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From the Editor

Good mining practices and value added issues, particularly in implementing the application of the Law No.4/2009 concerning mineral and coal mining in this country, always dominate the main topic along this edition. Those issues are really significant, because in the early 2016, this law has officially been implemented. All raw minerals may not be exported prior to being processed in smelters. However, the mineral product grade (concentrate) may be exported for a limited time for mining companies in completing the construction of smelter until January 2017. This regulation absolutely become a guidance of the implementation to ban export of ores in the early 2014. There are six minerals banned to be exported, in which they must be exported with grade of reaching 100%, i.e. gold, bauxite, iron ore, nickel, coal and copper. Even currently, President Joko Widodo strictly supervises the implementation of the regulation. Supporting this supervision, the Indonesia’s Corruption Eradication Commission (Komisi Pemberantasan Korupsi/KPK) is involved to the verification of the mining activities in the country in implementing those issues.

It is predicted that the government must cope with the impacts that can happen when the regulation implemented. One of these impacts absolutely includes termination of employment. The problem, of course, will be a concern for the mining employees. For this reason, the government should give a policy that still permit to export concentrate with certain grade limits until the construction of smelters. Besides saving the employees, this regulation can be a concession for regional economy, because the mining operation still carries out.

Articles related to this law emphasise that holders of mining licences must increase value added of mineral and coal resources in the implementation of mining operation, processing and utilisation. The holders of mining licence of operation and production must domestically conduct process the mineral and coal. It is also stressed that environmental issues are the main points to be managed wisely. In addition, most small-scale mining always gives rise to degraded environment and causes air and water pollution to the communities around the mining operation. This issue must be solved in order to create a healthy environment and to make a harmonious living between the mining company and the surrounding communities.

Five papers published in this journal are contributed by researchers and lecturers from R&D institutions and universities. Some of the authors are well-known figure for their discipline and have contributed their brilliant ideas to improve the mineral and coal technology. The rest is young researchers who are interested in managing a good environment due to mining operation in this country.

From all the papers published in this journal, R&D institutions should do something new to anticipate all the above challenges rather than to cope with all problems. It is really expected that the Law 4/2009 and related regulations must be implemented to accommodate the good mining practices and value added issues including the aspects of exploration, mining environment and economics of the mineral and coal commodities, which are perfectly processed in line with the user demands. Of course, this opportunity should be developed and this is a big challenge for researchers and engineers to prove their capabilities for the better future of this country.

The Editor
Abstract Index

DDC 549
Wahyudi, Tatang and Faizal, Erwin (R&D Centre for Mineral and Coal Technology, PT L’Oreal Manufacturing Indonesia)
Mineralogy Characters of Cijulang Phosphate Rocks Related to Bioleaching Process
Karakter Mineralogi Batuan Fosfat Cijulang pada Proses Bioleaching
IMJ, Vol. 19, No. 2, June 2016, P. 65 - 77

Research on potency test of selected phosphate solubilizing microfungi (PSM) isolates had been conducted. The purpose was to obtain the most potential indigenous microfungi to solubilizing phosphate in bioleaching process. Identification with moist chamber showed that the selected PSM belonged to Penicillium genera. Bioleaching process through measuring process growth and oxalic acid production was effective on the 8th day. Chemical analysis showed that bioleaching process using selected indigenous PSM of phosphate rock was able to increase P₂O₅ content from 38.40 to 49.70% or improve around 11.30%. Experimental condition for such a recovery was -140+200# of sample size an 5% of percent solid. Mineralogy characters of the leached phosphate rocks showed some micro cracks as well as encapsulation by clay minerals. Not all phosphor element was leached by oxalic acid produced by microfungi.

Keywords: phosphate rocks, phosphate solubilizing microfungi (PSM), indigenous, bioleaching, Penicillium

DDC 669.0283
Amalia, Dessy; Sariman and Azhari (R&D Centre for Mineral and Coal Technology)
Potency of Making the Chemical Manganese Dioxide (CMD) from East Nusa Tenggara Pyrolusite
Potensi Pembuatan Mangan Dioksida dari Pirolusit Nusa Tenggara Timur
IMJ, Vol. 19, No. 2, June 2016, P. 79 - 87

Chemical manganese dioxide has not yet commercially developed in Indonesia. It is supplied by import sector. The fact that Indonesia has manganese resources as many as 60,893,820 tons is inconsistent with above condition. Research on CMD making employed pyrolusite as the raw material with size of -100+150 mesh. The material was then reacted with sulfuric acid 6% and various concentration of molasses as reductant from 10, 20, 30, 50 and 100 %. The manganese sulfate leachate was then purified using sodium hydroxide and then filtered to have a nonferrous manganese sulfate. The Mn was precipitated from manganese sulfate using sodium bicarbonate. The precipitated manganese carbonate was then calcined at 600°C by injecting the air at various flow rates (100, 200, 300, 400 cc/minute) and different calcination time (2, 3, 4 hours) to get manganese dioxide. The best extracted Mn reached 97.58% using 50% of molasses as a reductant. The precipitation of manganese carbonate had produced sodium carbonate as an impurity. The calcination had not yet changed the manganese carbonate into manganese dioxide due to extremely high calcination temperature.

Keywords: pyrolusite, molasses, precipitation, calcination,

DDC 691.4
Widodo; Subari and Erlangga, Bagus D. (Research Center for Geotechnology; Center for Ceramic)
Characterization of Karangnunggal Kaolin as Raw Materials for Ceramic
Karakterisasi Kaolin Karangnunggal untuk Bahan Baku Keramik
IMJ, Vol. 19, No. 2, June 2016, P. 89 - 96

Kaolin from Karangnunggal had been characterized. This kaolin has a brownish white in color and is associated with tuff. To identify characteristics, the samples was analyzed by XRD, optical microscope, AAS, and SEM. The results showed that the kaolin consisted of kaolinite, halloysite, cristobalite, dickite, muscovite, illit and hematit while petrographic analysis describes halloysite, kaolinite, dickite, and quartz. SEM analysis showed the crystal forms such as kaolinite, halloysite and dickite; while chemical analysis confirmed that kaolin composition comprised SiO₂ = 65.78 %, Al₂O₃ = 19.55 %, Fe₂O₃ = 0.90 % and LOI = 8.29 %. Based on characterization results Karangnunggal kaolin originated from tuff alteration. Referring to such properties, this kaolin can be used as raw material for white ceramic products such as sanitary, ceramic tiles and insulation.

Keywords: kaolin, XRD, petrographic, SEM, chemical, utilization
Solvent extraction method is one of the methods to reduce ash content in coal to improve the energy efficiency and reduce negative environmental impacts. The use of 1-methyl naphthalene (1-MN) as a solvent in the weight ratio of coal to solvent of 1:3, 1:6 and 1:9 using three coal samples obtained from a coal washing plant, namely ROM (run of mine), DC (dirty coal) and RC (reject coal) was performed. Results show that the ash content of the extracted coals no or significantly low amount (<0.3%) ash contents. The highest extraction yield was obtained at 15.38 % (daf) at DC coal sample and coal to solvent ratio of 1:9, while the lowest at 3.09 % (daf) at ROM coal sample and coal to solvent ratio of 1:3. In addition, the extraction process with a solution of 1-MN also able to reduce moisture content of the coals, as a result the caloric value of the coals were significantly increased.

Keywords: solvent, ash, extraction yield, moisture, caloric value

Coal gasification is a chemical reaction that has a purpose to change the original solid coal into gaseous compounds. Converting the coal into gaseous compounds will make the combustion process easier and results in increasing combustion efficiency. The sulfur and nitrogen are also easier to be separated in order to obtain cleaner flue gas. This paper presents kinetic analysis of coal gasification reactions in mini gasifier (or known as GasMin in Bahasa) reactor. The results show that the increase of the air-coal ratio (ACR) affected the maximum temperature of the reactor, which means that an increase of the intake air flow rate will increase the amount of oxygen for combustion reaction. Meanwhile, the increase of the team coal ratio (SCR) will increase flow rate of the mixture of air-steam feed. As a result, the ability of coal gasification has also increased. This will increase gasification efficiency around 3-5% which then will also increase the gas yield. The maximum value of SCR was 0.06, further than that of the yield gas and the q-value will slightly decrease. The simulation result showed that the producer gas was dominated by CO with 26.72% mole fraction; H2 with 14.06% mole fraction, and N2 with 47.88% mole fraction. Meanwhile CO2, CH4 and O2 mole fraction were 5%, 0.24%, and 1.20% respectively.

Keywords: coal, gasification, mini gasifier, kinetic reactions.
MINERALOGY CHARACTERS OF CIJULANG PHOSPHATE ROCKS RELATED TO BIOLEACHING PROCESS

KARAKTER MINERALOGI BATUAN FOSFAT CIJULANG PADA PROSES BIOLEACHING

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ABSTRACT
Research on potency test of selected phosphate solubilizing microfungi (PSM) isolates had been conducted. The purpose was to obtain the most potential indigenous microfungi to solubilizing phosphate in bioleaching process. Identification with moist chamber showed that the selected PSM belonged to Penicillium genera. Bioleaching process through measuring process growth and oxalic acid production was effective on the 8th day. Chemical analysis showed that bioleaching process using selected indigenous PSM of phosphate rock was able to increase P₂O₅ content from 38.40 to 49.70% or improve around 11.30%. Experimental condition for such a recovery was -140+20# of sample size an 5% of percent solid. Mineralogy characters of the leached phosphate rocks showed some micro cracks as well as encapsulation by clay minerals. Not all phosphor element was leached by oxalic acid produced by microfungi.

Keywords: phosphate rocks, phosphate solubilizing microfungi (PSM), indigenous, bioleaching, Penicillium

ABSTRAK
Penelitian mengenai uji potensi isolat mikrofungi pelarut fosfat (MPF) terseleksi dari batuan fosfat bertujuan untuk memperoleh isolat mikrofungi asli batuan fosfat yang paling potensial dalam melarutkan fosfat dari batuannya melalui proses bioleaching. Mikroba terseleksi dengan aktifitas pelarutan tertinggi termasuk ke dalam genus Penicillium. Proses bioleaching melalui pengukuran parameter profil pertumbuhan dan kadar asam oksalat, efektif pada hari ke-8. Analisis kimia basah menunjukkan bahwa proses bioleaching dengan MPF asli batuan fosfat terseleksi dapat meningkatkan kadar P₂O₅ dari 38.40 sampai 49.70% atau bertambah sekitar 11.30% sedangkan kondisi percobaan yang digunakan untuk mencapai perolehan seperti di atas adalah -140+20# ukuran contoh dan persen padatan 5%. Karakter mineralogi batuan fosfat yang terdeteksi adalah rekahan mikro dan penyelaputan partikel fosfat oleh mineral lempung. Pengamatan secara mikroskopis menunjukkan bahwa tidak semua unsur fosfat tertindih oleh asam oksalat yang dihasilkan mikrofungi.

Kata kunci: batuan fosfat, mikrofungi pelarut fosfat (MPF), asli, bioleaching, Penicillium
INTRODUCTION

Phosphorus is one of the major nutrients, second only to nitrogen in requirement for plants. Its application is mostly for chemical, fodder, detergent and fertilizer industries. Development of world fertilizer industries in 2009 showed that almost 90% of natural phosphates were used as raw material for superphosphate fertilizer (Sastramiharja et al., 2009). The fact that as an agricultural country, Indonesia requires superphosphate fertilizer around 800,000 tons a year (Budi and Purbasari, 2009) makes the import of superphosphate fertilizer still required. Normally, Indonesian phosphate deposits are distributed sporadically within limestone caves performing relatively small quantity such as available at Cijulang - West Java (Figure 1). Yet, the newest data regarding Indonesian phosphate reserve are not yet available. In Java, 20 million tons of phosphate resources were already identified. They are included in 48 locations; however, such a figure may bigger than that of identified ones as the guano deposits of Sumatera, East and South Kalimantan as well as Sulawesi have not yet been explored. Moreover, the exploration of marine phosphate deposits has also not yet been conducted. If so, the figure related to Indonesian phosphate resources may increase significantly.

Most of Indonesia phosphate rock deposits contain low P_2O_5 content, namely less than 20%. Such deposits are suitable only for small scale mining (Wahyudi et al., 2008; Kasno et al., 2009). A good phosphate rock deposit used for superphosphate fertilizer should have minimum P_2O_5 content around 43% (Ridwan, 2011). Improving P_2O_5 content can be conducted both physically and chemically. The former can be accomplished through calcination and magnetic separation while the later is carry out by acidic method using sulphuric, hydrochloric and phosphoric acids. However, the use of such methods has some disadvantages such as high energy and chemical reagent consumptions. The use of chemical reagent also provides hazardous residues that are harmful to the environment. An alternative to change such methods is bioleaching - a biotechnology that beneficiates micro fungi capability to dissolve the phosphate rocks (Saeed et al, 2002).

Phosphate solubilizing microfungi (PSM) play an important role in supplementing phosphorus to the plants, allowing a sustainable use of phosphate fertilizers. The fungi are involved in a range of process that effect the transformation of soil phosphorus (P) and thus are integral component of the soil ‘P’ cycle. Many of them are capable of the soil ‘P’ cycle (Bulut, 2013). PSM application in the field has been reported to increase crop yield. Several mechanisms like lowering pH by acid production, ion chelation and exchange reactions in the growth environment have been reported to play a role in phosphate solubilization by PSM. Among PSM, species of Aspergillus, Penicillium and yeast have been widely reported solubilizing various forms of inorganic phosphates (Blackwell, 2011).
Wahyudi et al. (2008) had improved the P<sub>2</sub>O<sub>5</sub> content through bioleaching using *Aspergillus niger*. However, the fungi used for bioleaching was not derived indigenously. The leaching was optimized by varying grain size of the sample and its percent solid. Chi et al., (2007) stated that the finer the processed sample, the easier the contact between the mineral and the bioleaching agent. Referring to Chi’s statement, Wahyudi et al. (2009) found that the best sample size for bioleaching was -140+200# instead of -200# and the 20% was the minimum condition for percent solid to get economically bioleaching process. Yet, the effectivity of bioleaching decreased when the %solid increased. Based on such an argument, it needs to conduct isolate potential test of phosphate solubilizing microfungi.

Microfungi produce organic acid that can free all phosphatic compounds within the phosphate rock such as AlPO<sub>4</sub>, FePO<sub>4</sub> and Ca(PO<sub>4</sub>). The free phosphate is then used by plants. Roni et al. (2013) stated that the best organic acid to solve the phosphor from its clusters was citric acid followed by oxalic acid and the acetic acid while Chi et al. (2007) had been investigated that sulfuric acid produced by *Acidithiobacillus ferrooxidans* started effective on the 5<sup>th</sup> day of bioleaching process and increased the P<sub>2</sub>O<sub>5</sub> contents as many a 9%.

Bioleaching study on increasing P<sub>2</sub>O<sub>5</sub> content by Wahyudi et al. (2008) showed that the highest oxalic acid production occurred at the 10<sup>th</sup>-day. Some factors affecting their bioleaching process included type of microfungi, percent solid and particle size. Using PSM of *Aspergillus niger* and particle size of -140+200#, the increasing P<sub>2</sub>O<sub>5</sub> was much better than that of particle size of -200#. Nevertheless, Chi et al (2007) who used *Acidithiobacillus ferrooxidans* with varying particle size from 400, 270, 140, 70 and 50# showed that particle size of 270# provided the best quantity to increase the P<sub>2</sub>O<sub>5</sub> content. Referring to Wahyudi's and Chi’s studies, it showed that different microorganism worked better at different particle sizes when solubilizing the phosphor. *Aspergillus niger* was good for coarser particles than 270# while the *Acidithiobacillus ferrooxidans* was competent for fine particle.

The objective of this study is to evaluate mineralogy characters related to bioleaching process. The fact that not all phosphate element of Cijulang phosphate rocks dissolved implies that there are some obstacles during the leaching. By studying tailings mineralogy and other bioleaching cases, problem related to bioleaching performance might be solved.

**METHODOLOGY**

Samples for conducting the study were taken from Cijulang, West Java. The phosphate rocks were then prepared by crushing and sieving the materials to -140+200# and -200# and percent solid of 20%. PSM selection applied methods that were conducted by Widawati et al. (2008), namely rehydration centrifugation (RC) and sodium dodecyl sulfonate (SDS) methods. They were followed by moist chamber method for identifying the selected PSM. PSM selection was determined by potential test of phosphate dissolution within Pikovskaya medium. The selected PSM was represented by the biggest clear zone occurred around the colony. Microfungi growth was analyzed by total plate account method while the oxalic acid profile from bioleaching were evaluated. Previously, the samples were also characterized their mineralogy characters by optical microscope, X-ray diffraction (XRD) and scanning electron microscope-electron dispersive spectrometer (SEM-EDS) methods while its chemical composition employed AAS. Characterization using those instruments was also conducted to the tailings from bioleaching.

**RESULTS AND DISCUSSION**

Bioleaching test using indigenous PSM improve P<sub>2</sub>O<sub>5</sub> content of phosphate rock from Cijulang. Though the leaching provided promised results, some phosphor elements still remained within the tailings. It meant that the indigenous PSM only leached some phosphate minerals due to some mineralogical characters. Mineralogical study on the tailings showed some features regarding the effect of leaching process.
Raw Material Study

Phosphate minerals available within the phosphate rocks consist of various apatites, namely carbonate fluorapatite (francolite) - \((\text{Ca, Mg, Sr, Na})_{10}(\text{PO}_4,\text{SO}_4,\text{CO}_3)\text{F}_{2-3}\), carbonate hydroxyapatite (dahlite) - \(
\text{Ca}_5(\text{PO}_4,\text{CO}_3)\text{F}\) and chlorapatite - \(
\text{Ca}_5(\text{PO}_4)\text{Cl}\). XRD analyses showed that Cijulang phosphate rock contained dahlite, calcite - \(\text{CaCO}_3\), montmorillonite - \(\text{Na(Al, Mg)}_2 \text{Si}_4\text{O}_{10}(\text{OH})_2\cdot\text{H}_2\text{O}\) and quartz - \(\text{SiO}_2\).

The fact that dahlite was the phosphate mineral within Cijulang phosphate rocks was confirmed by optical microscope test. The results showed fibrous radiating masses - a special habit of dahlite (Figure 2). In mineral processing point of view, such a feature is an advantage as it will facilitate the leaching reagent to permeate into dahlite body. This will increase the \(\text{P}_2\text{O}_5\) content. Yet to get the desired content, many factors should be considered in processing the phosphate.

Statistically, the optical microscope tests exhibit that the original phosphate rock samples (not fractionated) own dahlite only 5.40% (Figure 3). Of various minerals occur within phosphate rocks, clay minerals that might be montmorillonite seem the dominant one. Its portion within the rocks is 59.05% followed by calcite (20.80%), quartz (6.41%), rock fragments (6.30%) and opaque minerals (2.04%). Those five minerals are categorized impurities and should be noted when the dahlite is processed. SEM-EDS analysis using X-ray method also ascertained that the main phosphate mineral of Cijulang phosphate rock was dahlite. SEM photomicrograph (Figure 4) displayed radiating features of dahlite. The mapping process showed at least eight elements detected within samples. Those are calcium (Ca), carbon (C), phosphor (P), sulfur (S), aluminum (Al), silicon (Si) and iron (Fe). The first three element is dahlite component; the C and Ca are also the elements of calcite while Al, Si and Fe are silicate mineral components. Of the eight-mapped elements; calcium, carbon, phosphor and aluminum, silicon, iron showed strong signal to be well mapped. Sulfur seemed a noise within this sample. Its quantity (0.82%) was supposed to be the cause (Table 1). The material might be came as transported element from somewhere through leaching water. Two detected silicate components, aluminum and silicon, might be came from weathered volcanic rocks where the phosphate rocks associated. Similar to the result of SEM-EDS analysis, XRD analysis of Cijulang phosphate rocks showed that three minerals dominated the material (Figure 5). Those are hydroxyapatite, calcite (\(\text{CaCO}_3\)) and quartz (\(\text{SiO}_2\)). Hydroxyapatite (HA) was a naturally occurring mineral form of calcium apatite with the formula \(\text{Ca}_5(\text{PO}_4)\text{OH}\) but is usually written \(\text{Ca}_{10}(\text{PO}_4)\text{OH}\) to denote that the crystal unit cell comprises two entities. It is one of the phosphate minerals that is known as dahlite and is produced and used by biological micro-environmental systems.

Analyzing composition of Cijulang phosphate was also accomplished through chemical analysis using wet method. The analyzed sample consisted of three types, namely head sample (HS) and fraction ones. The original sample (HS) contained \(\text{P}_2\text{O}_5\) around 17.28% which was then increased to 38.4 and 37.6% when ground into -140+200# and -200# (Table 2).

The grinding process seemed to liberate phosphate mineral from its host. Not only was the \(\text{P}_2\text{O}_5\) content within Cijulang phosphate rock high but also the \(\text{CaO}\) substance was also significant. Kusumo et al. (2000) stated that high \(\text{CaO}\) content had a value added for a phosphate rock to be a natural fertilizer as such a material could increase soil basicity. Though the \(\text{P}_2\text{O}_5\) content of Cijulang phosphate is relatively high, it is unqualified to be used for super phosphate fertilizer (Ridwan, 2011). It needs improving the content until satisfies the specification for phosphate fertilizer.
Figure 2. Two dahlite performances showing fibrous radiating masses. D belongs to dahlite and C is calcite.

Figure 3. Composition of Cijulang phosphate rocks that consists of dahlite, calcite, quartz, clay minerals, opaque minerals and rock fragments.
**Figure 4.** SEM-EDS analysis of Cijulang phosphate rocks detected fibrous radiating performance and phosphate-forming elements.

**Table 1.** Result of SEM-EDS analysis of Cijulang phosphate rocks.

<table>
<thead>
<tr>
<th>Element</th>
<th>(keV)</th>
<th>mass%</th>
<th>Error%</th>
<th>A%</th>
<th>Compound</th>
<th>mass%</th>
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<td>7.01</td>
<td>1.83</td>
<td>3.8326</td>
</tr>
<tr>
<td>P</td>
<td>2.013</td>
<td>5.25</td>
<td>0.63</td>
<td>214</td>
<td>P2O5</td>
<td>12.04</td>
<td>2.67</td>
<td>6.7698</td>
</tr>
<tr>
<td>S</td>
<td>2.307</td>
<td>0.62</td>
<td>0.62</td>
<td>9.66</td>
<td>SO3</td>
<td>2.06</td>
<td>0.40</td>
<td>1.2755</td>
</tr>
<tr>
<td>Ca</td>
<td>3.590</td>
<td>2.184</td>
<td>0.25</td>
<td>13.76</td>
<td>CaO</td>
<td>30.56</td>
<td>6.67</td>
<td>27.3861</td>
</tr>
<tr>
<td>Fe</td>
<td>6.393</td>
<td>5.02</td>
<td>1.05</td>
<td>2.27</td>
<td>FeO</td>
<td>6.46</td>
<td>1.41</td>
<td>6.7918</td>
</tr>
<tr>
<td>Total</td>
<td>100.00</td>
<td>139.00</td>
<td>100.00</td>
<td>15.53</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 5. Result of XRD analysis showing four detected minerals, namely calcite, hydroxyl apatite, (Na, Mg) silicate and quartz.

Table 2. Composition Cijulang phosphate rocks, HS = head sample, -140+200# and -200# samples = fractioned phosphate rocks

<table>
<thead>
<tr>
<th>Sample code</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>14.16</td>
<td>7.71</td>
<td>5.35</td>
<td>26.9</td>
<td>17.28</td>
</tr>
<tr>
<td>-140+200#</td>
<td>0.75</td>
<td>2.68</td>
<td>0.33</td>
<td>46.62</td>
<td>38.4</td>
</tr>
<tr>
<td>-200#</td>
<td>0.65</td>
<td>3.08</td>
<td>0.32</td>
<td>46.81</td>
<td>37.6</td>
</tr>
</tbody>
</table>
Bioleaching Tests

Most of soil microbes have potency as bio-fertilizer, mainly those that lives within rhizosphere. One of them relates phosphatic-solvent microbes. Such microbes have a capability to increase the growth and production of the plants (Widawati et al., 2008). Yet its mechanism has not been known but it is supposed to involve complex process including dissolution of polypeptide compounds, oxidation and reduction (Ruangsanka, 2014). Samples for isolating microbes were phosphate rocks. To remove the water content that might be still available within samples, the samples used wind-drying method as the method was relatively secured from composition destruction (Sterflinger, 2000). Isolated PSM was accomplished by testing the potency of phosphate dissolution in Pikovskaya medium (Malviya et al., 2011). Clear zone formation within the medium showed that the microorganism were available. The clear zone occurred due to the dissolution of tricalcium phosphate or $\text{Ca}_3(\text{PO}_4)_2$. The selected PSM was determined by the largest dimension of the clear zone surrounding the colony (Ginting et al., 2006; Maryanti, 2006). Figure 6 shows the selected PSM available in Cijulang phosphate rocks and successfully isolated for bioleaching

Identification of selected PSM isolates showed that the isolated PSM belonged to *Penicillium* sp. genus. Such the microfungi had grown-fast character and spread fast in various environments in either soil, air, or rotten plants (Blackwell, 2011; Kiziewicz et al., 2013).

When conducting bioleaching; two items should be observed, namely the growth of *Penicillium* sp. and produced oxalic acid during the leaching (Yasser et al. 2014). A series of bioleaching tests had been conducted using 6 combinations of particle size and percent solid (Table 3) and found that during 10-day leaching, the microfungi had shown the growing capability since Day-1 and continued through Day-8 but then declined from Day-9 through 10. Of 6 variables, sample with label $P = \text{-140+200+5\%}$ retained higher cell development compared to other samples and showed the colony number around $68 \times 10^6$ CFU/ml. Yet the figure showed that the *Penicillium* sp. resulted from selection test did not undergo adaptation phase as the fungi came indigenously from the phosphate rocks. The adaptation phase is not always necessary if the growing medium and environment of the fungi was similar to the previous ones.

Referring to the oxalic contents that were produced during the process, it was found that the acid increased exponentially since Day 1 through Day 10; however, there were no significant differences of the content among six varying samples. Overall, the quantity of produced oxalic acid when leached by the fungi varied from 75 to 85%. Sample with labelled $P = \text{-140+200+5\%}$, $P = \text{-140+200+12.5\%}$ and $P = \text{-140+200+20\%}$ yielded similar produced oxalic acid quantity, namely 85%. Comparing cell development and oxalic acid production, the acid production was in accordance with microfungi growth. Start on Day 1 through 8, the fungi grew exponentially (Figure 6) and were followed by stationary phase on the next day; later, the cells died on Day 10. The oxalic acid was optimally produced on Day 8. High concentration of oxalic acid detected after cell mortality indicated that the acid was not used as a nutrition for growing phase but accumulated as intermediate compound within fungi metabolism.

Leaching experiment showed that particle size of -140+200# and percent solid of 5% provided the highest oxalic acid (Figure 7). It seemed that such parameters were the optimum condition for the experiment. Employing various sample feeds and indigenous microfungi, it showed that the increase of $P_2O_5$ content varied from 37.6 - 38.4% to 47.4 - 49.7% (Table 3). The highest recovery was achieved by experiment that used sample with size of -140+200# and percent solid of 5%. The increase of $P_2O_5$ and CaO occurred due to the phosphate mineral was leached and releasing P element to be $P_2O_5$ while the Ca developed into CaO (Wahyudi et al., 2008).
Figure 6. The selected PSM for dissolving phosphate element showing the biggest clear zone (A) and identified PSM (*Penicillium* sp)

Figure 6. The growth of indigenous phosphate solubilizing microfungi during bioleaching process
In its activity, the phosphate solubilizing microfungi releases several organic acids such as citric, glutamic, succinic, lactic, oxalic, glyoxal, malic, fumaric, tartaric and aceto butyrate acids. The increase of the acids results in decreasing the pH sharply and dissolving Ca-phosphate. A stable complex compound of Ca$^{2+}$, Mg$^{2+}$, Fe$^{3+}$ and Al$^{3+}$, known as chelate, is also developed and releases the phosphor (Raharjo et al., 2007). The phosphate solubilizing microfungi (PSM) of Cijulang phosphate rocks, *Penicillium* sp. produced the oxalic acid and leached the phosphate rock. Referring to the 49%-P$_2$O$_5$ content (Table 3), it seems that such a microfungi is prospective to leach the rocks.

### Table 3. Result of bioleaching test for Cijulang phosphate rocks using indigenous *Penicillium* sp.

<table>
<thead>
<tr>
<th>Feed Condition</th>
<th>Particle Size</th>
<th>% Solid</th>
<th>P$_2$O$_5$ Content</th>
<th>CaO Content</th>
<th>P$_2$O$_5$ Content</th>
<th>CaO Content</th>
<th>P$_2$O$_5$ Increase (%)</th>
<th>CaO Increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-140+200#</td>
<td>5%</td>
<td>12.5%</td>
<td>38.4</td>
<td>4.6%</td>
<td>4.2%</td>
<td>11.3</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-200#</td>
<td>5%</td>
<td>12.5%</td>
<td>37.6</td>
<td>4.6%</td>
<td>4.3%</td>
<td>10.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tailings Characterization After Bioleaching

Bioleaching by *Penicillium* sp. could increase the P$_2$O$_5$ to 49% and exceeded the minimum specification for triple phosphate fertilizer. Therefore, it is necessary to do a characterization for tailings after bioleaching. Moreover, if referring to the leaching result that was only 49%, not at least 80%. Such a study can help improving leaching implementation. SEM-EDS analyses using X-ray mapping method of the after-leaching materials showed the feature of non-leached dahlite mineral as shown in Figure 8. The illustration showed that after bioleaching some dahlite minerals were completely leached by the fungi (D1), another was partly
leached (D2). The phosphorus pentoxide was still available within both minerals, noted by the green color, however, such concentrations were not as many as that of Dahlite D3. The red color of the D3 implied that the P_2O_5 were not completely leached. Mineralogical characters of the D3, such as less particle porosity or unliberated particles, were supposed to be the cause; the oxalic acid produced by the fungi could not optimally reach such particles. Mineralogical condition of the tailings from bioleaching also found the unleached calcite due to encapsulation by clay mineral (Figure 9). Such condition results in ineffective contact between calcite and the lixiviants.

CONCLUSIONS

Carbonate hydroxyapatite known as dahlite - Ca_5(PO_4,CO_3)F are the main phosphate mineral found within Cijulang phosphate rock. The rocks also contain calcite, quartz, clay mineral, opaque mineral and rock fragments. The clay mineral is supposed to be montmorillonite. Encapsulation performance found within the sample is supposed to be the cause imperfect leaching as the contact between the lixiviants and desired particles turns out to be ineffective.

The potential indigenous PSM found in Cijulang phosphate rocks is *Penicillium sp.* The fungi is effective enough to dissolve phosphor element within the rocks. Bioleaching using such a microfungi, -140+200# of feed size and 5% of percent weight provided the highest P_2O_5 solubilization, namely 49%. The figure exceeds the requirement of P_2O_5 for superphosphate fertilizer (43%). Prior bioleaching, the content of P_2O_5 within the rocks is only 38.4% but then increases 11.3%.

![Figure 8. SEM-EDS analysis of the phosphate tailings came from bioleaching process](image-url)
The study of adaptive characters for the microfungi and its capability in improving the P$_2$O$_5$ within phosphate rocks can be conducted to evaluate its potency when the fungi is directly inoculated on the superphosphate fertilizer. Changing the stirring method from rotary shaking to agitation when conducting bioleaching will result effective infiltration of microfungi mycelium.

ACKNOWLEDGEMENTS

The authors would like to thank Head of Microbiology Laboratory, Padjadjaran University for his permission to use laboratory facilities during the research, Pak Rachmat of Cijulang for providing phosphate rock samples and Staff of Preparation Laboratory, Research Development Centre for Mineral and Coal Technology for their assistance to prepare the samples.

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Mineralogy Characters of Cijulang Phosphate Rocks to... Tatang Wahyudi and Erwin Faizal


ABSTRACT
Chemical manganese dioxide has not yet commercially developed in Indonesia. It is supplied by import sector. The fact that Indonesia has manganese resources as many as 60,893,820 tons is inconsistent with above condition. Research on CMD making employed pyrolusite as the raw material with size of -100+150 mesh. The material was then reacted with sulfuric acid 6% and various concentration of molasses as reductant from 10, 20, 30, 50 and 100 %. The manganese sulfate leachate was then purified using sodium hydroxide and then filtered to have a nonferrous manganese sulfate. The Mn was precipitated from manganese sulfate using sodium bicarbonate. The precipitated manganese carbonate was then calcined at 600°C by injecting the air at various flow rates (100, 200, 300, 400 cc/minute) and different calcination time (2, 3, 4 hours) to get manganese dioxide. The best extracted Mn reached 97.58% using 50% of molasses as a reductant. The precipitation of manganese carbonate had produced sodium carbonate as an impurity. The calcination had not yet changed the manganese carbonate into manganese dioxide due to extremely high calcination temperature.

Keywords: pyrolusite, molasses, precipitation, calcination

INTRODUCTION
Manganese is the twelfth most common element in earth’s crust and fourth ranked after iron, aluminum and copper as widely used metal. More than 90% manganese is used as metallurgical product in steel manufacturing. The second largest is used as...
a dry cell battery (Webb, 2008). Those added values of manganese have not yet applied in Indonesia as reported by Ministry of Energy and Mineral Resources (Anon, 2014).

Indonesia has manganese resources as many as 60,893,820 tons (Anon, 2015). The manganese had previously been exported without any processing until the Ministry of Energy and Mineral Resources Regulation No. 8, 2015 issued a regulation regarding the minimum limit of major element percentage for metal commodities. Therefore some processing efforts have to be accomplished to fulfill the regulation.

Methods for processing the ore usually depend on the ore grade. High grade manganese ores are generally treated to produce ferromanganese (FeMn) and silicon manganese (SiMn) through pyrometallurgy technique while the low grade ores are processed through hydrometallurgy method into chemical manganese dioxide (CMD) or electrolytic manganese dioxide (EMD) to replace the roasting step by reductive leaching (Sumardi, 2013).

Reductive leaching is a leaching process in reductive condition. The condition has to be applied in order to transform Mn(IV) from manganese ore into Mn(II) as seen in Figure 1. It is shown that the manganese ore leaching has to be managed in reductive condition within acid circumstances or low pH. The kinetics of manganese reductive leaching is controlled by diffusion through insoluble layer of the associated minerals (Su et al., 2010).

Leach liquors resulted from leaching usually dissolve undesirable elements. Some treatments are needed to increase the liquor concentration through purification to eliminate or separate undesirable metals. Several options of purification process include precipitation, cementation, solvent extraction, ion exchange etc. Carbonate precipitation of manganese solution using ammonium carbonate is suitable to separate nickel and cobalt as well as manganese in ammine complexes solution to solid carbonates (Baba et al., 2014).

Some researches regarding reductive leaching of manganese ore especially pyrolusite have been conducted using sulfuric acid with different reducing agent or additive. Sponge iron is proved to be a good additive by Bafghi et al. (2008). The efficiency of Mn dissolution after 10-minute-reaction was 98% at room temperature using the particle size of −250+150 μm and the H2SO4 to MnO2 molar ratio of 0.8 as well as sulfuric acid to MnO2 molar ratio of 3.0. The result has a better performance than that of previous researchers that used ferrous iron as the additive.

![Figure 1. Eh- pH system of Mn-Fe-H2O at 25°C (Sumardi, 2013)](image-url)
Another research on manganese reductive leaching from pyrolusite using sulfuric acid as solvent had also been conducted by Nayl et al. (2011). The leaching was performed optimum condition using H₂O₂ as a reductant. The optimum condition of the leaching was achieved at 40°C for 90 minutes using 4.0 M H₂SO₄ and 0.8 M H₂O₂ on particle size of 44–37 μm pyrolusite. The manganese leaching efficiency was 92%.

Various reductants have been applied but the organic reductant has approved to be simple and efficient to leach pyrolusite (Su et al., 2009). The organic one is also environmental friendly. Some of them that can be used as reducing agent are molasses, hay, corn cob and sawdust (Sumardi, 2013). The use of corn cob as reductant in reductive pyrolusite leaching had been conducted by Ali et al. (2106). The siliceous manganese ore were diluted in 1.9 mol/dm³ sulfuric acid solution. Best manganese extraction was 92.8% and accomplished in 60 minutes at 90°C and 4 grams of corn cob.

Su et al. (2009) had conducted reductive pyrolusite leaching using sulfuric acid as a solvent and molasses of alcohol wastewater as the reductant. The optimum condition for such a leaching was performed by 1.9 mol/L H₂SO₄ and 2.0 mL/g of alcohol-wastewater molasses based on Mn content in pyrolusite. The reductive leaching conducted at 90°C for 120 minutes and resulted Mn efficiency more than 93%. While, the recoveries of Fe and Al about 37 and 25% respectively. Another research dealing with pyrolusite reductive leaching was conducted using molasses from sugar production waste. The highest percentage of manganese dissolution reached up to 95.33% using condition 70°C-temperature, 6%-sulfuric acid (H₂SO₄), 10%-percent solid, 100 g/L- molasses, 200-rpm and 6-hour leaching time. Chemical reaction of the leaching was as follows (Sumardi, 2013):

\[
C₆H₁₂O₆ + 12MnO₂ + 24H^+ → 6 CO₂ + 12Mn^{2+} + 18H₂O
\]

Previous research (Su et al., 2009; Sumardi, 2013) proved that molasses is a good reductant. However some improvements are required to get a higher extraction percentage. This research tried to seek a better molasses composition to have higher manganese dissolution efficiency than previous ones using molasses as a reductant. Nevertheless, the manganese sulfate production using molasses as a reductant has not yet available to be applied for making the chemical manganese dioxide. The potency of chemical manganese dioxide production using molasses as a reductant through hydrometallurgy method needs to be proved.

**METHODOLOGY**

The experiments used manganese ore from East Nusa Tenggara. The ore was dried by oven at 110°C for 24 hours then was prepared through sampling and milling to get representative samples size of -100+150 mesh. The sample was then reacted within 2-mole/L sulfuric acid and various molasses concentration (10; 20; 30; 50; 100 %) as reductant at 90°C in 6 hours. Equipments for process was shown in Figure 2. The leachate from filtered leaching solution heated at 70°C along with 10-% NaOH until pH 5-6 as seen in Figure 3 to precipitate the ferrous hydroxide. Then the solution was filtered to separate ferrous hydroxide. Remained solution was heated to 50°C and added with sodium carbonate to pH 9 to get precipitated manganese carbonate. The manganese carbonate was then calcined in tube furnace at 600°C with various air rate (200; 300; 400) cc/minute for 2 hours. The best air rate was used for next experiments using various calcination temperatures. Figure 4 showed the flowchart of the process.
Figure 3. Ferrous precipitation from leaching solution

Figure 4. The flowchart regarding the process to get manganese dioxide
RESULTS AND DISCUSSION

XRD analyses of manganese ore showed (Figure 5) pyrolusite (MnO₂) and manganite (Mn(OH)₃ along with quartz (SiO₂). However the presence of potassium was also detected by X-ray mapping (SEM-EDS method) test result as shown in Figure 6. Through SEM photo-micrograph test, it is known that manganese mineral is associated with silicate mineral.

Mineral composition is supported by chemical composition as presented in Table 1. It is showed that the manganese as the primary component followed by SiO₂ as the major impurity. The amount of Al, Mg, and Ca present the silicate content in the ore. Manganese contents in the ore used as a basic calculation for sulfuric consumption. Result of the manganese ore leaching is presented in Table 2 and illustrated in Figure 7.

Figure 5. XRD pattern of manganese ore

Figure 6. (a) SEM photo-micrograph of manganese ore and (b) X-Ray mapping analysis of the ore
The result also proved that molasses is a good reductant for manganese ore reductive leaching. Mn extraction improved as the molasses concentration increased to 50% (97.58%) and decreased when 100% concentration of molasses were added. The excessive amount of molasses will trigger others element besides Mn reduction; the elements consumed more sulfuric acid. Constant amount of sulfuric acid would reduce Mn dissolution rate than that of previous molasses concentration.

The best Mn extraction which is used 50% of molasses concentration was purified from ferrous ion with sodium hydroxide (NaOH) addition to precipitate the ferrous. Remained solution was added with sodium carbonate (Na$_2$CO$_3$) to precipitate the manganese carbonate as visualized in Figure 8. Confirmation of the precipitated mineral composition was conducted through XRD analysis as shown at Figure 9 that affirmed the precipitate was manganese carbonate.
In terms of making CMD, the manganese carbonate was calcined in a tube furnace equipped with a compressor to supply the air. The product was shown in Figure 10. Calcination was performed firstly at 600°C with various air flow rates. As seen in Table 3, the MnO₂ content under condition of 300 cc/minute air injection is bigger therefore it continued to perform at various temperatures as seen in Table 4. Different temperatures of calcination would produce different MnOx crystal form along with MnO and MnO₂. The possible MnOx phase that can be produced were Mn₃O₄, Mn₅O₈ even Mn₂O₃ (Ren et al., 2014).

According to TGA test for MnO₂ and MnCO₃ under air and argon atmosphere, the MnCO₃ would transform to MnO at 450°C while MnO₂ to Mn₂O₃ at 550°C and further transformation into Mn₃O₄ at 950°C (Saputra et al., 2013). The XRD test of manganese carbonate calcination at 600°C resulted transformation into manganese oxide-haussmanite (Mn₃O₄) containing sodium sulfate (Na₂SO₄) as an impurity (Figure 10). The presence of sodium sulfate was considered to occur during precipitation of manganese carbonate. The precipitation of such a material was illustrated as follows:

\[ \text{MnSO}_4 + \text{Na}_2\text{CO}_3 \rightarrow \text{MnCO}_3 + \text{Na}_2\text{SO}_4 \]

while illustration for calcination process was shown below:

\[ 2 \text{MnCO}_3 + \text{O}_2 \rightarrow 2 \text{MnO}_2 + 2 \text{CO}_2 \]
Table 3. Mn content in calcined manganese carbonate at 600°C for 2-hour reaction with various air flow rate (200, 300, 400 cc/minute)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Content (%)</th>
<th>200 cc/minute</th>
<th>300 cc/minute</th>
<th>400 cc/minute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn Total</td>
<td>55.2</td>
<td>56.7</td>
<td>56.68</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>43.16</td>
<td>40.44</td>
<td>44.8</td>
<td></td>
</tr>
<tr>
<td>MnO₂</td>
<td>34.78</td>
<td>40.17</td>
<td>34.78</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Mn content in calcined manganese carbonate for 2-hour leaching using 300 cc/minute of air with various temperature (600, 700, 800°C)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Content (%)</th>
<th>600°C</th>
<th>700°C</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn Total</td>
<td>56.7</td>
<td>54.47</td>
<td>55.82</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>40.44</td>
<td>44.57</td>
<td>46.19</td>
<td></td>
</tr>
<tr>
<td>MnO₂</td>
<td>40.17</td>
<td>31.73</td>
<td>31.73</td>
<td></td>
</tr>
</tbody>
</table>

Figure 10. XRD test on calcined manganese carbonate at 600°C for 2-hour leaching using 300 cc/minute air as the oxidant.
CONCLUSIONS

Molasses has a good ability as a reductant. Optimum amount of 50% concentration of molasses can extract 97.58% of Mn from pyrolusite. Precipitation of Mn from manganese sulfate leachate can be conducted using sodium bicarbonate but yielded sodium sulfate as an impurity. Therefore, it is suggested to use ammonium carbonate to precipitate the manganese in terms of avoiding the formation of sodium carbonate. The change of manganese carbonate into manganese dioxide has not yet succeeds but it turns into haussmanite because the calcination temperature that applied was too high. It is suggested to apply calcination temperatures below 600°C.

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REFERENCES


CHARACTERIZATION OF KARANGNUNGGAL KAOLIN AS RAW MATERIALS FOR CERAMIC
KARAKTERISASI KAOLIN KARANGNUNGGAL UNTUK BAHAN BAKU KERAMIK

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ABSTRACT
Kaolin from Karangnunggal had been characterized. This kaolin has a brownish white in color and is associated with tuff. To identify characteristics, the samples was analyzed by XRD, optical microscope, AAS, and SEM. The results showed that the kaolin consisted of kaolinite, halloysite, cristobalite, dickite, muscovite, illit and hematit while petrographic analysis describes halloysite, kaolinite, dickite, and quartz. SEM analysis showed the crystal forms such as kaolinite, halloysite and dickite; while chemical analysis confirmed that kaolin composition comprised SiO₂ = 65.78 %, Al₂O₃ = 19.55 %, Fe₂O₃ = 0.90 % and LOI = 8.29 %. Based on characterization results Karangnunggal kaolin originated from tuff alteration. Referring to such properties, this kaolin can be used as raw material for white ceramic products such as sanitary, ceramic tiles and insulation.

Keywords: kaolin, XRD, petrographic, SEM, chemical, utilization

INTRODUCTION
Indonesia has a lot of kaolin deposit showing variation in types and qualities. Kaolin is a rock consists of kaolinite mineral. Besides kaolinite, other minerals available within kaolin include dickite Al₂Si₂O₅[OH]₄, smectite (AlMg)₂ Si₆ O₂₀(OH)₁₀, illite, ((K,Na)(Al,Mg,Fe))₂(Si,Al)₄O₁₀(OH)₂,(H₂O)), and halloysite Al₄Si₄O₁₄[OH]₄ (Ajayi and Adefila, 2012). Kaolin is a hydrous aluminum silicate composition (Al₂O₃ 2SiO₂ 2H₂O). Volcanic rocks and hydrothermal alteration are indicators of kaolin formation.
In nature, there are three types of kaolin, namely residual kaolin (weathering the acid rocks such as granit and rhyolite), hydrothermal (alteration of alkali feldspar minerals by hot ground water) and sedimentary kaolins (deposition process from the origin to another sedimentation environment). The quality of kaolin is determined by chemical composition, mineral composition, brightness, shape and size of the granules. Kaolin in general can be used as raw materials for ceramics, paint, rubber, cosmetics, paper, and pesticides (Boch and Niepce, 2007; Kamseu et al., 2007).

Fialips et al. (1999) stated that kaolin crystallography and chemical characteristics of kaolin vary significantly and depend on the origin of the sediment deposits. Kaolin can be resulted from weathering the source rock (granite, feldspar, mica, and tuff) and was contaminated by other minor minerals to get different color. Cases et al. (1986) and Murray (2007) stated that detailed investigation of crystallography and mineralogy are needed to identify possible applications of the minerals within industry it was combined with chemical and physical characters. Identifying kaolinite minerals can be used X-ray diffraction analysis (Berry et al., 2006).

Specifically in ceramic industry, kaolin is usually used for manufacturing white ceramic such as tiles, sanitary and insulators. To make white ceramic hard porcelain is also used additional materials such as feldspar and silica with the ratio of 50 % kaolin, 25 % K-feldspar, and 25 % silica (Fialips et al., 1999). In ceramic body, kaolin serves as a binder or plasticity, feldspar as a buster and silica as a filler. Such composition when burned at high temperature will produce mullite, but mainly depended on the use kaolin. Pure kaolin that well-ordered kaolinite can give good results of mullisation after a burning process above 1,000° C. For disordered kaolinite, mullite will be formed at temperatures of bigger than 1,200° C (Septawendar et al., 2007).

The purpose of this study is to determine kaolin characterization including mineral content, chemical analysis, grain size, moisture content, and the properties of the ceramic. This data are used to determine potential utilization of raw material for white ceramic (whiteware ceramics) such as tableware, sanitary and ceramic tiles. The expected benefits of this research is to increase the value-added of Karangnunggal kaolin.

**METHODOLOGY**

This research used primary and secondary data. The secondary data included internet, books, and existing literatures. This secondary data is used as supporting data during research activities in the field and laboratory to help find solutions in discussion. Primary data was obtained through two activities that is field and laboratory researches.

The field research consists of identification kaolin deposit and kaolin sampling; whereas laboratory research consists of chemical analysis, X-ray diffraction (XRD), petrographic analysis, scanning electron microscope (SEM), water content, grain size, and properties of ceramic. The results of chemical analysis, XRD, petrographic, SEM, water content, and a large grain size is used to determine the quality kaolin as ceramic raw materials. To evaluate kaolin properties for ceramics, a specimen of 1 cm x 1.5 cm x 12 cm was made and burned at 1,050° C for 6 hours. The specimen was then characterized by measuring the dry shrinkage, shrinkage fuel, dry flexural strength, and thermal flexural strength.

Kaolin sample (Figure 1) were taken from Sarimanggu, Karangnunggal within coordinates of 7° 36' 45.7" S and 108° 7' 36.9" E. The sediment was found in a lens form. The material showed yellowish-white in color, and it was slightly oxidized as well as rather plastic. The source rock was supposed to be from tuff breccia alteration. Kaolin also came due to sedimentary occurrences.

**RESULTS AND DISCUSSION**

Based on petrographic analysis Karangnunggal kaolin shows flow structure and gas holes due to the differences in lava density and viscosity, and gas evaporation as well. Based on petrographic analysis, its composition comprises colloform halloysite (45 %), flake dickite (10 %), kaolinite 6 %, iron oxide 5 %, feldspar 3 %, and quartz 2 %. The thin section of such a material is shown in Figure 2.
Kaolin for ceramics should contain the alkali (K₂O and Na₂O). Such materials help in sintering process due to its smelted character is not too strong. Quartz may control and enhance mechanical strength of the ceramics while the iron oxide results in color change of the ceramics to creamy brown after burning process.

Based on SEM analysis (Figure 3), Karangnunggal kaolin was composed by kaolinite, illite and halloysite. Kaolinite minerals looked like fan sheets while halloysite was in fine grains, and illite was in a flake shape. Karangnunggal kaolin was formed from feldspatic due to hydrothermal alteration and is associated with tuff, which then formed kaolin minerals such as kaolinite and halloysite. The content of illite in kaolin was smaller than that of kaolinite and halloysite. If the illite was greater than that of kaolinite, it would affect the color of white ceramic body due to the iron content within illite.
XRD analysis showed (Figure 4) that Karangnunggal kaolin contained kaolinite, dickite, halloysite, cristobalite, illite, muscovite and hematite. After peak calculation Karangnunggal kaolin comprised of dominant cristobalite (45.0 %), halloysite (25.2 %), kaolinite (8.8 %), dickite, illite, and hematite with a small peak intensity (Table 1).

Referring to Table 1, halloysite and kaolinite were the dominant minerals within Karangnunggal kaolin. This clay mineral is similar to Cameroon kaolin (china clay) that can be used for manufacturing the body a white ceramic types for both hard and soft porcelain (Berry et al., 2006). Halloysite can reduce the combustion temperature in the sintering process of ceramic (Murray, 2007).

Chemical analysis showed that Karangnunggal kaolin comprised several oxides such as SiO\(_2\) = 65.78 %, Al\(_2\)O\(_3\) = 19.55 %, Fe\(_2\)O\(_3\) = 0.90 % (Table 2). The SiO\(_2\) and Al\(_2\)O\(_3\) belonged to the main compound in ceramic material. The compound of Fe\(_2\)O\(_3\) may reduce the ceramics brightness, so its content should be less than 1% (Celik, 2010).

**Figure 4. XRD diffractogram of Karangnunggal kaolin**

**Table 1. Quantitative mineral of Karangnunggal kaolin**

<table>
<thead>
<tr>
<th>No</th>
<th>Mineral</th>
<th>Formula</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cristobalite</td>
<td>(SiO(_2))</td>
<td>45.0</td>
</tr>
<tr>
<td>2</td>
<td>Halloysite</td>
<td>(Al(_2)Si(_2)O(_3))[OH] (_4)</td>
<td>25.2</td>
</tr>
<tr>
<td>3</td>
<td>Kaolinite</td>
<td>(Al(_2)Si(_2)O(_3))[OH] (_4)</td>
<td>8.8</td>
</tr>
<tr>
<td>4</td>
<td>Dickite</td>
<td>(Al(_2)Si(_2)O(_3))[OH] (_4)</td>
<td>6.9</td>
</tr>
<tr>
<td>5</td>
<td>Muscovite</td>
<td>(K(_2)Fe(_3)Si(_2)O(_8))(H(_2)O)</td>
<td>8.5</td>
</tr>
<tr>
<td>6</td>
<td>Illite</td>
<td>(K(_2)O)(Al(_2)O(_3))(Si(_2)O(_5))(OH)(_2)(H(_2)O)</td>
<td>4.8</td>
</tr>
<tr>
<td>7</td>
<td>Hematite</td>
<td>(Fe(_2)O(_3))</td>
<td>0.8</td>
</tr>
</tbody>
</table>

**Table 2. Result of chemical analysis for Karangnunggal kaolin**

<table>
<thead>
<tr>
<th>No</th>
<th>Oxides</th>
<th>Unit</th>
<th>% Weight</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SiO(_2)</td>
<td>%</td>
<td>65.78</td>
<td>Gravimetric</td>
</tr>
<tr>
<td>2</td>
<td>TiO(_2)</td>
<td>%</td>
<td>0.64</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>3</td>
<td>Al(_2)O(_3)</td>
<td>%</td>
<td>19.55</td>
<td>Titration</td>
</tr>
<tr>
<td>4</td>
<td>Fe(_2)O(_3)</td>
<td>%</td>
<td>0.90</td>
<td>Atomic Absorption Spectroscopy (AAS)</td>
</tr>
<tr>
<td>5</td>
<td>MnO</td>
<td>%</td>
<td>0.01</td>
<td>AAS</td>
</tr>
<tr>
<td>6</td>
<td>MgO</td>
<td>%</td>
<td>0.02</td>
<td>AAS</td>
</tr>
<tr>
<td>7</td>
<td>CaO</td>
<td>%</td>
<td>0.12</td>
<td>AAS</td>
</tr>
<tr>
<td>8</td>
<td>Na(_2)O</td>
<td>%</td>
<td>1.54</td>
<td>AAS</td>
</tr>
<tr>
<td>9</td>
<td>K(_2)O</td>
<td>%</td>
<td>0.60</td>
<td>AAS</td>
</tr>
<tr>
<td>10</td>
<td>P(_2)O(_5)</td>
<td>%</td>
<td>0.56</td>
<td>Spectrophotometry</td>
</tr>
<tr>
<td>11</td>
<td>H(_2)O(_2)</td>
<td>%</td>
<td>0.66</td>
<td>Gravimetric</td>
</tr>
<tr>
<td>12</td>
<td>H(_2)O(_3)</td>
<td>%</td>
<td>0.98</td>
<td>Gravimetric</td>
</tr>
<tr>
<td>13</td>
<td>SO(_2)</td>
<td>%</td>
<td>0.35</td>
<td>Gravimetric</td>
</tr>
<tr>
<td>14</td>
<td>(LOI)</td>
<td>%</td>
<td>8.29</td>
<td>Gravimetric</td>
</tr>
</tbody>
</table>
Compared to SiO₂ and Al₂O₃ compounds counted by Suhala and Arifin (1997) that was around 46.54 % and 39.50 %, it may be said that Karangnunggal kaolin was low level kaolin. However, the content of alkali (K₂O and Na₂O) at 2.14 % is almost the same as kaolin from Jebus West Bangka, at which such kaolin can be made for decorative ceramic using casting or slip casting system (Subari and Primasari, 2013). High content of SiO₂ and low content of Al₂O₃ affect to decreasing dry shrinkage and shrinkage of fuel when burned at temperature of 1,050° C (Hartono, 1993).

SiO₂ and Al₂O₃ oxides in ceramic materials serves as a framework/filler of ceramic body. The content of Fe₂O₃ and TiO₂ provides a certain color on the ceramic body. The oxides of alkali can serve to lower the melting temperature in the combustion process while loss of ignition (LOI) which consist of organic compounds and water, affect the nature of the plasticity of kaolin (Septawendar et al., 2007). Fe₂O₃ can provides the unwanted color, on white ceramic namely beige brown (Choudhary et al., 2012). However, Fe₂O₃, CaO, and MgO as impurities of Karangnunggal kaolin do not affect the color of white ceramic body after a burning process at high temperatures (above 1,050° C). The iron oxide (Fe₂O₃) will also affect degree of whiteness and serves as one of the parameters to determine the kaolin for ceramic raw materials. If the content is below 1.0 %, when the material is burned at high temperatures (above 900° C) will appear white. On the contrary; if the Fe₂O₃ content above 1.0 % it will yield cream color after burning process.

Yellowish brown color of impurities iron compound will reduce the whiteness, inhibit proliferation properties of optical fibers, lower the translucent nature of the product, and limit use in the industry. Luévanos et al. (2011) examined concentrations of iron contained in kaolin. The study discusses the reduction of iron content in kaolin influenced by oxalic acid concentration. Iron content in kaolin will decreases with the increase of oxalic acid concentration. Decreasing iron content up to 0.5 % will not affect the color of the white ceramic body (Lee et al., 2007). Based on whiteness analysis (Table 3) it is known that the quality of Karangnunggal kaolin has a degree of 48.05 %. This means that Karangnunggal kaolin has lower quality.

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>Whiteness (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Kaolin</td>
<td>48.05</td>
</tr>
<tr>
<td>2</td>
<td>Kaolin + 5 % Citric acid</td>
<td>51.48</td>
</tr>
</tbody>
</table>

After using a mixture solution of 5 % citric acid, kaolin whiteness turns into 51.48 % or increased to whiteness of 3.43 %. To improve kaolin whiteness can actually be conducted by magnetic ferro filter. The increase reaches above 50 % (Subari and Wahyudi, 2014). The 51.48 % of Karangnunggal kaolin whiteness is lower than that of whiteness from Bangka kaolin that retains 65%. Based on the results of the burning test fuel at 1.400° C shows that whiteness of 51.48 % within Karangnunggal kaolin did affect the color after it burned at high temperatures. When combustion temperature is lowered, the color after the burning process do not change in atmospheric conditions.

The water content of the Karangnunggal kaolin sample, analyzed by moisture content method, is 4.75 %. Such a figure is suitable for ceramic raw materials for either porcelain, solids pottery or non solid pottery (Nuntiya and Prasanphan, 2006). Meanwhile, results from grain size analysis show that the amount of >2 micron is 56.30 %. The results are quite good and can be used as raw materials in the manufacturing of glaze and ceramics body (Nugroho et al., 2000).

Kaolin grains size will affect the flexural strength of ceramic products; the larger the grain size of the material, the more reduced the bending strength (Johnson et al., 2012). Kaolin with grain size ≤ 2 μm is estimated to produce a dry flexural strength and flexural strength. Large grains size will affect the flexural strength of ceramic products, while the grain size result in smaller flexural strength of the ceramic body (Johnson et al., 2012). Kaolin with a grain size of <2 μm retaining quantity of 56.30 % are less plastic. As a result, both dry flexural strength and thermal flexural strength of the ceramic body will save fuel if incinerated at 1,200-
1,300°C. Yet the kaolin with similar size but its quantity is bigger than 80% normally retains plasticity and high dry strength characters. As a result, such a kaolin can be used for stoneware-ceramics type (Johnson et al., 2012). The fact that the large grain size fraction of <2 μm is less and the content of SiO₂ is high enough (65.78 %), means that Karangnunggal kaolin is less plastic. To increase the Karangnunggal kaolin plasticity, it can be added ball clay materials.

After burning at 1,400°C, the kaolin showed white in color and it is almost melt rather dense as well as non-porous. Referring to such characters Karangnunggal kaolin can be used as a raw material for manufacturing white ceramic products as porcelain body to stoneware. According to Johnson et al. (2012) kaolin with such properties can also be used for porous ceramic, but it needs to be mixed with sawdust material. After burning process 1,050°C, seven specimens of Karangnunggal kaolin (KK1 to KK7) showed dry shrinkage of 7.54 %, firing shrinkage of 2.48 %, dry flexural strength of 18.29 kg/cm², and thermal flexural strength in of 47.58 kg/cm² (Table 4).

The total amount of shrinkage factors, as a combination of dry shrinkage (7.54 %) and firing shrinkages (2.48 %), is 10.02 %. This result is smaller compared to the amount of dry and firing shrinkages of ball clay that is 10.50 % (Septawendar et al., 2007). The fact that the average value of dry shrinkage is 7.54 %, shows that this kaolin has plastic properties. Compared to kaolin studied by El Quahabi et al. (2014) that has less plastic characters, the plasticity of Karangnunggal kaolin is much better because the dry shrinkage of El Quahabi kaolin is around 2-6 %.

Referring to firing shrinkage value, Karangnunggal kaolin has firing shrinkage of 2.48 %. It is better than the kaolin studied by Baccour et al. (2009). Such kaolin is burned at temperature of 1,050°C producing firing shrinkage of 3.12 % (KK6). The differences in the amount of firing shrinkage is due to the different content of the alumina. Kaolin studied by Baccour et al. (2009) has 18.8% of alumina. It is lower than that of Karangnunggal kaolin with alumina content of 19.55 %.

The average value of dry flexural strength of Karangnunggal kaolin is low (18.29 kg/cm²), because the X-RD semi-quantitative data showed cristobalite content is bigger than that of clay minerals such as halloysite, kaolinite and dickite. Similar condition occurred to the average value of thermal flexural strength of 47.58 kg/cm². Such a strength (47.58 kg/cm²) is also low, because most kaolin when burned at temperatures 1,050°C is still in metakaolin form and mullite did not occur. Mullite can increase mechanical strength of the ceramic body, especially when it is in needle shape (Leonard and Kjell, 2004).

Karangnunggal kaolin including types of disordered kaolinite, will form mullite and can improve the mechanical strength after being burned at temperature above 1,200°C (Kamseu et al., 2007). After the burning process at a temperature above 1,100°C, kaolin will change to mullite and cristobalite (Septawendar et al., 2007). Its reaction can be seen in equation 1.

However, Georges-Ivo et al. (2008) stated that kaolin was already changed into mullite the burning kaolin at 1,050°C. Its reaction can be seen in equation 2.

\[
\text{[M}_{x}\text{O}_{y}\text{][aAl}_{2}\text{O}_{3}\text{bSiO}_{2}\text{]cH}_{2}\text{O} \rightarrow 3\text{Al}_{2}\text{O}_{3}2\text{SiO}_{2} + \text{SiO}_{2} + \text{M}_{x}\text{O}_{y}\text{[SiO}_{2}2\text{Al}_{2}\text{O}_{3}] \quad \text{.....................................(1)}
\]

\[
\text{Al}_{2}\text{Si}_{2}\text{O}_{5}(\text{OH})_{4} + \text{Al}_{2}\text{Si}_{2}\text{O}_{5}(\text{OH})_{4} + \text{KAl}_{2}(\text{AlSi}_{2})\text{O}_{10}(\text{OH})_{2} + \text{SiO}_{2} \rightarrow 5\text{SiO}_{2} + \text{K}_{2}\text{SiO}_{4} + \text{Al}_{2}\text{O}_{3}\text{SiO}_{2} \quad \text{.....................................(2)}
\]

\[
\text{mullite phase glass phase} \quad \text{M}_{x}\text{O}_{y} = \text{alkali which contained in clay}
\]

\[
\text{Al}_{2}\text{Si}_{2}\text{O}_{5}(\text{OH})_{4} + \text{Al}_{2}\text{Si}_{2}\text{O}_{5}(\text{OH})_{4} + \text{KAl}_{2}(\text{AlSi}_{2})\text{O}_{10}(\text{OH})_{2} + \text{SiO}_{2} \rightarrow 5\text{SiO}_{2} + \text{K}_{2}\text{SiO}_{4} + \text{Al}_{2}\text{O}_{3}\text{SiO}_{2} \quad \text{.....................................(2)}
\]

Kaolinite dickite illite quartz kaolinite mullite
Combustion of kaolin at high temperatures will produce different colors due to differences in Fe$_2$O$_3$ content. Kaolin contains 19-26 % Al$_2$O$_3$ and 1.5-3 % Fe$_2$O$_3$ and after being burned at high temperatures (>900° C) produces material with creamy yellowish or brownish in color (Subari and Wenias, 2007; Ramaswamy and Raghavan, 2011). Karangnunggal kaolin containing 19.55 % (Al$_2$O$_3$) and 0.90 % (Fe$_2$O$_3$), and burned at 1,050° C produced light beige kaolin due to its iron content is <1.5 %; (0.90 %).

### CONCLUSIONS AND SUGGESTION

Based on characterization of Karangnunggal kaolin, the material can be used for white ceramic products such as sanitary, ceramic tiles and insulation. Low composition of Fe$_3$O$_4$ in Karangnunggal kaolin (0.90 %) is an advantage as it can be used for white ceramic without affecting the brightness of the colors when it is burned at high temperatures (≥1,050° C). To increase ceramics strength, it is suggested to mix kaolin with mullite. Drilling exploration needs to be conducted in terms of assessing the potential kaolin deposit.

### ACKNOWLEDGMENTS

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### REFERENCES


THE USE OF 1-METHYL NAPHTHALENE AS COAL ASH REMOVAL SOLVENT

PENGGUNAAN 1-METIL NAFTALEN SEBAGAI LARUTAN PENGHILANGAN KADAR ABU DALAM BATUBARA

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ABSTRACT

Solvent extraction method is one of the methods to reduce ash content in coal to improve the energy efficiency and reduce negative environmental impacts. The use of 1-methyl naphthalene (1-MN) as a solvent in the weight ratio of coal to solvent of 1: 3, 1: 6 and 1: 9 using three coal samples obtained from a coal washing plant, namely ROM (run of mine), DC (dirty coal) and RC (reject coal) was performed. Results show that the ash content of the extracted coals no or significantly low amount (<0.3%) ash contents. The highest extraction yield was obtained at 15.38 % (daf) at DC coal sample and coal to solvent ratio of 1:9, while the lowest at 3.09 % (daf) at ROM coal sample and coal to solvent ratio of 1:3. In addition, the extraction process with a solution of 1-MN also able to reduce moisture content of the coals, as a result the calorific value of the coals were significantly increased.

Keywords: solvent, ash, extraction yield, moisture, calorific value

ABSTRAK

Metode ekstraksi pelarut merupakan salah satu metode untuk mengurangi kadar abu dalam batubara sehingga meningkatkan efisiensi energi dan mengurangi dampak negatif terhadap lingkungan. Penelitian penggunaan 1-metil naftalen (1-MN) sebagai pelarut dengan rasio antara batubara dan pelarut 1: 3, 1: 6 dan 1: 9 dengan menggunakan tiga buah contoh batubara yang diperoleh dari pabrik pencucian batubara, yaitu ROM (run of mine), DC (dirty coal) dan RC (reject coal) telah dilakukan. Hasil penelitian menunjukkan bahwa kadar abu batubara hasil ekstraksi tidak ada atau sangat rendah (<0,3%). Perolehan tertinggi sebesar 15,38% (daf) diperoleh pada contoh batubara DC dengan rasio antara batubara dan pelarut 1: 9, sedangkan perolehan terendah pada 3,09% (daf) untuk contoh batubara ROM dengan rasio batubara dan pelarut 1: 3. Selain itu, proses ekstraksi dengan larutan 1-MN juga mampu mengurangi kadar air dari batubara, sehingga nilai kalori batubara meningkat secara signifikan.

Kata kunci: pelarut, abu, perolehan, kadar air, nilai kalor

INTRODUCTION

The Indonesian Government has set an ambitious target to add approximately 35,000MW installed power generation within a period of 5 years (2014-2019). With a projected economic growth of 6-7 percent a year, additional electricity capacity in this country needs at least 7,000 MW per year. Approximately about 25,000 MW of the project will use coal as fuel. This project has been confirmed in the document of the National Medium Term Development Plan (Anonymous, 2014).

Coal was selected as a source of electricity due to the price of coal is cheaper than diesel. However, there are some consequences of the use of coal, specifically the environmental problem of pollution and emissions. The main problem associated with the environment in the coal is ashes. Coal
ash is the waste that is left after coal is burned in coal-fired power plants. It includes fly ash, bottom ash, boiler slag, flue gas desulfurization residue and other solid fine particles which possess major environmental problems. Depending on where the coal was mined, coal ash typically contains heavy metals including arsenic, lead, mercury, cadmium, chromium and selenium, as well as aluminum, antimony, barium, beryllium, boron, chlorine, cobalt, manganese, molybdenum, nickel, thallium, vanadium, and zinc. Arsenic is one of the most common, and most dangerous (Pandey et al., 2011). Most of Indonesia’s coal resources, the ash content is low (generally < 10%). However, in some areas the ash content in coal is relatively high so it needs to be washed. In addition, during the process of mining, a portion of the roof and floor material may be taken along with the coal seam in order to create adequate working height for the equipment and miners. The position of the coal at the roof or bottom layer usually has high ash content due to contamination of overburden (Ghasemi et al., 2014).

It is also necessary to remove the ash from coal to be combusted directly in the new generation integrated gas combined cycle (IGCC) gas turbines to overcome issues like erosion and corrosion of turbine blade and fouling due to coal ash deposition. Thus, it is advantageous to upgrade coals in terms of ash and moisture contents. A new cost-effective and efficient process is therefore essential to remove the ash and upgrade the low-rank lignite and sub-bituminous coals. One such technology could be the production of ash-free coal (AFC). It could be a preferred feed for some applications, such as direct combustion in the gas turbines (Okuyama, et al., 2004). Utilization of AFC directly in a gas turbine as fuel can generate a power system of higher thermal efficiency without damaging the turbine blades (Wijaya and Zhang, 2011).

From those point of views, the ash content in coal should be minimized. The reduction/removal of ash content has been implemented in coal washers in Indonesia as pre-combustion clean coal technology. The choice of process depends on factors such as the type of coal being treated, the market requirement and the economics. The washed coal is expected to have a low ash content. If the raw coal has high ash content, thereof the yield is low. In the coal washing plant, approximately 30% of which is reject coal, because of the very high ash content. Consequently, the reject coal would be excessive. The disposal of this huge quantity of rejects in an environment friendly manner poses a real problem.

The reject coal that has high contain of ash, could be further processed through ash removal using solvent. There are two main types of chemical treatment of coals to produce clean coal. The first one, aiming to produce the upgraded coal using strong acids or alkalis to dissolve all the minerals leaving the organic coal matrix under hydrothermal conditions is termed as ultra clean coal (UCC). The second process uses organic solvents to dissolve organic matter and precipitating back the ash free coal known as hyper-coal (Okuyama, et al, 2004) is termed here as ash free coal (AFC). However, the coal from the UCC process may contain around 0.5% ash and cannot be directly fired in the gas turbines. Another possible concern could be associated with the corrosiveness and biodegradability of strong acids and alkali reagents used and consequently disposal of the waste solution.

This research was aimed to get the processing condition of ash removal using coals from a coal washing plant in East Kalimantan. According to the previous research (Umar, et al, 2015), to remove the ash content in coal through organic solvent extraction, among the organic solvents of metoxy etoxy acetic acid (MEAA), 1-methyl naphthalene (1-MN) and 1-methyl 2-pyrolidinon (MP) that have been tested, 1-MN is the best solvent that produces coal with the lowest ash content.

1-MN is a naphthalene-related compound that is also called alpha methyl-naphthalene. It is a clear liquid with the formula of $C_{11}H_{10}$ (Hardacre et al, 2010). A naphthalene molecule can be viewed as the fusion of a pair of benzene rings (Figure 1). It is classified as a benzenoid polycyclic aromatic hydrocarbon (PAH) with a density of 1g/cm$^3$, molar mass of 142.2 g/mol, cetane number of zero, and was previously used as the lower reference for cetane number. As derivate of naphtelene, 1-MN provides an excellent solubilizing medium for poorly soluble aromatic compounds. In many cases it is more efficient than other high-boiling solvents, such as dichlorobenzene,
benzonitrile, nitrobenzene and durene. As a non-polar, 1-MN can solve the polar such ash mineral matter in coal.

Solvent extraction of coal using 1-MN can produce AFC that has significantly much lower ash content than that of the raw coal (Lee, 2012). However, there are some limitations of AFC preparation process, such as low product yield and use of residual coal discharged.

From the foregoing discussion, it is found that most of the works on thermal extraction of coal to produce AFC, have been performed using bituminous and sub-bituminous coals from the Australian, Indonesian, South African and American origins (Rahman, et al., 2013, Shui et al, 2013). However, in spite of abundant availability of reject coal from a washing plant, there was no study available in literature for preparation of AFC using industrial solvents, such as heavy aromatic hydrocarbons and hydro treated heavy aromatic hydrocarbons. Therefore, the reject coal also be used as coal itself. Therefore, one of the objectives of this study is to investigate the effect of 1-MN in various concentration through coal to solvent ratio on the extraction yield of extracted coals.

**METHODOLOGY**

The raw coal samples were obtained from mining and coal washing plant (CWP) in East Kalimantan. There were run of mine (ROM), dirty coal (DC) and reject coal (RC). To support this research, analysis of inherent moisture, ash, volatile matter, fixed carbon, and calorific value were conducted to the both of coal samples. The result of analyses is given in Table 1.

As explained above, during the process of mining, a portion of the roof and floor material may be taken along with the coal seam, the ROM coal that comes directly from a mine has relatively high ash content of 27.07% (Table 1). The buyer, on the other hand, may demand certain specifications depending on the intended use of the coal. DC is coal taken from CWP shortly before washing (feed of CWP). This coal has lower ash content compared to the ROM i.e. 25.47%. The lower ash content might be caused by the pre-separation of impurities before going into a washing machine. The RC is the waste from CWP, including substances such as coal fines, soil, sand, and rock. So that the coal has a very high ash content of 54.66%. This coal is usually discarded and disposed.

Their moisture content is as low as 4.42, 4.89 and 3.05% respectively of ROM, DC and RC. Despite of low inherent moisture content, the calorific value of the coals are relatively low due to the high of ash content. The calorific value of the RC only 2.843 cal/g.

The coal samples was ground into fine particles of less than 75µm in diameter before being served to the solvent treatment through these steps:
- Coal was dried at 40°C in an oven;
- Dried coal crushed using hammer mill to be 2.3 mm in diameter size.
- Crushed coal ground using rock lab and sieved using 200 mesh sieving to get coal with diameter size of 75µm.
Table 1. Analysis result of raw coal samples in air dried basis (adb)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Samples mark</th>
<th>Unit</th>
<th>Standard Methods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROM</td>
<td>DC</td>
<td>RC</td>
</tr>
<tr>
<td>Inherent moisture</td>
<td>4.42</td>
<td>4.89</td>
<td>3.05</td>
</tr>
<tr>
<td>Ash</td>
<td>27.07</td>
<td>25.47</td>
<td>54.66</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>31.61</td>
<td>32.06</td>
<td>22.43</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>36.9</td>
<td>37.58</td>
<td>19.86</td>
</tr>
<tr>
<td>Calorific value</td>
<td>5.185</td>
<td>5.271</td>
<td>2.843</td>
</tr>
</tbody>
</table>

A stainless steel vibrating autoclave with a capacity of 500 mL was used for this experiment (Figure 2). Coal was charged into the autoclave together with 1-MN solvent. The ratios between coal and solvent were 1:3; 1:6 and 1:9 wt. %. After sufficiently purging the autoclave with nitrogen, the coal in the autoclave was heated up to 300°C at which it was kept for 1 hour under sufficient agitation (Umar, et al., 2014). Then the coal was separated into residue, filtrate and gaseous product consisting of CO₂, H₂O and a negligible amount of hydrocarbon gases (Fujitsuka, et al., 2013) at the treatment temperature by opening the valve connecting the autoclave and the reservoir by filtration at room temperature (Figure 3). The filtrate was further heated in a vacuum oven to separate extracted coal and solvent fraction. The solvent can be used for the next process. Residues and extracted coals then were dried, weighed and analysed to proximate and calorific value analysis.

Figure 2. Stainless steel vibrating autoclave

Figure 3. Separation apparatus
The extraction yield was calculated based on dry ash-free basis (daf) from the weight of dry extracted coal produced using the following Equation (Rahman, et al., 2013).

\[
\text{Extraction yield (wt%, daf)} = \frac{\text{Weight of dry extracted coal}}{\text{Weight of feed coal (daf)}} \times 100\%
\]

RESULTS AND DISCUSSION

The extracted coals and residues were characterized to understand the thermo-chemical changes occurring before and after the solvent extraction using 1-MN. The results of proximate analysis and calorific value of both can be seen in Table 2 and 3 respectively.

The extracted coals show no or significantly low amount (< 0.3%) ash contents (Table 2). This is possibly due to the ability of polar components present in the coal being dissolved in non-polar solvent of 1-MN. Okuyama, et al., 2004 reported that 1-MN is an effective recoverable solvent for coal extraction under mild conditions at 202 °C and atmospheric pressure. The more the addition of 1-MN is not correlated with the decreasing of coal content (Figure 4).

Figure 4 shows that coal to solvent ratio of DC and RC coal samples is not significantly affected on ash content. Nonetheless of ROM. The more the amount of solvent the less the ash content. The DC coal sample with the ratio of coal to solvent of 1:6 has the highest ash content of 0.2, while the lowest ash content reached by DC and RC coal samples with the ratio of coal of 1:3 and 1:9 respectively. In fact, the ratio of coal to solvent is not affected the ash content of the coal samples, where the ash content for all of the coal samples are very low. So that the difference can be ignored. According to Siefert and Litster, 2013, the ash content of < 0.3% can be directly fired in the gas turbines of the IGCC.

The use of 1-MN also decreased the inherent moisture content in the extracted coals. As a result the calorific value also increased significantly. The decreasing of inherent moisture is parallel with the coal to solvent ration. The more the 1-MN, the high the moisture content (Figure 5). This occurrence could be caused by more and more the water (as a part of the 1-MN) is remained in the extracted coal.

### Table 2. Proximate analysis and calorific value of extracted coal (adb)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample mark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROM</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
</tr>
<tr>
<td>Inherent moisture, %</td>
<td>0.30</td>
</tr>
<tr>
<td>Ash, %</td>
<td>0.18</td>
</tr>
<tr>
<td>Volatile matter, %</td>
<td>62.78</td>
</tr>
<tr>
<td>Fixed carbon, %</td>
<td>36.74</td>
</tr>
<tr>
<td>Calorific value, cal/g</td>
<td>8,767</td>
</tr>
</tbody>
</table>

### Table 3. Proximate analysis and calorific value of residue (adb)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample mark</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ROM</td>
</tr>
<tr>
<td></td>
<td>1:3</td>
</tr>
<tr>
<td>Inherent moisture, %</td>
<td>6.46</td>
</tr>
<tr>
<td>Ash, %</td>
<td>28.04</td>
</tr>
<tr>
<td>Volatile matter, %</td>
<td>37.32</td>
</tr>
<tr>
<td>Fixed carbon, %</td>
<td>28.18</td>
</tr>
<tr>
<td>Calorific value, cal/g</td>
<td>5,613</td>
</tr>
</tbody>
</table>
Different with moisture content, the calorific value of the extracted coal are not directly correlated in line with the coal to solvent ratio (Figure 6). The calorific value of the ROM and DC extracted coals decreased due to the increasing of coal to solvent ratio, in line with the increasing of inherent moisture. While the RC extracted coal, the calorific value of the extracted coal in the ratio of 1:6 is the lowest parallel with the highest ash content of the coal.

In the residue fraction, the ash content of ROM and RC increased while the ash content of DC decreased (Table 3). The increasing of the ash content indicating the possible enrichment of heavy aromatic hydrocarbon components in those residue coals. The increasing of moisture content indicating the enrichment of the hydrogen in the hydrocarbon components. Consequently the calorific value of the residues are higher compared with the corresponding raw coals.
Similar observations were also reported by Takanohashi et al. 2008.

As can be seen in Table 4 above, the extraction yield relatively low between 3.09 and 15.38 % daf. However, the rate of the extraction yield increases rapidly with the increase of coal to solvent ratio (Figure 7). This is possibly due to the enhanced coal and solvent interaction and consequently, higher solvent induced thermal relaxation of coal molecules is occurring and releasing mainly small molecules and free radicals from the cross-linking coal structure to the solvent (Sonmez and Giray, 2011).

![Figure 6. The effect of coal to solvent ratio on calorific value of extracted coal](image)

Table 4. Extraction yield of 1-MN treatment

<table>
<thead>
<tr>
<th>Coal sample/coal to solvent ratio</th>
<th>Coal initial weight g, dry ash free</th>
<th>Extracted coal g, dry</th>
<th>Extraction yield %, dry ash free</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>17.13</td>
<td>0.53</td>
<td>3.09</td>
</tr>
<tr>
<td>1:6</td>
<td></td>
<td>1.21</td>
<td>7.09</td>
</tr>
<tr>
<td>1:9</td>
<td></td>
<td>1.57</td>
<td>9.17</td>
</tr>
<tr>
<td>DC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>10.57</td>
<td>0.43</td>
<td>4.06</td>
</tr>
<tr>
<td>1:6</td>
<td></td>
<td>1.36</td>
<td>12.82</td>
</tr>
<tr>
<td>1:9</td>
<td></td>
<td>1.63</td>
<td>15.38</td>
</tr>
<tr>
<td>RC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:3</td>
<td>17.41</td>
<td>0.56</td>
<td>3.20</td>
</tr>
<tr>
<td>1:6</td>
<td></td>
<td>0.72</td>
<td>4.11</td>
</tr>
<tr>
<td>1:9</td>
<td></td>
<td>1.05</td>
<td>6.04</td>
</tr>
</tbody>
</table>
The highest extraction yield was obtained at 15.38 % (daf) at DC coal sample and coal to solvent ratio of 1:9. Rahman, et al., 2011, reported the extraction yield by using Canadian coal and 1-MN as solvent was 2.6% at temperature of 200°C (473 K) and 31.3 % at temperature of 300°C (673 K). Okuyama et al., 2004 investigated 20 different coals of Chinese origin mainly bituminous and extracted with 1-MN. The extraction yields were within the range 30–70% at 633 K and these yields were largely dependent on the coal characteristics. They found that the extraction yield of brown coals is less than 30% (daf) and Algerian sub-bituminous coal was maximum 47% at 300°C. The low extraction yield, one possible reason could be the loss of significant amount of gaseous products from high oxygen containing reactive coals during high temperature soaking period in the reactor. Besides, the extracted coal liquid may have some soluble components that may dissolve in solvent and does not tend to precipitate upon dilution. It is also possible that low molecular weight volatile components present in the extracted coal liquid may be lost due to natural evaporation. Consequently, it produces less extracted coal yields. The new study of Okuyama, et al., 2014, heating rate affected on the coal extraction yield and the property of the extraction products. The rapid heating, higher than 1000°C/min of heating rate, improved coal extraction yield compare to the conventional heating, lower than 100°C/min. This effect appeared with the coal which had lower extraction yield by the conventional heating.

The extraction yields of RC extracted coal are the lowest compare with that of the extracted coals of ROM and DC at a same treatment condition (Figure 8), except for the RC at the ratio of coal to solvent 1:3, the extraction yield of the RC is slightly higher than that of the ROM coal. It could be understood, because the RC raw coal has a very high ash content, and mostly inherent impurities that consisting of organic constituents that previously formed part of the tissues of the plants from which the coal was derived. Most impurities is chemically or colloidal combined with coal substance (Li et al., 2014).
Low extraction yield, remained high residues. Rom and DC residues which have ash content of about 28 wt% and 21 wt % respectively (Table 3). But, since the residual coal with high ash content contains low moisture (less than 10%) and it has high calorific value of more than 5,600 cal/g, the residues can be utilized effectively for power generation or steam generation using fluidized bed combustors. The residue coals also have high reactivity and can be used as reducing agent in the synthetic rutile production from ilmenite resources (Komatsu, et al., 2009). Beside that, the residues could be returned to the coal mining in a lower price and/or recycled again to the coal washing plant. There is a lot of example that coal washed residue is sold about half of the price (Okuyama, et al, 2004).

CONCLUSIONS

Solvent extraction of three coal samples obtained from a coal washing plant, namely ROM (run of mine), DC (dirty coal) and RC (reject coal) was performed using 1-Methyl Naphtalene (1-MN). The effect of coal to solvent ratio on preparing extracted coals was examined. The following conclusions were obtained:
- The ash content of the extracted coals shows no or significantly low amount (<0.3%) ash contents. This is possibly due to the ability of polar components present in the coal being dissolved in non-polar solvent of 1-MN.
- The highest extraction yield was obtained at 15.38 % (daf) at DC coal sample and coal to solvent ratio of 1:9, while the lowest at 3.09 % (daf) at ROM coal sample and coal to solvent ratio of 1:3
- The low extraction yield, one possible reason could be the loss of significant amount of gaseous products from high oxygen containing reactive coals during high temperature soaking period in the reactor. While the extraction yield increases with increasing coal to solvent ratio.
- The extraction process by using 1-MN also able to reduce moisture content and the calorific value of the coals were significantly increased.
- The residue will be returned to the coal mining and/or recycled again to the coal washing plant. The calorific value of more than 5,600 cal/g is acceptable to be utilized as the fuel for power plant

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The authors gratefully acknowledge the head of R&D Center for Mineral and Coal Technology (tekMIRA) for making this research possible. We are also expressing our deep gratitude to PT Kaltim Prima Coal (PT KPC) for their full support during coal sampling. Thanks also go to the staffs of coal laboratory of tekMIRA for their full assistance during laboratory works.
REFERENCES


ANALYZING CHEMICAL KINETICS OF COAL GASIFICATION IN MINI GASIFIER REACTOR

ANALISIS KINETIKA REAKSI GASIFIKASI BATUBARA PADA REAKTOR GASIFIKASI MINI

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ABSTRACT
Coal gasification is a chemical reaction that has a purpose to change the original solid coal into gaseous compounds. Converting the coal into gaseous compounds will make the combustion process easier and results in increasing combustion efficiency. The sulfur and nitrogen are also easier to be separated in order to obtain cleaner flue gas. This paper presents kinetic analysis of coal gasification reactions in mini gasifier (or known as GasMin in Bahasa) reactor. The results show that the increase of the air-coal ratio (ACR) affected the maximum temperature of the reactor, which means that an increase of the intake air flow rate will increase the amount of oxygen for combustion reaction. Meanwhile, the increase of the team coal ratio (SCR) will increase flow rate of the mixture of air-steam feed. As a result, the ability of coal gasification has also increased. This will increase gasification efficiency around 3-5% which then will also increase the gas yield. The maximum value of SCR was 0.06, further than that of the yield gas and the q-value will slightly decrease. The simulation result showed that the producer gas was dominated by CO with 26.72% mole fraction; H2 with 14.06% mole fraction, and N2 with 47.88% mole fraction. Meanwhile CO2, CH4 and O2 mole fraction were 5%, 0.24%, and 1.20% respectively.

Keywords: coal, gasification, mini gasifier, kinetic reactions.
et al., 2013) and is ready to be used in terms of the availability and technology. However, environmental impact becomes important issues that hinder the success of coal as an alternative energy. Therefore, utilization technology should be developed to produce clean and efficient energy, both as a direct or indirect burning.

Coal gasification is a process to utilize coal energy without the conventional combustion. The coal is gasified and its gas product is used as a feedstock for numerous end-use products. Potential end-uses include power generation, liquid fuels and chemical feedstock (Skodras et al., 2015). The kinetic rates and extents of the gasification process vary and typically serve as functions of temperature, pressure, reactor and configuration, gas composition, and the nature – chemical composition and properties – of the coal being gasified (Muller et al., 2003; Slavinskaya et al., 2009; Speight, 2013a; Speight, 2013b). Generally, the reaction rate (i.e., the rate of coal conversion) is higher at higher temperatures, whereas reaction equilibrium may be favored at either higher or lower temperatures, depending on the specific type of gasification reaction (Speight, 2015).

Numerous studies have dealt with the kinetic model of coal gasification. He et al. (2013) has developed a steady state kinetic model for an industrial-scale pressurized Lurgi gasifier using the simulator Aspen Plus. The thermodynamic efficiencies of the gasifier and the entire gasification system have been investigated in considerable detail via simulation studies. The simulation results show that the oxygen/coal ratio exerts a strong impact on the exergetic efficiency profile of the combustion zone within the Lurgi gasifier. Gomez and Mahipney (2015) conduct study that demonstrates a consistent method to perform gasification in the chemically controlled temperature range between 750°C and 900°C. In addition, the apparent activation energy was estimated independent of the kinetic model. The effect of coal bed thickness was studied and compared between steam and CO2 gasification. Zoulalian et al. (2015) proposed model that presents a simple method to handle the evolution of the total surface area and of the reactive surface area. The model was applied to coal and wood char for O2, CO2 and H2O gasification experiments (taken from the literature). The experiments were conducted in a thermo balance and an analytical differential fixed bed under gasification conditions with negligible diffusional resistances.

Since 2010, Research and Development Center for Mineral and Coal Technology (Puslitbang tekMIRA) has conducted a research regarding a design for mini gasifier (GasMin). The development of GasMin had been successfully accomplished through changing the reactor diameter and height; it was increase the efficiency to 50% (Sofaeti, 2013). GasMin is appropriate to be used for substituting oil or LPG in small-scale industries. The investment of GasMin is reasonable and the energy need for small-scale industries is satisfied. In addition, GasMin is categorized as a clean coal technology as it produces low NOx, SOx and particulates (Sofaeti and Daulay, 2014). This paper presents kinetic analysis of coal gasification process in mini gasifier (GasMin) reactor.

METHODOLOGY

Research of GasMin was conducted at Coal Technology Center, Palimanan – Cirebon, West Java and the simulation of kinetic analysis accomplished at the Laboratory of Research Center for Engineering Science, Gadjah Mada University using the simulation COMSOL. Characteristics of coal used for research were shown in Table 1. Prior to the kinetic study, reactor condition of the GasMin fixed bed was summarized in Table 2 and schematic diagram of the GasMin coal gasification was shown in Figure 1.

Table 1. Characteristics of coal

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Proximate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Moisture content</td>
<td>%, adb</td>
<td>16.52</td>
</tr>
<tr>
<td></td>
<td>Ash content</td>
<td>%, adb</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>Volatile matter</td>
<td>%, adb</td>
<td>42.22</td>
</tr>
<tr>
<td></td>
<td>Fixed carbon</td>
<td>%, adb</td>
<td>40.43</td>
</tr>
<tr>
<td>2</td>
<td>Ultimate</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>%, adb</td>
<td>67.93</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>%, adb</td>
<td>6.45</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>%, adb</td>
<td>0.71</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>%, adb</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>O</td>
<td>%, adb</td>
<td>23.99</td>
</tr>
<tr>
<td>3</td>
<td>HHV</td>
<td>Kkal/kg, adb</td>
<td>5.852</td>
</tr>
</tbody>
</table>
Coal gasification involves thermal decomposition of coal, reaction of coal carbon and other pyrolysis products with oxygen, water, and fuel gases such as methane (Table 3). In fact, coal gasification is often considered to involving two distinct chemical stages, namely (1) de-volatilization of the coal to produced volatile matter and char followed by (2) char gasification that is complex and specific to the conditions of the reaction. Both processes contribute to the complex kinetics of the gasification process.

The rate of a gasification reaction mainly depends on the reactivity of the fuel and the reaction potential of the gasifying medium. Process temperature and pressure also affect the reaction rates. The combustion reactions are faster than gasification and occur first rapidly to consume the oxygen. Basu (2010) claims that the water-gas reaction is the fastest char reactions while Blasi (2009) states that in gasification, water-gas reaction occurs two to five times faster than the boudouard reaction. An interesting estimation is presented about the relative reaction rates of these three reactions compared to combustion reaction at 800°C and 10 kPa overpressure. These rates are presented in Table 4.
Table 2. Chemical reactions in the coal gasification process

<table>
<thead>
<tr>
<th>Type</th>
<th>Reaction</th>
<th>Enthalpy (298.15 K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis</td>
<td>Coal → C + volatile</td>
<td>+131.3 kJ/(gmol C)</td>
</tr>
<tr>
<td>Gasification</td>
<td>C + H₂O(g) → CO(g) + H₂(g)</td>
<td>-393.5 kJ/(gmol C)</td>
</tr>
<tr>
<td>Combustion</td>
<td>C + O₂(g) → CO₂(g)</td>
<td>-75 kJ/(gmol C)</td>
</tr>
<tr>
<td>Hydrogasification</td>
<td>C + 2 H₂(g) → CH₄(g)</td>
<td>+131.3 kJ/(gmol C)</td>
</tr>
<tr>
<td>Dissociation</td>
<td>C + CO₂(g) → 2 CO(g)</td>
<td>+172.5 kJ/(gmol C)</td>
</tr>
<tr>
<td>Shift reaction</td>
<td>CO(g) + H₂O(g) → CO₂(g) + H₂ (g)</td>
<td>-41.2 kJ/(gmol CO)</td>
</tr>
<tr>
<td>Hydrocracking</td>
<td>volatile + H₂(g) → CH₄(g)</td>
<td>-75 kJ/(gmol C)</td>
</tr>
<tr>
<td>Volatile gasification</td>
<td>volatile + H₂O(g) → CO(g) + 2 H₂ (g)</td>
<td>+ 206 kJ/(gmol H₂O)</td>
</tr>
</tbody>
</table>

Table 3. Relative reaction rates of four char reactions (Basu, 2010)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Relative reaction rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + 1/2 O₂ → CO</td>
<td>105</td>
</tr>
<tr>
<td>Water-gas</td>
<td>103</td>
</tr>
<tr>
<td>Boudouard</td>
<td>102</td>
</tr>
<tr>
<td>Methanation</td>
<td>3 x 10⁻³</td>
</tr>
</tbody>
</table>

The combustion reactions are more than a million times faster than that of other carbon reactions but methanation reaction is quite slow in atmospheric pressure compared to the other reactions, and it is often ignored (Lu and Wang, 2011). The equations for simulation of reaction kinetics of coal gasification were as follows (COMSOL, 2012):

\[ R_B^* = k_B e C_0 C_B \left\{ \frac{P \chi_3}{RT_R} \left( \frac{P}{RT_R} \right)^2 \frac{\chi_2 \chi_3}{K_B C_1} \left( 1 + \frac{P}{RT_R} (\gamma_1 C \chi_1 + \gamma_2 C \chi_2 + \gamma_3 C \chi_3) \right) \right\} \]

Gasification

\[ R_C^* = \frac{k_C e C_0}{RT_R} \left( \frac{P}{RT_R} \right) \left( \frac{\chi_4}{K_C C_1} \right) \left( 1 + \frac{P}{RT_R} (\gamma_4 C \chi_4 + \gamma_5 C \chi_5) \right) \]

Combustion

\[ R_D^* = k_D e C_0 C_D \left\{ \left( \frac{P}{RT_R} \right)^2 \frac{\chi_3}{K_D C_1} \left( 1 + \frac{P}{RT_R} (\gamma_3 C \chi_3 + \gamma_6 C \chi_6) \right) \right\} \]

Hydrogasification

\[ R_E^* = k_E e C_0 C_E \left\{ \frac{P \chi_5}{RT_R} \left( \frac{P}{RT_R} \right)^2 \frac{\chi_2 \chi_5}{K_E C_1} \left( 1 + \frac{P}{RT_R} (\gamma_5 C \chi_5 + \gamma_2 C \chi_2) \right) \right\} \]

Dissociation

\[ R_F^* = k_F e \left( \frac{P}{RT_R} \right)^2 \left( \frac{\chi_1 \chi_2}{K_F C_1} \right) \]

Shift Reaction

\[ R_F^* = k_F e \left( \frac{P}{RT_R} \right)^2 \left( \frac{\chi_1 \chi_2}{K_F C_1} \right) \]
\[
R_G^* = k_G \epsilon C_0 C_G \left( \frac{P}{RT_R} \right)^2 \left( \frac{P}{RT_R} \frac{Z_6}{K_{G}\epsilon C_1} \right) \left( 1 + \frac{P}{RT_R} \left( \gamma_{3v} \chi_3 + \gamma_{6v} \chi_6 \right) \right)
\]

Hydrocracking

\[
R_H^* = k_H \epsilon C_0 C_H \left( \frac{P\chi_1}{RT_R} \right)^3 \left( \frac{P}{RT_R} \frac{Z_2 \chi_5^2}{K_{H}\epsilon C_1} \right) \left( 1 + \frac{P}{RT_R} \left( \gamma_{1v} \chi_1 + \gamma_{2v} \chi_2 + \gamma_{3v} \chi_3 \right) \right)
\]

Volatile gasification

\[P = \text{gas pressure}\]
\[R = \text{universal gas constant},\]
\[T_R = \text{reactor temperature}\]
\[k_B = \text{reaction rate coefficient H}_2\text{O with coal}\]
\[k_H = \text{the reaction rate coefficient H}_2\text{O with volatile matters},\]
\[k_C = \text{the reaction rate coefficients O}_2 \text{ with coal},\]
\[k_D = \text{hydrogen reaction rate coefficients with coal}\]
\[k_G = \text{hydrogen reaction rate coefficients with volatile matters},\]
\[k_E = \text{CO}_2 \text{ reaction rate coefficients with coal,}\]
\[k_F = \text{reaction rate coefficients shift.}\]
\[Y_{1C} = \text{absorption coefficient of H}_2\text{O on the surface of coal}\]
\[Y_{2C} = \text{mass transfer coefficient equilibrium CO on the surface of coal}\]
\[Y_{3C} = \text{equilibrium mass transfer coefficient on the surface of coal}\]
\[Y_{4C} = \text{equilibrium coefficient of mass transfer of O}_2 \text{ on the surface of coal.}\]
\[Y_{5C} = \text{equilibrium coefficient of mass transfer of CO}_2 \text{ on the surface of coal.}\]
\[Y_{6C} = \text{coefficient of CO}_2 \text{ adsorption on the surface of coal}\]
\[Y_{1V} = \text{absorption coefficient of H}_2\text{O on the surface of volatile matters.}\]
\[Y_{2V} = \text{mass transfer coefficient equilibrium CO on the surface of volatile matters}\]
\[Y_{3V} = \text{equilibrium mass transfer coefficient on the surface volatile matters.}\]
\[Y_{4V} = \text{each is equilibrium mass transfer coefficient H}_2 \text{ at the surface of the volatile matters.}\]
\[Y_{5V} = \text{each is the mass transfer coefficient equilibrium CO and CO}_2 \text{ on the surface of coal.}\]
\[Y_{6V} = \text{each is equilibrium mass transfer coefficient H}_2 \text{ and CO}_2 \text{ at the surface of the volatile matters.}\]

The values of these parameters depend on the reactor temperature and the coal surface reactivity against H\textsubscript{2}O, CO, H\textsubscript{2}, O\textsubscript{2} and CO\textsubscript{2} as well. The relations between reaction rate coefficient (k) and equilibrium coefficient (K) with the temperature is stated according to the Arrhenius equation.

**RESULTS AND DISCUSSION**

**Reaction Kinetics of the GasMin**

Figure 2 shows that the molar flow rate of oxygen decreased rapidly at approximately 0.2 meters from the input of the reactor, instead of CO\textsubscript{2} that increased rapidly in the same range. It shows that the approximately 0.2 meters from the reactor input stands for the combustion zone. In this zone, the oxygen reacts with coal to produce CO\textsubscript{2} gas. Meanwhile, the 0.0-0.2 m serves as the ash chamber zone. No reaction occurs in this zone. Coal combustion is an exothermic reaction result in increasing the reactor temperature. The rate of gasification reaction increases along with the increase of reactor temperature. Gasification reaction rate has a maximum value at the end of the combustion zone when the temperature of the gas inside the reactor reaches the maximum value.
Figure 2 also shows the increase in the molar flow rate of hydrogen ($H_2$) and carbon monoxide ($CO$). Meanwhile, the molar flow rate of $CO_2$ and $H_2O$ has decreased as a result of the gasification reaction. The total amount of gas molar flow rate increases due to the formation of compounds of gas because of coal gasification reaction. This initial calculation made with assumption the reactor was adiabatic. In other words, the wall of reactor was considered perfectly insulated so there was no heat flow through. Thus, the gasification reaction stopped when the reaction equilibrium was achieved. At equilibrium, the reactor temperature and gas composition values were constant against the axial position of the input reactor. The results show that the gas output of reactor was dominated by $CO$ with 26.72% mole fraction; $H_2$ with 14.06% mole fraction, and $N_2$ with 47.88% mole fraction. Meanwhile $CO_2$ mole fraction was 5%, $CH_4$ mole fraction was 0.24% and $O_2$ mole fraction was 1.20%.

**Effect of Inlet Air Position on Distribution of Axial Temperature in the Reactor**

Figure 3 shows that the maximum temperature of the reactor was not affected by the inlet air temperature. Changing the temperature of the inlet air ($T_{ia}$) has a consequence in shifting combustion zone. This also affects the condition of producer gas. Increasing the $T_{ia}$ will shift the combustion zone more upward of the reactor as shown in Figure 1 because the pressure and the volume of the input air also increase. As a result, gasification reaction becomes imperfect if the reactor is not long enough. Thus if the ACR is 2.4 and $T_{ia}$ is 100°C, the combustion zone must be at least 0.25 m from the bottom of the reactor.

Figure 4 shows effect of inlet air temperature on some important components producer gas (CO, $H_2$, $CH_4$ and $CO_2$), the gas mass flow rate, calorific value gas, and producer gas energy. The heating value was calculated based on producer gas components that can be burned. Thus, the calorific value (q-value; in units of $kJ / gmol$) can be calculated by equation (8).

$$q-value = X_1LHV_1 + X_2LHV_2 + X_3LHV_3........(8)$$

$LHV_1$, $LHV_2$, and $LHV_3$ each is a lower calorific value of combustion of $CO$, $H_2$, and $CH_4$. Energy on producer gas ($Q$, in units kW) can be calculated with mass flow of producer gas ($M_G$) and calorific value (equation 9).

$$Q = M_G \times (q-value)..............................(9)$$
Mole fractions increases with the increase of air temperature entering reactor. Meanwhile the mole fraction of CO\textsubscript{2} decreases. An increase in the mole fraction of CO and CH\textsubscript{4} indicates that the gasification reaction increases dominantly. The high mole fraction of CO\textsubscript{2} indicates that the combustion reaction remains high. Gasification reaction shown by high temperature of the entering reactor air is also indicated from the higher gas molar flow rate.

**Effect of Variation the Air-Coal Ratio**

Flow rate of the coal mass is expected to remain at 50 kg / hour. Thus, if the ACR is 3, the air mass flow rate should be 150 kg / hour. Figure 5 shows the correlations between the axial temperature distribution without value adjustments and the ACR at a constant inlet air temperature in the reactor. In this case, the value of inlet air temperature reactor (T\textsubscript{ia}) is assumed to be fixed at 100 °C.
The increase of the ACR affects the maximum temperature of the reactor as the increase in the intake air flow rate will also increase the amount of oxygen for establishing combustion reaction. Thereby, the amount of coal combustion reaction increases resulted in increasing the maximum reactor temperature. Figure 5 also shows the increase of ACR effect on the increase of air inlet position and combustion zone shift. Due to the addition of air flow rate, while the volume that passes through the fixed inlet results in the pressure of the air flow rate increases and the position of the air inlet shifts to the right side. It should be considered when designing the reactor to have enough space for reactions of the oxidation and reduction.

Figure 6 shows the correlation among mole fraction some important components of gasification (CO, H₂, CH₄ and CO₂), flow rate of producer gas, calorific value of producer gas and energy of producer gas as well as the flowing ACR.
The mole fraction of CO reduced when ACR increased. This means that the increase of ACR value in line with combustion on the gasification. Another symptom of decline rate gasification process is the mole fraction of $\text{H}_2$ and $\text{CH}_4$ is slightly reduced by the increase of the ACR value. The gasification decreases causes calorific value (q-value) of producer gas as well as the energy of producer gas were reduced. According to equations 1 and 2, all oxygen reacts with carbon results in unnecessary addition of the ACR value increased combustion reaction rather than gasification.

**Effect of Variation the Steam-Coal Ratio**

Inlet air flow rate was assumed to be fixed at 120 kg/h and the coal mass flow rate was 50 kg/h. It meant that Steam-Coal Ratio (SCR) = 2.4. The flow rate of water vapors varied from 0 up to 8 kg/hour meaning that SCR values varied from 0 to 0.16. Figure 7 shows the correlation axial temperature distribution of the ACR. The value of inlet air temperature reactor ($T_{ia}$) was assumed to be fixed at 100°C.

Increasing the SCR value would lessen the maximum reactor temperature due to the increase value in SCR that resulted in the increase of steam amount that occurred within the air inlet. As a result, the steam increase would improve the reaction of gasification.

Figure 8 showed the relation among mole fraction of some important gasification components ($\text{CO}$, $\text{H}_2$, $\text{CH}_4$ and $\text{CO}_2$), flow rate of producer gas, calorific value of producer gas, and energy of producer gas to the SCR. It showed that the increase of SCR value slightly increased the CO mole fraction of producer gas. It occurred because the increase of the SCR would—increase the amount of steam and enhanced the gasification. When the value of SCR increased, the increase in the mole fraction of CO led to an increase in calorific value (q-value) and energy of producer gas.
At fixed air flow rate, increasing the SCR would increase the total flow rate of the air-steam mixture in reactant, therefore the ability to gasify coal also increased. This led to increase the gasification efficiency, about 3-5%. As a result, the gas yield increased. The maximum value of SCR was 0.06, bigger than that such a figure, the yield gas and energy of producer gas will decrease. This occurred because the energy from the combustion decreased and would decrease the fulfillment of energy needs for gasification.

CONCLUSIONS

Simulation of chemical reaction shows that the reactor gas output dominated by CO (26.72% mole fraction), H₂ (14.06% mole fraction), and N₂ (47.88% mole fraction). Meanwhile CO₂ mole fraction is 5%, CH₄ mole fraction is 0.24% and O₂ mole fraction is 1.20%. These results are similar with the field experiment of GasMin. The result also shows that the inlet air temperature did not affect the maximum temperature of reaction. The increase of the ACR enlarged the maximum reactor temperature as the increase of the incoming air flow rate was used for establishing combustion reaction. The SCR increased the total flow rate of the air-steam mixture feed; therefore the ability to gasification of coal had also improved. This led to the increase of gasification efficiency, about 3-5%. This in turn would increase the yield gas. The maximum value of SCR was 0.06. If bigger than that such a figure, the yield gas and energy of producer gas would decrease.

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