別紙様式８

研　究　主　論　文　抄　録

論文題目　Critical Fluid Technology in Food Industry for Extraction and Particle Generation
（食品工業における抽出および粉粒体調製のための超臨界流体技術）

熊本大学大学院自然科学研究科　複合新領域科学　専攻　衝撃エネルギー科学　講座
（　主任指導　後藤　元信　　教授　）

論文提出者　アスキン　ルーハン
(Ruhan ASKIN UZEL)

主論文要旨

Extraction with supercritical fluids is a unit operation in chemical engineering that could be employed for a variety of applications. The goal of this project was to establish new approaches in supercritical technology in food industry. Therefore, supercritical fluids and their common applications for both carbon dioxide and water were briefly explained. Furthermore, supercritical fluid technology was applied on basis for natural products from mushroom called *Ganoderma lucidum* and a new hybrid vegetable called *Petit vert.* In the following sections, a general overview of supercritical fluids, the importance and recent industrial applications of supercritical fluid technology, as well as fundamental aspects which were studied in this work was described in more detail. Moreover, as carrying crucial importance for food packaging industry, removal of oligomers from PET (polyethylene terephthalate) by hydrothermal treatment has been studied in following chapters. Finally, a novel system design for particle generation has been investigated in separate chapter.

Being one of the objectives of this work, a method was established for extraction from grinded form of *Ganoderma lucidum* with water in sub-critical conditions and with $SCCO_2$ at distinct temperatures to obtain extracts rich in water-soluble organic compounds (WSOC), including mostly beta glucans and triterpenoids including ganoderic acids and alcohols respectively. $SCCO_2$ experiments were carried out at pressures of 10, 20 and 30 MPa and temperatures ranging from 40 to 60 $^{\circ}C$ with and without modifier. Ethanol was used as modifier at flow rates of 0.1, 0.2 and 0.4 mL/min. The CO_2 flow rate was maintained at 4 mL/min for 2 hours extraction time. The extracts were analyzed by HPLC. The temperatures for batch-scale sub-critical water extraction kept constant at different time intervals starting from 373 up to 573 K. For semi-continuous scale experiments, samples were extracted once with water at 373, 423, 448 and 473 K, respectively, working at pressure around 10 MPa to keep the water in the liquid state. The flow rate used was 1 mL/min. The extracts were analyzed by TOC for water soluble organic compound recovery. The highest yield obtained at

473 K as 78.1 % and as 57.4 % for batch- and semi continuous scale experiments respectively. It was also demonstrated that the modified $SCCO_2$ extraction is suitable for the extraction of *Ganoderma lucidum*.

Water has been shown to be capable of extracting different classes of compounds from *Petit vert* depending on the temperature used in hydrothermal treatment. Hot compressed water was continuously delivered into a reactor while gradually rising the temperature from 25 to 200 °C at 5 MPa and its flow rate was 1 ml/min for different experimental time combinations. The extract from the reactor was cooled and each fraction was collected at the volume having range from 10 ml up to 40 ml. Next, pectin was separated from *Petit vert* using semi continuous flow reactor. The quantitative analysis of the pectin was measured as the amount of a galacturonic acid according to the dimethylphenol method. It was found that the pectin was rapidly extracted when the temperature of the reactor reached 200 °C from the analysis of each fraction. As a result of the cation analysis, K^+ was detected as an indicator element in a large amount having peak a little ahead from the extraction peak of pectin.

A rapid, alternative technique for the extraction of low molecular weight oligomers from PET (polyethylene terephthalate) polymer film was reported. Traditionally, PET has been extracted using liquid–solid Soxhlet extraction but this has proved to be extremely time consuming. In this work, cyclic trimer and other low molecular weight oligomers have been extracted from PET film using water at sub-critical conditions. The determination and identification of the extracts has been performed using HPLC and GPC.

Finally, in order to combine the extraction technique with particle formation process, a novel system was designed. The apparatus is divided into three sections: a supercritical fluid delivery unit (a water source, a circulating heater, an HPLC pump), a solute dissolving and extracting unit (a pre-heater, an extraction vessel and an oven), and a crystallizing-separating unit (nozzle and collector). The extraction vessel placed in the oven was heated to the desired temperature and accurately controlled to within range of 2 °C difference. The pressure in the stainless steel extraction vessel (10 mL) was monitored by a pressure gauge. The solution left the extraction vessel and was led to the crystallizer where it was throttled across an expansion nozzle. The pre-expansion temperature was monitored by a temperature controller (T1 -C). When the supercritical solution depressurized through the nozzle to ambient conditions, it experienced a rapid expansion and resulted in precipitation of the solute in the collection chamber as powder. Precipitated sample particles were analyzed with laser diffraction in order to have an idea about the size distribution of the product. SEM analysis was done respect to particle size and shape. Molecular weight distributions were determined via size-exclusion chromatography (SEC). The sample weight change with increasing temperature was evaluated by a thermogravimetric analyzer (TGA 2050, TA Instruments). The crystal structures and melting points of original and precipitated powder were examined by an X-ray-diffractometer.