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論　　文　　名	「Evaluation of Various New Technologies for Valuable Materials Production from Green Macroalgae （緑藻類からの有用物質生産に関する複数新技術の評価）」
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Summary

The worldwide demand for fossil fuels, climate change and global warming, fuel security, and economics are driving the use of renewable energy sources. Renewable energy resources such as solar, wind, and hydro energies may be used to generate electricity or heat either directly or indirectly, but biomass is the only renewable energy source capable of reducing CO_2 emissions and also producing chemical commodities and liquid fuels (biofuels) for storage and as a transport fuel. With an annual production of biomass up to 1.7-2 × 10^{11} tons in the world, only 6 × 10^9 tons of it is currently used for food and non-food applications. As approximately 50% of global biomass is thought to be generated in a marine environment, therefore marine biomass has great potential of alternatives to fossil fuels. Amount them, macroalgae is a significant source of renewable energy and bio-chemicals in coming years. Simple cultivation, possible productiveness, high photosynthetic efficiency, the avoidance of land use, and also easier manufacturing process (no lignin removal) with a higher CO_2 fixation ability are the main advantages of macroalgae as great alternative source of energy and bio-chemicals.

These advantages motivated researchers all over the world to report substantial amounts of academic works showing possibility of energy and valuable materials production from macroalgae. More recently there has been an increasing interest into utilization of innovative green techniques instead of using traditional ones for avoided environmental impacts and its greenhouse gas reduction benefits which consequently increase the economical and ecological feasibility of the techniques. Obviously, using different techniques cause different impacts on the utilization and treatment of the samples. To the best of our knowledge, there is no available report on comparing the

various innovative methods for treatment and conversion of the macroalgae to the energy and bio-chemicals. On the other hand there is no available report on industrialization and economic feasibility study of the mentioned techniques.

The present study has been dealt with utilization and application of four kinds of new technologies for a selected macroalgae (*C. fragile*) as model of green macroalgae, a low-cost and abundant marine biomass. In addition, the data obtained from laboratory scale experiments were used for evaluation of industrialization of the processes in pilot plant scale.

The first objective of this study was to evaluate and develop efficient environmentally friendly techniques for conversion of *C. fragile* into valuable compounds such as soluble sugars, fatty acids, organic acids, and pure fibers. Some of the techniques have been utilized for first time in this research work. The second objective was to provide the sufficient information in order to comparison between the effect of different innovative methods on conversion yield and production of valuable materials. The third objective was industrialization of each process and its economical assessment individually. The major and important results of the thesis are summarized as follows:

In chapter one, the general introduction and importance of the present work as well as review of previous research works were presented.

In chapter two, application of subcritical water as green innovative technique for hydrolysis and decomposition of *C. fragile* was investigated in order to obtain value-added bio-based substances. A batch type subcritical water reaction system was used to perform laboratory experiments over the whole temperature range of subcritical water and different reaction times. As an interesting and main finding, it was observed that hydrolysis and decomposition reactions were effectively carried out without utilization of any organic solvent, acid, base, and/or enzyme. Significant increases of total organic carbon (TOC) in the water phase proved that bio-macro polymers of the initial sample such as polysaccharides were hydrolyzed using subcritical water; they showed maximum amount at around 210 ºC. The results indicated that cellulosic parts of macroalgae could be successfully decomposed to water-soluble sugars (including mixtures of poly-, oligo-, di-, and mono saccharides) using subcritical water treatment. The optimum condition for the best yield was achieved at temperature of 210 ºC. Several other valuable compounds such as furfural and 5-hydroxymethylfurfural were also produced from decomposition of the algae, which can be classified as main building block materials. The amount of oil extracted was relatively low probability due to hydrolyzing reactions of oily compounds under subcritical water conditions. Water insoluble residual solid after treatment had a high carbon content compared to initial sample, which caused an increased energy density in the solid and consequently increased heating values of the solid. The results proved that the solid residue can be a very good alternative energy resource compared to initial algae before treatment.

In chapter three, treatment and liquefaction of *C. fragile* under batch type subcritical ethanol was studied at temperatures ranging from 100 to 205 °C for different reaction times ranging 2 to 15 min. Due to the transesterification reaction in ethanolic medium, very valuable bio-oil compounds such as hexanoic acid ethyl ester, n-hexadecanoic acid, ethyl myristate, ethyl oleate, ethyl palmitate, EPA, heptadecanoic acid ethyl ester, and etc. produced and identified. The maximum yield of bio-oil products was obtained at 200 ºC after 15 min. reaction time. The solid residue composition was analyzed as well. The results indicated that subcritical ethanol could successfully extract all extractives from the algae and result almost very pure cellulose with less hydrolyzed amount of the cellulose fibers which is an industrially interested bio-material and could be applied in bio-fiber and pharmaceutical industries. Since residual solid also showed high energy density, it could also be alternative energy resource as well. As an advantage of the technique, ethanol is a green solvent which after reaction could be easily purified and recycles back to the reaction system.

In chapter four, thermogravimetric analysis (TGA) and differential thermogravimetric (DTG) techniques as other new methods were proposed to determine the (kinetic) pyrolysis behavior of the macroalgae. In fact, prior to scale up a pyrolysis system, it is necessary to evaluate the influence of different parameters such as pyrolysis temperature, particle size, and heating rate, and so on. Pyrolysis was carried out by vary the heating rates from 5 to 50 °C/min. The weight losses occurring in correspondence to temperature rises were continuously recorded with a computer working in coordination with the instrument. Effect of particle size (ranging between <75 and >1400 μm) and initial sample weight (ranging between 5-25 mg dry sample) have been studied. The results showed approximately 6.5% moisture content of dried sample, 58% volatile materials, 10.5% fixed carbon, and 25% ash content (depending on the experimental conditions). To estimate kinetic parameters, the solid state non-isothermal (isoconversional) method was used. This method is applied for the description of more complex processes where lots of chemical reactions are running simultaneously, while their mechanisms are not exactly known. Finally, the kinetic parameters as well as value of activation energies for three pyrolysis stages of *C. fragile* were obtained with the methods of Flynn, Ozawa, Wall (FOW), Friedman, Kissinger-Akahira-Sunose (KAS), and Coats-Redfern.

In chapter five, the effect of ultrasonic irradiations as more innovative technique on *C. fragile* was investigated. The reaction carried out at three different amplitude and time at constant temperature of 22 °C using water and ethanol as reaction media. The efficiency of the method has been evaluated by analyzing of decomposition products such as saccharification yield, bio-oil production, and the purity of extracted fibers. At higher power of sonication system, the soluble sugars yield reached to 20% after 20 min due to the cell disruption and saccharification reaction. The maximum dissolution of sample which obtained by sonication was 59% after 10 min. However, this amount is around 15% after 20 min. reaction in ethanolic medium. Higher dissolution in water medium compared to ethanolic phase clearly proves that sonication solvent has great influence on the reaction efficiency. With utilization of ethanol medium the valuable fatty acids ethyl esters such as EPA and phytol were produced. Heating value of remained solid obtained from sonication in water medium was higher than those obtained from ethanolic medium (13 MJ/kg). As conclusion, by using sonication technique it is possible to completely extract valuable materials along with production of very pure cellulosic fibers which has industrial interest owing to their high durability and low weight.

In chapter six, based on the experimental data obtained from previous chapters (i.e. sub and supercritical water, subcritical ethanol, pyrolysis, and ultrasonic treatment methods), we attempted to simulate large pilot plants for macroalgae conversions. Four continuous processes were designed and simulated by Aspen Plus® software for decomposition of macroalgae at capacity of 10 kg/h. Subsequently, by understanding the mass balance and energy balance of each process, an economic assessment revealed the cost and benefit of each process individually. The estimated cost of 10 kg/h subcritical water pilot plant, Subcritical ethanol pilot plant, pyrolysis pilot plant, and sono-assisted pilot plant without considering the purification process cost, manufacturing and utility cost, were 12, 14, 11, and 10 JPY/h, respectively. However, the final products for each system (bio-oil, cellulosic fiber, methane gas, and carbon dioxide) represent absolutely high value of profit for them. In fact the simulation proved that it is possible to successfully scale up the data obtained from bench scale to larger ones. Results revealed that all proposed new technologies have benefit in even large scales; however, for precise simulation processes there are several other thermodynamic parameters which must be considered and evaluated.

In chapter seven, general conclusions of the present work were given.

審査結果の要旨

本論文は、陸域から排出された炭素や栄養塩を基に海域で生産された海産バイオマスを、効率よく回収し有用な資源として利用する、いわゆる海産バイオマス有効利用システムの構築を前提に、システム全体の経済成立性を確保するため、海産バイオマスのうち緑藻類のミル（*C. fragile*、大阪湾内でよく見られる海藻）から単価の高い有用物質を抽出するための技術開発を行ったものであり、以下の成果が得られている。

（1）亜臨界水処理技術を用いてミルからの有用物質抽出を行う場合、210℃、10MPa で 10 分程度反応させるのが最も有用な物質が取れる条件であることを明らかにし、その場合、最も多く抽出できる物質が多糖類、オリゴ糖類、単糖類などの糖類で、その他にセルロースが取れること、非常に微量であるもののアラキドン酸（ARA）が抽出できることを示した。

（2）亜臨界アルコール処理技術を用いてミルからの有用物質抽出を行う場合、200℃、10MPa で 10 分程度反応させるのが最も有用な物質が取れる条件であることを明らかにし、その場合、最も多く抽出できる物質がセルロースで、その次に多糖類、オリゴ糖類、単糖類などの糖類と、それと同程度アラキドン酸を含むバイオオイルが取れることを示した。

（3）熱重量分析（Thermogravimetric Analyses）処理技術を用いてミルからの有用物質抽出を行う場合、どの条件においても、生成物中のうち炭分が占める割合が多く、バイオオイルも抽出できるものの、アラキドン酸やエイコサペンタエン酸（EPA）などの商品価値の高い成分は抽出できないことを示した。

（4）超音波処理技術を用いてミルからの有用物質抽出を行う場合、媒体は水よりアルコールのほうがよいことを明らかにし、常温、20kHz で振動素子の振幅を 10μm とした場合、最も多く抽出できる物質がセルロースで、その次に多糖類、オリゴ糖類、単糖類などの糖類が取れること、わずかではあるもののエイコサペンタエン酸が抽出できることを示した。

（5）亜臨界水処理、亜臨界アルコール処理、熱重量分析処理、超音波アルコール処理の４つの技術を用いたパイロットプラントのランニングコストを計算し、実験から得られたデータを基に生産品の利益を見積もって比較した結果から、これらの技術の中では、単価の高いアラキドン酸が比較的多く生産できる亜臨界アルコール処理が最も経済的に有利であることを示した。

以上の研究成果は、海産バイオマス有効利用システムの計画・設計とって非常に有益であるとともに、申請者が自立して研究活動を行うに必要な能力と学識を有することを証したものである。学位論文審査委員会は、本論文の審査ならびに最終試験の結果から、博士（工学）の学位を授与することを適当と認める。

以上