

Dewatering and upgrading of Loy Yang lignite using hydrothermal treatment coupled with mechanical expression

劉, 祥春

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氏 名 : 劉 祥春

論 文 名 : Dewatering and upgrading of Loy Yang lignite using hydrothermal treatment coupled with mechanical expression (水熱処理と機械圧搾を用いたロイヤング褐炭の脱水と品質向上に関する研究)

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論 文 内 容 の 要 旨

The trend of the utilization of lignite is increasing because of the continuing increase in global energy demands, the decrease in high-rank coal reserves, and the wide availability of low-rank coal. However, lignite contains a high water content, which is the most important factor that limits its wide utilization. Therefore, it is necessary for lignite to dewater. On the other hand, dewatered lignite is easy to re-adsorb water. So far, dewatering and re-adsorption mechanisms of lignite are still not fully understood.

Hydrothermal treatment coupled with mechanical expression (HT-ME) is one of the most appropriate techniques. In this study, HT-ME was employed to remove water from Loy Yang (LY) lignite in order to explore dewatering and re-adsorption mechanisms, which facilitate the improvement of dewatering techniques and utilization, storage, and handling of lignite. For the HT-ME, HT stage was conducted without adding extra water and ME stage was performed at low temperature (110 °C) under atmosphere environment. To reveal dewatering and re-adsorption mechanisms, the effects of HT-ME on special physicochemical properties of the treated samples were systematically examined. Combustion performance of the HT-ME treated samples was also studied. Freeze drying (FD) technique was conducted to support and supplement HT-ME results.

The thesis consists of seven chapters. In **Chapter 1**, characteristics of lignite and previous literature related to lignite dewatering (i.e., dewatering techniques and the changes in some physicochemical properties of lignite during drying processes) were presented. Afterwards, the significances and purposes of this thesis were elucidated.

Chapter 2 focused on the changes in the hydrogen bonds (HBs) during low temperature HT process considering the forms of water in all of the samples. This can help to understand dewatering mechanism. HBs were determined using Fourier transform infrared (FT-IR) spectrum, which was obtained using diffuse reflectance infrared Fourier transform (DRIFT) method. The number of absorption bands, their peak positions, and the area of each peak in each spectrum were determined by curve-fitting analysis with the mixed Gaussian and Lorentzian function. The results showed that water was linearly and relatively easily removed at temperatures lower than 173 °C, which was referred to as non-interfacial water. At temperatures higher than 173 °C, dewatering slope increased, suggesting the existence of another form of water, which was relatively difficult to be removed and was named as interfacial water. Furthermore, the strength of each HB from low to high was 8.74, 14.50, 20.06, 26.36, and 32.59 kJ/mol, respectively. OH- π HBs changed apparently compared with the other four types of HBs because its strength is the weakest among these five types of HBs. The trend of the number of OH- π HBs decreased with the increase in HT temperature.

In **Chapter 3**, the changes in the gaseous, liquid, and solid products obtained from HT and HT-ME were investigated to describe the process of HT-ME dewatering, which can further help to explain dewatering and re-adsorption mechanisms. Gaseous, liquid, and solid products were characterized by gas chromatography, total organic carbon (TOC) analyzer, inductively coupled plasma atomic emission spectroscopy, high-performance liquid chromatography, and FT-IR. The results showed that volume and TOC value of wastewater increased with increasing HT temperature. Contents of monovalent cations (Na^+ and K^+) in wastewater increased significantly in temperature range 100 to 150 °C. As to divalent cations (Mg^{2+} and Ca^{2+}), their contents increased apparently from 150 to 200 °C and 150 to 250 °C, respectively. One possible

explanation of this is that divalent cations are more strongly bound to carboxyl groups than monovalent cations. Volatile matter, fixed carbon, and acidic groups (i.e., phenolic hydroxyl and carboxyl groups) changed slightly below 150 °C. Above 150 °C, volatile matter and acidic groups decreased with increasing processing temperature and an opposite trend was observed for fixed carbon. These indicate that both HT and HT–ME upgrade LY lignite. Furthermore, water contents of HT treated samples decreased significantly by using the following ME treatment, indicating that the next ME treatment is useful for further dewatering. Combined with the results of Chapter 2, dewatering mechanism was proposed.

Chapter 4 focused on equilibrium water contents (EWCs) in samples obtained from HT and HT–ME across a range of relative humidities (RHs) to investigate the performance of EWC and its mechanism, which can provide useful guidelines for water re-adsorption of lignite and its storage. Mesopore volume was calculated based on N₂ gas adsorption isotherm using Barrett, Joyner, and Halenda proposed method. The results showed that at RHs lower than 10%, the factor that controls EWC is water molecules–active sites interactions and one to two water molecules are associated with each carboxyl group, while in RH range 10–42%, the amount of monolayer water gains in significance and ca. two water molecules are bound to each monolayer water molecule. Within RH range 42–92%, EWC is primarily controlled by monolayer water content and mesopore volume. At RHs higher than 92%, EWC is determined by comprehensive factors such as macropores and cracks. Furthermore, EWC was generally higher than residual water content (RWC) below a RWC of ca. 5% and the opposite relationship was observed for sample with RWC above ca. 16%.

In **Chapter 5**, combustion performance of HT and HT–ME treated samples was investigated using thermogravimetric analysis to evaluate the effects of HT–ME on upgrading in combustion aspect. The relationships between various physicochemical properties (i.e., amounts of volatile matter and fixed carbon, specific surface area, and pore volume) and combustion performance were also investigated. The activation energy was calculated using the Kissinger–Akahira–Sunose method. The results showed that the ignition temperatures for samples treated using HT and HT–ME were higher than that for raw lignite and increased with increasing processing temperature, suggesting that HT and HT–ME decrease the reactivity of LY lignite. The maximum combustion rates and average activation energies of the treated samples were higher than those of raw lignite. Activation energy increased with increasing extent of conversion because combustion of volatile matter changes to char burning with the increase in extent of conversion. The activation energy for char combustion is higher than that for volatile matter.

In **Chapter 6**, LY lignite was dewatered by FD to check and supplement HT–ME results. RWC, sorption behavior, and pore size distribution were investigated. Furthermore, kerosene coating by adsorption method to study effect of covering oxygen-containing functional group on restraining water re-adsorption was also investigated. The results showed that non-interfacial and interfacial water contents determined by FD were 1.258 and 0.093 (g/g-lignite, d), which coincide quite well with those by HT method. The moisture holding capacity (MHC) of the FD treated samples was lower than that of raw lignite. This is because of their residual water contents, which determine the final water re-adsorption capacity. Moreover, adding kerosene by adsorption method decreased MHC because kerosene is coated on the surface of the lignite, which mainly covers oxygen-containing functional groups. For direct-mixing method in this study, it can decrease MHC because kerosene is coated both on the surface and in the pores of the lignite. Both of these two methods prevent water re-adsorption. The adsorption method is better than the direct-mixing method because water re-adsorption content decreased by the former is similar to that by the latter while the former consumes less kerosene.

Chapter 7 summarized the main conclusions of this thesis and provided some recommendations.