentrations of 0.5%, 1.5%, 2.5%, and 3.5%. The average yield of humic acid from raw lignite is 2.85%. % - 11.05%; while pre-treatment lignite ranges from 8.13% - 26.92%. This shows that using 0.5% - 3.5% KOH concentrations does not produce the maximum yield of humic acid from raw or pre-treatment lignite. Similar research conducted in various places on lignite showed similar results [1, 2, 18], which stated that KOH concentrations of 0.5%, 1.5%, 2.5% and 3.5% did not produce maximum humic acid content.

4. Conclusions

In this study, low rank coal (lignite) from the Sajau Formation in the Berau Basin, Indonesia, was used to extract humic acid using different concentrations of KOH solution, namely 0.5%, 1.5%, 2.5%, 3.5%, and 4.5% used as alkali treatment for humic acid production. Proximate analysis of lignite treated with HNO_3 indicated a decrease in fixed carbon and ash; and an increase in moisture and volatile matter content. The results of the ultimate analysis of lignite treated with HNO_3 found a decrease in carbon concentration, with a significant increase in oxygen; and slight changes in nitrogen, hydrogen and sulfur elements. This informs that there has been a carboxylation process, nitration reaction during the HNO_3 oxidation process. The maximum humic acid production was found in treated lignite using a KOH concentration of 4.5%; which is indicated by an increase of around 155% more than untreated lignite. Based on this study, it can be concluded that the Sajau Formation lignite coal can be used as a raw material for producing and extracting humic acid on a commercial scale.

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