

学位論文概要

題目 Development of new mass spectrometry analysis for hydrothermal reactions
(水熱反応のための新規質量分析法の開発)

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The utilization of renewable energy resources is desirable owing to several issues, including the depletion of petroleum resources and global warming. Among many kinds of renewable resources, marine biomass (macroalgae) could be a promising feedstock for bioproduct and biofuel production. However, appropriate pretreatment is needed prior to its effective utilization. Owing to the high-water content of macroalgae, pretreatment under hydrothermal conditions is more favorable. This is because, during the hydrothermal process, water is used as a reaction medium, and thus the drying of feedstock prior to the pretreatment is unnecessary. Furthermore, it was reported in previous studies that hydrothermal pretreatment employed a simple process and was economical.

In order to propose a complete reaction pathway for biomass, detailed information of its decomposition products is required. Previously, many studies, including those from our group, have researched model compounds of kelp under hydrothermal reactions. However, in these cases, to analyze the product, samples were collected after a cooling down process. During the cooling down process, the temperature changes, and chemical reactions may take place with the opportunity that some of the products may change their form during the process, and may be lost during sampling. To address these problems, a rapid and real-time analysis is needed, which can provide new findings and understanding. However, the process of sampling the products under the hydrothermal reactor condition is difficult and poorly developed. To circumvent these problems, the purpose of this research is to design and develop a rapid and real-time analysis by using the mass spectrometric method to identify the decomposition products of model compounds of kelp; glucose, mannitol and mannuronic acid under the hydrothermal conditions for the first time.

The research methodologies employed in this study were coupling two types of the reactor; 1st a batch reactor and 2nd a continuous reactor, with a quadrupole mass analyzer via custom-built connection fittings. The effect of reaction temperatures ranging from 140 to 220 °C and residence times between 2.5 and 20 min on decomposition products of the model compounds of kelp was studied to observe the intermediate compounds and to clarify the fundamental reaction mechanism, including its reaction kinetics. The results of MS analysis, mass spectrometry of cold effluent, and high-performance liquid chromatography (HPLC) were compared and discussed.

First, the results of in-situ mass spectrometry (in-situ MS) analysis using batch reactor were reported. For glucose, in-situ MS analysis observed furfural and levulinic while HPLC could not. For mannitol, the formation of acids like formic acid and levulinic acid could not be observed by HPLC. Mannitol decomposition products like formic acid were not observed by HPLC or once-quenched spectrum at low temperature. The mass spectra of once quenched method showed the similar results as HPLC, but it was completely different from in-situ analysis. Due to the successful development in situ MS analysis system, the quantitative analysis of the products that are needed for the kinetics is discussed. The quantitative in-situ MS analysis was also developed to reinvestigate the kinetics of glucose and mannitol under hydrothermal conditions. The decomposition kinetics was successfully obtained, and the first-order reaction kinetics well expressed the overall decomposition of both glucose and mannitol. The reaction rate constants for the reactions in the decomposition network were determined using the quantitative in-situ MS analysis. The both analyses gave a similar reaction rate constant for the compounds that could be detected by HPLC. This indicates the validity of the in-situ MS analysis. In-situ MS analysis with batch reactor was successfully developed, but only enabled us to simultaneously identify the products after reaction.

At last, to elucidate a complete reaction pathway for biomass decomposition, a different MS analysis method is developed. The real-time analysis using MS (real-time MS analysis) was set-up and designed. Glucose was used as a first model compound to study the effect of hydrothermal pretreatment parameters. It was found that no fructose was observed using conventional HPLC at 200 °C for 10 min of residence time, indicating the effectiveness of MS analysis.

In conclusion, a new methodology for rapid and real-time MS analysis was developed successfully. The MS analysis gave different results from conventional HPLC method. Some of the products could not be obtained by HPLC. This specifies the effectiveness of the MS analysis over the conventional HPLC method and this analysis allows kinetics development including the intermediates.