Pretreatment of Coal by Acid Leaching As Feedstock Preparation For Co-Gasification With Biomass

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Abstract. Co-gasification process of coal and biomass is believed to be one of the promising way to produce hydrogen. The mixing of coal and biomass can solve the problems that usually happened during gasification of pure coal or pure biomass. Furthermore, the presence of synergistic effect between coal and biomass may increase the hydrogen production due to Alkali and Alkaline Earth Metal (AAEM) content in the biomass. However, the synergistic effect may be hindered by the presence of silica in the coal. The present study focuses on the reduction of silica content of coal by acid leaching. Based on the result, it is found that the use of hydrofluoric acid may significantly reduce the silica content shown by the reduction of ash content in the coal. Furthermore, acid leaching process also causes the increase of surface area of the coal which may increase the possibility of AAEM attachment to the surface and thus the gas production may increase as well.

1. Introduction
Provide an adequate background, context of the problems based on the literature review. State Gasification is thermal conversion of carbonaceous materials into synthesis gas in limited oxygen condition with gasifying agent [1]. It can be used to utilized coal cleanly as Indonesia has abundant reserve of coal. However, 92% of Indonesia coal is in low-rank state, such as subbituminous and lignite [2]. Gasification of low-rank coal results in low gas yield as it contains higher amount of volatile matter [3]. To increase gas yield, catalyst can be added to the sample to increase its reactivity. It is known that alkaline and alkaline earth metal (AAEM) can be used as the gasification catalyst as it can increase the carbon reactivity toward gasification reaction, especially in producing hydrogen [4]. AAEM can be found naturally in biomass. Co-gasification of coal and biomass could increase carbon conversion and gas yield as well, especially hydrogen [5]. Thus, not only decreasing the non-neutral CO2 emission, co-gasification process may also increase the overall gasification efficiency [6]. Catalytic effect in co-gasification process occurs due to the existence of AAEM in biomass [7] and they are volatilized during gasification and may attach to the coal surface so that the reactivity of the coal may increase as well. This synergistic effect makes co-gasification attractive to be applied. However, silica content in coal may hinder the synergistic effects. Silica deactivates AAEM by converting them to form metal silicate which has no catalytic effect [8]. Therefore, silica content in coal must be reduced before it is used as the gasification feedstock.

Mineral content, including silica, in coal can be removed by demineralization process, such as acid leaching method [9-13]. When coal is rinsed with strong acid solution, some of the mineral (including silica) is expected to be leached out so that the mineral content in coal reduced to some extent. It is expected that by reducing the silica content, the gas production from co-gasification process of coal and biomass increase since the catalytic activity of AAEM will not be hindered. Furthermore,
Giudicianni et al. (2014) stated that demineralization of the feedstock may promote the char porosity [14]. The present study is done to determine the effect of acid solution concentration, temperature, reaction time, and particle size during acid leaching process of coal. Two main parameters are examined; mineral content and surface area of the leached coal. Low mineral content in coal makes it more reactive towards catalytic gasification and higher surface area means more volatilized AAEM attached to the coal surface and it may increase the coal reactivity as well.

2. Methods

2.1 Raw Material Preparation

Two types of low-rank coal are used in this experiment. The proximate and ultimate analysis of the coal samples were done at TEKMIRA, Bandung, and the results are shown in Table 1. The coal has particle size of 14-48 mesh and -48 mesh. Coal is dried at 105-110°C overnight.

| Table 1. Proximate and ultimate analysis of sub-bituminous and lignite coal. |
| Parameter         | Sub-bituminous | Lignite | Unit | Basis* |
|-------------------|----------------|---------|------|--------|
| Proximate         |                |         |      |        |
| Moisture          | 13.54          | 13.81   | %    | adb    |
| Ash               | 5.86           | 8.58    | %    | adb    |
| Volatile matter   | 42.62          | 41.14   | %    | adb    |
| Fixed carbon      | 37.98          | 36.47   | %    | adb    |
| Ultimate          |                |         |      |        |
| Total sulfur      | 0.99           | 0.86    | %    | adb    |
| Carbon            | 54.41          | 51.57   | %    | adb    |
| Hydrogen          | 5.19           | 4.92    | %    | adb    |
| Nitrogen          | 1.15           | 0.97    | %    | adb    |
| Oxygen            | 32.40          | 33.10   | %    | adb    |

*adb = air dried basis

2.2 Demineralization of Coal

Demineralization process was done by washing coal with acid solution. 250 ml of hydrofluoric acid (HF) with concentration of 1 M, 2 M, and 3 M were used to leach 10 gram of coal samples. Coal was dispersed in HF solution in a teflon beaker and stirred by a magnetic stirrer for 2, 3, or 4 hours. Liquid was then separated by using a filter funnel, while the solid (coal) is then washed with aquadest until the pH of water is neutral. Demineralized coal was dried in the oven at temperature of 105-110°C before further analysis.

2.3 ORF Primary Frames

Demineralized coal was analyzed to measure its ash content, mineral composition, and surface area. Ash content were determined by gravimetry method. Certain amount of coal sample was weighted and then calcined at 700°C for 2 hours to remove all the burnable matter. The remain unburned component was weighted and it is determined as the ash content. Surface area of demineralized coal was analyzed by Surface Area Analyzer (QUANTACHROME NOVA e-4200) performed at Laboratorium Instrumen Analisis Labtek X ITB. Since the ash sample was limited mineral composition of coal ash was analyzed by Scanning Electron Microscopy with Energy Dispersive X-Ray (SEM-EDX, HITACHI SU3500) done at Pusat Penelitian Nanosains dan Nanoteknologi (PPNN) ITB.

3. Results and Discussion
3.1 Decreasing of Ash Content
For the demineralization process, the effect of acid solution concentration, temperature, and reaction time towards decreasing of ash content is determined. Figure 1 and figure 2 show ash content of demineralized coal which indicated by yellow colour as the highest ash content (10%) and dark blue as the lowest ash content (1%) for both types of coal. In subbituminous coal, the decreasing of ash content is 2.79–4.89%. The similar results obtained by Bolat et. al. (1998) and Steel (2001) for ash content of coal demineralized by HF which achieved the degree of demineralization up to 79%.

The present experiment utilized full factorial design (FFD) with center point which is repeated three times. For demineralization of subbituminous coal, analysis of variance (ANOVA) for factorial design is shown in Table 2. It can be seen that the main factor (i.e. concentration, temperature, and time) and interaction factor are considered significant as indicated by P-value which is smaller than α which is set to 5%. Furthermore, the R² value is 99.68%, indicating that the deviation of equation model is close enough with the experimental data. Thus, the model used in this case is quite accurate. Regression result of all parameters and experiment data for demineralization of subbituminous coal solution is shown in equation 1. This equation is using coded units with 1 as higher value, -1 as lower value and 0 as middle value.

\[ \text{Content}_{\text{ash}} = 0.037033 - 0.002311 C - 0.001127 T + 0.000868 R + 0.003807 C T + 0.002311 C R - 0.006149 C T R + 0.003898 C T P_t \]  \tag{1} 

| Source                  | DF | Adj SS   | Adj MS  | F-Value | P-Value |
|-------------------------|----|----------|---------|---------|---------|
| Model                   | 7  | 5.5E-04  | 7.9E-05 | 135.03  | 0.001   |
| Linear                  | 3  | 5.9E-05  | 2.0E-05 | 33.54   | 0.008   |
| Concentration (C)       | 1  | 4.3E-05  | 4.3E-05 | 72.99   | 0.003   |
| Temperature (T)         | 1  | 1.0E-05  | 1.0E-05 | 17.35   | 0.025   |
| Time (R)                | 1  | 6.0E-06  | 6.0E-06 | 10.29   | 0.049   |
| 2-Way Interactions      | 2  | 1.6E-04  | 7.9E-05 | 135.55  | 0.001   |
| C*T                    | 1  | 1.2E-04  | 1.2E-04 | 198.06  | 0.001   |

### Table 2a. ANOVA of demineralization of subbituminous coal with HF solution.

| Source                  | DF | Adj SS   | Adj MS  | F-Value | P-Value |
|-------------------------|----|----------|---------|---------|---------|
| Model                   | 7  | 5.5E-04  | 7.9E-05 | 135.03  | 0.001   |
| Linear                  | 3  | 5.9E-05  | 2.0E-05 | 33.54   | 0.008   |
| Concentration (C)       | 1  | 4.3E-05  | 4.3E-05 | 72.99   | 0.003   |
| Temperature (T)         | 1  | 1.0E-05  | 1.0E-05 | 17.35   | 0.025   |
| Time (R)                | 1  | 6.0E-06  | 6.0E-06 | 10.29   | 0.049   |
| 2-Way Interactions      | 2  | 1.6E-04  | 7.9E-05 | 135.55  | 0.001   |
| C*T                    | 1  | 1.2E-04  | 1.2E-04 | 198.06  | 0.001   |

### Table 2b. ANOVA of demineralization of subbituminous coal with HF solution.
### 3.2 Molecular Dynamics Results

Demineralization process using acid solution is expected to decrease the silica content in coal ashes. The relative decrease of silica content is shown in Table 3. In demineralization of coal with HF solution, the relative decrease of silica content in subbituminous and lignite coal are 75.24% and 92.57%. This result is corresponding to some literatures state that mixing coal with HF solution could decreases the silica content of coal ash [9, 15, 16]. Previous researchers have proven that demineralization can decrease the silica content in coal ash [9, 17, 16]. The decreasing of silica content can improve the co-gasification of coal and biomass. Rizkiana et al. (2014a) stated that silica content can deactivate catalyst in co-gasification process [4]. Using demineralization process, the catalytic activity during co-gasification process is expected to work more intensive.

| Source          | DF | Adj SS   | Adj MS   | F-Value | P-Value |
|-----------------|----|----------|----------|---------|---------|
| C*R             | 1  | 4.3E-05  | 4.3E-05  | 73.03   | 0.003   |
| 3-Way Interactions | 1  | 3.0E-04  | 3.0E-04  | 516.86  | 0.000   |
| C*T*R           | 1  | 3.0E-04  | 3.0E-04  | 516.86  | 0.000   |
| Curvature       | 1  | 3.3E-05  | 3.3E-05  | 56.64   | 0.005   |
| Error           | 3  | 2.0E-06  | 1.0E-06  |         |         |
| Total           | 10 | 5.6E-04  |          |         |         |

Table 3. Decreasing of silica content in coal ash after demineralization process.

| Coal type | Acid solution | Differential relative |
|-----------|---------------|-----------------------|
| Subbituminous | HF           | 75.24%                |
| Lignite   | HF           | 92.57%                |

\[
\text{SiO}_2 + 4 \text{HF} \rightarrow \text{SiF}_4 + 2 \text{H}_2\text{O} \quad \Delta G = -3.2 \text{ kJ/mol} \quad (2)
\]

\[
\text{C} + 4 \text{HF} \rightarrow \text{CF}_4 + \text{H}_2 \quad (3)
\]

Hypothetic reactions of HF with carbon (C) are also analyzed as written in equation 3. The reaction of acid solution with carbon could affect the demineralization process because mineral matters are dispersed in carbon matrix of coal. The main composition of coal is carbon, thus reaction between acid solution and carbon played a significant role in decreasing of mineral content. The reaction is analyzed by using Gibbs free energy as well and it is found that calculated \( \Delta G \) is also negative indicating that the reaction between HF and C are also likely to happen during demineralization process.

Furthermore, the effect of coal particle size in demineralization process is also examined in this experiment. The ash contents of demineralized coal with particle size variation is shown in Figure 3 for subbituminous coal, and Figure 4 for lignite coal. The effect of particle size in demineralization process using HF is not significant. Based on the Gibbs free energy calculation, HF could react spontaneously with carbon. Therefore, the mineral contents in coal matrix can to react with HF regardless the mineral are exposed to the surface of coal or not. HF coal can penetrate to the inner core of coal since it can react with the carbon matrix. Hence, in this case, the particle size does not affect demineralization process.
3.3 Surface area
In demineralization process, some reactions occur between mineral content in coal ash and acid solution as written in equation 2 and 3. Mineral content of coal is present in the coal matrix. The reaction between the mineral content and the acid solution causes the coal matrix to open to form pores in the coal. It causes the surface area of coal to increase. Data of surface area of raw subbituminous and lignite coal were 0.803 m²/g and 8.552 m²/g respectively. Both in subbituminous and lignite coals, the demineralization process using acid solution could increase the surface area of coal. Coal surface area data before and after demineralization process is shown in Table 4.

![Figure 3. Effect of particle size towards the ash content of demineralized subbituminous coal.](image)

![Figure 4. Effect of particle size towards the ash content of demineralized lignite coal.](image)

Table 4. Coal surface area before and after demineralization process.

| Sample no | Coal type   | Acid solution | Surface area (m²/g) |
|-----------|-------------|---------------|---------------------|
| 1         | Subbituminous | -             | 0.803*              |
| 2         | Subbituminous | HF            | 131.046             |
| 3         | Lignite      | -             | 8.552*              |
| 4         | Lignite      | HF            | 80.516              |

*raw coal

The increase of coal surface area may increase gas production in co-gasification process of coal and biomass [4]. The catalysis process occurring in co-gasification begins with the release of alkali and alkaline earth metal (AAEM) contents of the biomass. Then, the AAEM content is attached to the coal surface so as to increase the conversion in the co-gasification process [4]. Increasing the surface area of coal may increase the amount of AAEM that can attach to the coal surface. Therefore, an increase in the area of the coal surface can improve the reactivity of coal during the co-gasification process.

4. Conclusion
Demineralization of coal has been performed by using hydrofluoric acid. By measuring the mineral content of the treated coal, it can be concluded that the use of acid leaching successfully decreases the mineral content of the coal to some extent. The most decreasing mineral contents occurred for Si component as it can be removed up to 92% from its original content. Furthermore, acid leaching can also increase the coal surface area quite significantly. The total surface area increases from 0.8 to 131 m²/g for subbituminous coal sample. It indicates that coal pretreatment by acid leaching can increase the coal properties so that it is more reactive when it is used as the feedstock for gasification process.
5. References

[1] Basu P 2010 *Biomass Gasification and Pyrolysis Practical Design and Theory* (Cambridge: Academic Press)

[2] Badan Pengkajian dan Penerapan Teknologi (BPPT) 2016 *Outlook Energi Indonesia 2016* (Jakarta: Perpustakaan Nasional RI)

[3] Duan W, Yu Q, Liu J, Wu T, Yang F and Qin Q 2016 *J. Exp. And Kinetic Study Of Steam Gasification Of Low-Rank Coal In Molten Blast Furnace Slag Energy* 111 859-868.

[4] Rizkiana J, Guan G, Widayatno W B, Hao X, Huang W, Tsutsumi A and Abudula A 2014 *Effect Of Biomass Type On The Performance Of Co-Gasification Of Low Rank Coal With Biomass At Relatively Low Temperatures* 134 414–419.

[5] Rizkiana J, Guan G, Widayatno WB, Hao X, Li X, Huang W, and Abudula A 2014 *Promoting Effect Of Various Biomass Ashes On The Steam Gasification Of Low-Rank Coal* 133 282–288.

[6] Ali D A, Gadalla M A, Abdelaziz O Y and Ashour F H 2016 *Modelling of Coal-Biomass Blends Gasification and Power Plant Revamp Alternatives in Egypt’s Natural Gas Sector* 52 49-54.

[7] Iwaki H, Ye S, Katagiri S and Kitagawa K 2004 *Wastepaper gasification with CO₂ or steam using catalysts of molten carbonates* 270 237-243.

[8] Risnes H, Fjellerup J, Henriksen U, Moilanan A, Norby P and Papadakis K 2003 *Calcium Addition In Straw Gasification* 82 641-651.

[9] Steel K M, Besida J, O’Donnel T A and Wood D G 2001 *Production Of Ultra Clean Coal Part I—Dissolution Behaviour Of Mineral Matter In Black Coal Toward Hydrochloric And Hydrofluoric Acids* 70 171-192.

[10] Mukherjee S, Borthakur P C 2001 *Chemical Demineralization/Desulphurization Of High Sulphur Coal Using Sodium Hydroxide And Acid Solutions* 80 2037-2040.

[11] Behera S K, Chakrabory S and Meikap B C 2017 *Chemical Demineralization Of High Ash Indian Coal By Using Alkali And Acid Solutions* 196 102-109.

[12] Ratanakandilok S, Ngamprasertsith S and Prasassarakich P 2001 *Coal Desulfrization With Methanol/Water And Methanol/KOH* 80 1937-1942.

[13] Wu Z and Steel K M 2007 *Demineralization Of A UK Bituminous Coal Using HF And Ferric Ions*, 86 2194-2200.

[14] Giudicianni P, Cardone G, Cavaliere A and Ragucci R. 2014 *Effect of Feedstock Demineralization on Physico-Chemical Characteristics of Arundo Donax Derived Biochar* 37 85-90.

[15] Meshram P, Purohit B K, Sinha M K, Sahu S.K and Pandey B D 2015 *Demineralization Of Low Grade Coal* 41 745-761.

[16] Wijaya N and Zhang L 2011 *A Critical Review Of Coal Demineralization And Its Implication On Understanding The Speciation Of Organically Bound Metals And Submicrometer Mineral Grains In Coal* 25 1-16.

[17] Bolat E, Saglam S and Piskin S 1998 *Chemical Demineralization Of A Turkish High Ash Bituminous Coal* 57 93-99.