Development of direct mass analysis of hydrothermal reactions

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SUMMARY
In this research, in-situ mass spectroscopic analysis were designed and developed to identify the products from glucose conversion under hydrothermal pretreatment conditions. The in-situ analysis were performed by continuous reactor coupled with a quadrupole mass analyzer. The products of glucose during hydrothermal pretreatment under various temperatures (140-220 °C) and residence times (5-20 min) by real time analysis method and once quenched method have been investigated. Moreover, the results of products from the once quenched method were confirmed by high-performance liquid chromatography (HPLC). The fragmentation spectra from real time analysis showed that at 140 °C the products were mainly consisted of glucose, at temperature higher than 180 °C 5-hydroxymethylfurfural (5-HMF) was clearly observed.

1. Introduction
Hydrothermal pretreatment, pretreatment in hot compressed water, of marine biomass is a potentially viable approach to produce and convert biomass into valuable products. Moreover, this process is simple and economical. Hence, clear information about products of hydrothermal pretreatment of macroalgae by rapid and real time analysis is wanted. Mass spectrometry (MS) is attractive because of its high selectivity, sensitivity and high throughput. However, the real time analysis using MS during hydrothermal reaction have not been well developed. Therefore, the purpose of this study is to develop a methodology for real time analysis of hydrothermal pretreatment products using MS technology.

2. Experimental
A diagram of apparatus setup is shown in figure 1. A quadrupole mass spectrometer (ULVAC. Co.th, USA) was used as detector for all experiments. The in situ mass spectrometry was performed using continuous reactor coupled with quadrupole mass analyzer. To connect the reactor with the mass analyzer, connection fitting parts were designed and set up. Small orifice nozzle spray (0.1 mm) was used to reduce high pressure of hot liquid sample from reactor before passing through mass analyzer. The piping line of real time analysis for the hot sample liquid were kept at the same temperature with reactor by using a temperature control system. This apparatus

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Fig. 1 Real time analysis apparatus: continuous reactor coupled with quadrupole mass analyzer

setup used for investigate the effect of temperature and residence time on the decomposition of glucose. The residence times were controlled by feedstock flow rate. Data collection was processed using software for gas analysis Qulee QCS ver. 3.0. Glucose was used as model compound. Reaction temperature was changed in the range of 140-220 °C.

3. Results and discussions

Figure 2 shows the effect of temperature. At 140 °C the products were mainly consisted of glucose. At temperature higher than 180 °C 5-hydroxymethylfurfural (5-HMF) was clearly observed. Once cooled method gave completely different MS spectra, indicating importance of real time analysis.

4. Conclusion

The direct analysis of hydrothermal pretreatment product was developed successfully. Once quenched method gave different spectra, indicating importance of real time analysis.

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Fig. 2 Mass spectrum of glucose decomposition under various temperature of hydrothermal pretreatment process via real time analysis compared with commercial method.