The effect of demineralization towards gasification performance of low-rank coal

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Abstract. Gasification process is an alternative way to utilize low-rank coal. However, gas production is not very high due to the high content of volatile matters and high mineral content. One interesting way to increase gas production is by reducing the mineral content in the coal by acid leaching process. In the present study, acid leaching is occupied to pre-treat the coal by using HF solution so that the mineral content in the coal can be leached out. The results show that acid leaching process successfully decreased the ash content in the coal. However, in terms of gas production, it appears that acid leaching slightly decreases the total gas production. It could happen since acid processing of coal might increase its crystallinity and thus it becomes more difficult to be gasified.

1. Introduction
The increase in the world’s population becomes a great factor in the rise of energy demand [1]. The world’s energy consumption was at 13,105 million tons in 2015 and reached 13,276.3 million tons in 2016, while Indonesia’s energy consumption increases at 164.8 million tons and 175 million tons respectively [2]. One alternative in generating energy to meet the energy demand is through oxidation of hydrogen gas. Currently, 98% of hydrogen is produced from coal and 50% of it comes from the natural gas reforming process [3]. Coal places second after crude oil as an energy source until 2016 [2]. Hydrogen gas from coal can be utilized to generate a turbine to produce energy [4] and potentially used as fuel cell feedstock that is environmentally friendly in the future [5].

Since 2016, the use of coal as a fuel to generate energy has been declining to comply with the regulation to reduce CO2 emission in order to suppress environmental damage [6]. Indonesia Government in the United Nations Framework Convention on Climate Change (UNFCC). In Indonesia National Energy General Plan (RUEN), coal is viewed as a primary energy source that is capable of supplying energy for more than 30% of total energy in 2025. Based on its coal rank, lignite and sub-bituminous coal dominate in Indonesia at 24,641 million tons with bituminous and anthracite as minorities at 3,814 million tons [7]. Thermal decomposition of lignite and sub-bituminous coal discharges coal ash that contains high silica and sulfur content. Both components give off inhibition effect toward the coal utilization process.
Gasification is a conversion method of low ranked coal that allows maximum energy to be extracted with a minimum amount of residue and high carbon conversion [8-9]. Gasification emits less CO$_2$ compared to other coal utilization methods [10]. Gasification has high efficiency and flexibility in producing gas to generate electricity and synthesize liquid fuel [11-12]. Steam as gasification agent to gasification process intensifies hydrogen gas production. Potassium carbonate gives a favorable effect toward gasification process with steam as the gasification agent [13]. The increase of reaction rate results in raise of gas yield. However, SiO$_2$ content in coal ash is not preferable in gasification process as it inhibits gasification process.

Coal ash removal can be accomplished by using acid, base, alcohol, or combination of acid, base, and alcohol [14-18]. Literature concludes that acid solution gives the most effective result in coal mineral removal contained in coal ash. The coal ash removal process is called demineralization. Demineralization process improves the gasification process in 2 methods, silica removal, and pore formation to increase surface area. Several factors need to be considered in the demineralization process, they are type of acid solution, concentration, temperature, demineralization time, and coal particle size. The effect of factors mentioned previously can be seen in the reduction of coal ash produced after demineralization. Furthermore, the silica content in demineralized coal will diminish compared to the one in raw coal. This paper covers the effect of coal demineralization using HF solution toward coal gasification in removing silica and sulfur content.

2. Methodology
The experiment methodology includes material preparation, coal demineralization, coal gasification, and analysis and data interpretation.

2.1. Material preparation
Coal is crushed into sizes less than 232 μm (> 48 mesh) and then dried in an oven at 110°C for 14 hours. The determination of ash content in coal is achieved through combustion in a furnace at 750°C or 2 hours. Element content in ash is analyzed using EDS, while the composition of coal is determined through proximate and ultimate analysis. The two analyses of raw lignite (RL) and demineralized lignite (DL) are shown in Table 1.

| Parameter   | RC (%-weight) dry basis | DC (%-weight) dry basis |
|-------------|-------------------------|------------------------|
| Proximate   |                         |                        |
| Ash         | 9.54                    | 1.63                   |
| Volatile matter | 47.38                | 51.53                  |
| Fixed carbon | 43.08                   | 46.84                  |
| Ultimate    |                         |                        |
| Sulfur      | 1.07                    | 1.07                   |
| Carbon      | 64.38                   | 64.38                  |
| Hydrogen    | 3.74                    | 3.74                   |
| Nitrogen    | 1.14                    | 1.14                   |
| Oxygen      | 19.71                   | 19.71                  |

2.2. Coal demineralization
10g of dried coal is dissolved in a 250 mL HF solution in a Teflon glass. The solution low-rank for 4 hours at 70°C. Then, the solution is neutralized using aqua DM before being filtered. The solid residue from the filtration is later dried in an oven for 14 hours at 110°C before being stored in a desiccator.
2.3. Coal gasification

The gasification process is carried out with a fixed bed downdraft reactor for 80 minutes using steam as a gasification agent with steam production temperature at 90-92˚C. 3g of each raw lignite and demineralized lignite is used for the gasification process. Nitrogen, as gas carrier, is flown with a rate of 85 cm³/minute. The furnace used is heated beforehand with a heating rate of 6˚C/minute until the operating temperature in the reactor reaches 700˚C. The outlet gas is later condensed with cooling water at 14-16˚C. Condensed gas becomes tar while incondensable gas is stored in a gas bag every 10 minutes. The amount of incondensable gas produced is compared with the amount of fixed carbon in the feed sample per gram.

2.4. Analysis and data interpretation

Data obtained in material preparation and coal demineralization are processed, analyzed, and presented in graphs. Raw lignite and demineralized lignite contents are determined in proximate and ultimate analysis, while ash content determination from feed is done through ASTM D.3174. Synthesis gas compositions are analyzed using gas chromatography (GC) with thermal conductivity detector (TCD) that is connected with 2 types of columns, namely Porapak Q and Molesieve 5A. The GC result is further analyzed for graph fabrication. Surface area and char sizes obtained from gasification process are analyzed through nitrogen isothermal adsorption method.

3. Results and Discussion

3.1. Ash element content of Raw Lignite (RL) and Demineralized Lignite (DL)

Coal demineralization process is a pre-treatment one to reduce coal ash elements which are silica and alumina. Ash mineral content distribution in LC and DL is determined through EDS mapping analysis shown in Table 2.

| Element       | Compositions (%-weight) dry basis |
|---------------|----------------------------------|
|               | RL  | DL  |
| Carbon (C)    | 3.13| 0.66|
| Oxygen (O)    | 4.34| 0.67|
| Sodium (Na)   | 0.26| 0.04|
| Magnesium (Mg)| 0.20| 0.04|
| Aluminum (Al) | 0.41| 0.05|
| Silica (Si)   | 0.37| 0.03|
| Sulfur (S)    | 0.07| 0.02|
| Potassium (K) | 0.02| 0.002|
| Calcium (Ca)  | 0.02| 0.004|
| Phosphor (P)  | 0.05| 0.01|
| Iron (Fe)     | 0.67| 0.11|
| Total         | 9.54%|1.63%|

Coal that has been demineralized with HF has lower ash content compared to the raw lignite. HF not only dissolves silica but also almost all minerals in raw lignite. The result shows 91.7% silica content reduction, 90.3% aluminum content reduction, and also 88.9% potassium content. According to Steel et al. (2001) [19], HF solution is very reactive in dissolving all mineral components in coal but pyrite. At 3 M, HF is able to make aluminosilicate to be soluble in water.
3.2. Single fuel gasification: Raw Lignite (RL) and Demineralized Lignite (DL)

Feed characteristics determine the distribution of a carbon fuel gasification product [20]. Lignite coal contains complex organic compounds, namely vitrinite and liptinite, oxidized organic compounds, and water [21].

3.2.1. Gasification of RL and DL product conversion. The main products of coal gasification process generally composed of synthesis gas (H₂, CO, CO₂, and CH₄), liquid product (volatile matter and condensable gas, and char [21].

![Figure 1. Gas, liquid, and solid products of gasification process of RL and DL](image)

Figure 1 shows the distribution of RL and DL gasification products. The main components of liquid product include large aromatic compound (mixture of oxygenation, phenolic esters, phenolic alkyls, heterocyclic ethers, polyaromatic hydrocarbons, etc.) and alkali metal compounds [21]. As both components are soluble in HF solution, DL has lower liquid product conversion compared to RL. As for the gas product, DL synthesis gas conversion is less than the RL one, which means that demineralization treatment does not enhance synthesis gas conversion of RL gasification. Synthesis gas conversion depends on several factors, one of them is the char structure [22].

Carbon conversion of the DL gasification is higher than the RL one due to the demineralization process that improves lignite carbon conversion to char compared to RL. In gasification with H₂O medium, lignite ash with high silica content helps molecular breakdown of large hydrocarbons to smaller compounds such as methane and ethane [21]. Demineralization using HF and HCl upgrades the crystallinity of the char structure; therefore it is hard to break compared to coal without any pre-treatments [23]. This results in aromatic polycyclic hydrocarbons to have high densities to form bonds that are very strong and resistant to heat, making it difficult to decompose into liquid and gas products.

3.2.2. Gasification of RL and DL synthesis gas profile and trend. Based on Basu [22], solid-gas reactions that are likely to happen in char gasification process include Boudouard, methanation, and primary water-gas. After the synthesis gas is formed, a gas-gas reaction takes place, which forms a new gas compound. Common reactions include steam reforming and water gas shift. In determining the tendency of the gasification reaction, gas compositions of every 10 minutes are analyzed using Shimadzu Gas Chromatograph 2014 that has been calibrated with industrial standard synthesis gas. This experiment covers gasification process at low temperature and is kept constant at 700 ± 40°C. Figure 2 shows synthesis gas profile and H₂/CO ratio of RL gasification for 80 minutes.
Figure 2. (a) Synthesis gas profile and (b) H$_2$/CO ratio every 10 minutes of RL gasification

Generally, H$_2$ and CO$_2$ contents increase while CO gas yield decreases. This causes H$_2$/CO ratio to relatively rise until the 80$^{th}$ minute. At the 10$^{th}$ minute, H$_2$ gas yield is at its lowest while CO$_2$ and CO gas yield are quite high. This means that in the beginning, Boudouard reaction and water gas reaction dominate. The high CO$_2$ content is derived from residual pyrolysis result when a new gasification agent, steam, is released in the 0$^{th}$ minute. There is an increase in methane yield from the 0$^{th}$ minute to the 30$^{th}$ minute. This shows that a methanation reaction takes place from RL carbon and H$_2$. From the 0$^{th}$ minute to the 20$^{th}$ minute, a decrease in CO gas identifies Boudouard reaction rate drops and reaction sifts toward the primary water gas reaction, which is indicated by a rapid rise in H$_2$ concentration. Char conversion reaction is dominated by the primary water gas reaction marked by the increase in H$_2$ concentration, a drop in CO concentration, and constant CO$_2$ content.
Figure 3. (a) Synthesis gas profile and (b) H\textsubscript{2}/CO ratio every 10 minutes of DL gasification.

Figure 3 shows the synthesis gas profile and H\textsubscript{2}/CO ratio from gasification of DL. The results of synthesis gas profile from gasification of RL and DL have a similar pattern. Both results show a constant H\textsubscript{2} concentration until the 80\textsuperscript{th} minute. The synthesis gas profile of DL gasification fluctuates more compared to the RL one due to higher alkali and alkaline earth metal content in RL that gives a more stable gasification rate [24]. Methane gas that appears at the beginning of DL gasification is a residual gas produced from lignite pyrolysis, such as RL gasification [25-26]. However, DL gasification produces more methane than RL as methane cracking process in DL gasification is lower than the one in RL gasification [27]. According to Sun et al. (2007) [28] and Wei et al. (2011) [29], coal demineralization lessens catalytic effect toward the methane cracking process by Fe and Mg in coal ash. At the 40\textsuperscript{th} minute of DL gasification and the 60\textsuperscript{th} minute of RL gasification, a drip of steam condensate occurs that makes the primary water gas reaction producing more H\textsubscript{2} and CO\textsubscript{2}.

3.2.3. Gasification of RL and DL synthesis gas yield. Synthesis gas compositions depend on characteristics of carbon, type of gasification medium, and operating condition [20]. Figure 4 presents the yield of each component in synthesis gas from gasification of RL and DL.
RL gives better H₂, CO, CO₂, and CH₄ yield compared to DL. This shows that coal demineralization by HF leaching method slightly lessens the synthesis gas yield. The result is supported by research done by Murata et al. (1996) [30] that states HF leaching degrades conversion rate of char in coal gasification. It is possible that when the coal is pre-treated by a strong acid, the coal tends to be more crystalline; as such, it becomes more difficult to be gasified. Even though more pores are formed, the crystallinity of the carbon makes it harder to be gasified compared with the raw coal.

4. Conclusions
Acid leaching pre-treatment have been done for low rank coal by using HF solution. It appears to be the good method to demineralize coal. However, pre-treating the coal reduces gasification performance in terms of a decrease in synthesis gas and H₂ yield. An increase in char yield is caused by a drop in coal reactivity significantly that affects the catalytic effect on the overall gasification process. It is possible that pre-treatment using acid increases coal crystallinity as such it becomes more difficult to be gasified.

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