

論文の要旨

題目 HYDROTHERMAL PRETREATMENT OF MACROALGAE: DETAILED REACTION KINETICS AND MECHANISMS

(大型藻類の水熱前処理: 詳細な反応速度論及び機構)

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Hydrothermal process has been identified as a promising technology for pretreatment of wet biomass, particularly marine macroalgae. The key advantage of this technology is that it does not require any chemical solvent but only water as its reaction medium. Hence, drying of macroalgae prior to the hydrothermal process is certainly unnecessary. In fact, the potential of macroalgae as renewable resources has been extensively discussed in numerous studies. Most of the researchers highlighted the importance of pretreatment process of macroalgae in order to enhance the following processes. The remarkable point of macroalgae is that this biomass contains substantial amount of valuable carbohydrates. Thus, recovery and utilization of these carbohydrates are essentially desired. Owing to that, this research was initiated with the main idea is to study the behavior of carbohydrates in macroalgae, specifically kelp prior to its effective utilization.

The research methodology involved in this study consists of two (2) main sections, which are (i) hydrolysis of alginic acid for recovery of its uronic acids, and (ii) hydrothermal treatment process for kinetics study. In the first section, mild concentration of hydrochloric acid (HCl) was employed for the hydrolysis process, which was conducted for about 2.5 h in total, at round 90 °C. The desired uronic acids, mannuronic acid (MA) and guluronic acid (GA) were recovered separately via pH adjustment at 2.85. The undesired impurities were removed through additional washing and purified uronic acids were dried in desiccator prior to preservation in refrigerator. The later section was conducted by using continuous-flow reactor apparatus. The reaction temperatures ranged between 170 and 250, while residence times varied from 3 to 100 s. For all experiments, pressure was fixed at 25 MPa. Besides the carbohydrates in kelp (GA, MA), several other carbohydrates were also subjected to the hydrothermal treatment, which are glucuronic acid (uronic acid), mannose (aldohexose), and sorbitol (sugar alcohol). The products obtained after the hydrothermal treatment was quantitatively analyzed by using high performance liquid chromatography (HPLC).

The preparation of uronic acid from alginic acid was successfully conducted and the recovery yield was almost 50 %. The key point here is that the desired uronic acids were successfully obtained in a solid form, unlike the other previous studies. Certainly, this methodology employs simple processes to produce MA and GA in easy and quick way. On the other hand, the kinetics study indicated the susceptibility of GA and MA under hydrothermal condition, whose recovery yields were less than 10 % at 170 °C and 15 s of residence time. Similarly, high decomposition rate was observed for another type of uronic acid, namely glucuronic acid. Apparently, lower temperature range is desired for hydrothermal treatment of uronic acids. Perhaps, high reactivity of uronic acids was due to the high electronegativity of their functional group, which is carboxylic group.

The effect of functional group was further evaluated for a sugar family that consists of MA (carboxylic), mannose (aldehyde) and mannitol (hydroxyl). Basically, these sugar compounds have almost similar chemical structure except for the functional group. Among them, MA decomposed faster than the others while mannitol was less susceptible to degradation. Likewise, similar study was conducted on another sugar family that consists of glucuronic acid (carboxylic), glucose (aldehyde) and sorbitol (hydroxyl). The result showed a good agreement with the previous work, in which glucuronic acid exhibited the highest degradation rate. Unlike mannitol and mannose, different behavior was observed for sorbitol, which decomposed faster than glucose. Owing to that, additional study was conducted in order to investigate the effect of chemical structure on kinetics characteristics of these isomers. Apparently, the hydroxyl configuration in sorbitol caused to higher interaction between water and its carbon atoms, which consequently resulted to higher decomposition rate.

The kinetics parameters of various carbohydrates in macroalgae were calculated by using Arrhenius equation. Similar activation energies, E_a were obtained for GA, MA, and glucuronic acids, which are 20.6, 28.3, and 22.8 kJ/mol, respectively. However, the pre-exponential factors, A were increased in the order of GA (40.6 s^{-1}) < glucuronic acid (43.4 s^{-1}) < MA (281 s^{-1}). As for sorbitol, the E_a (28.3 kJ/mol) and A (42.9 s^{-1}) are higher than that of mannitol, 26.5 kJ/mol and 3.23 s^{-1} , respectively. Evidently, aldohexoses (mannose and glucose) showed the highest E_a and A than the uronic acids and sugar alcohols.