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SUBCRITICAL WATER EXTRACTION PROCESS FOR MICROALGAL BIODIESEL PRODUCTION

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By

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SUBCRITICAL WATER EXTRACTION PROCESS FOR MICROALGAL BIODIESEL PRODUCTION

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November 2020

Chair : Assoc. Prof. Mohd Razif Harun, PhD
Faculty : Engineering

Microalgae have been used as a substrate for biodiesel production due to their numerous advantages, including fast growth rate, non-edibility, and the ability to accumulate substantial amounts of carbohydrates, lipids, and proteins. However, current extraction technologies used to produce oil from microalgal biomass are expensive, unsustainable, involve lengthy processing steps and result in lower product yields. One of the newer extraction techniques is subcritical water extraction which offers lower production costs, milder operating conditions, and a shorter production period compared to other conventional methods, such as chemical and biological extraction. The current subcritical water extraction (SCW) for biodiesel production involves two steps: extraction and transesterification. These two steps can be combined in one-step by the proposed subcritical methanol extraction (SCM) process for microalgal biodiesel production.

In this study, SCW and SCM were used to treat *Chlorella pyrenoidosa*. The operational factors such as reaction temperature, reaction time and biomass loading influence the oil yield during the extraction process. In this study, response surface methodology was employed to identify the desired extraction conditions for maximum extraction yield. SCW experiments were carried out in batch reactors as per the central composite design with three independent factors: reaction temperature (170 to 370 °C), reaction time (1 to 20 min) and biomass loading (1 to 15%). The maximum oil yield of 12.89 wt.% was obtained at 320 °C and 15 min, with 3% biomass loading. Sequential model tests showed the good fit of experimental data to the second-order quadratic model. The extracted oil from SCW is converted to biodiesel via second-step, transesterification. Recent developments in subcritical studies utilize subcritical alcohol solvents as a single step process to produce biodiesel from algae. Here, the algal biomass is subjected to SCM in the second phase of this study. The effects of three operational factors: reaction temperature (140 to 220 °C), reaction time (1 to 15 min) and methanol to algae ratio (1 to 9 wt.%) were investigated. A maximum yield of crude biodiesel of 7.1 wt.% was obtained at 160 °C, 3 min reaction time and 7 wt.% methanol to algae ratio. The analysis of variance revealed that methanol to algae ratio is the most significant factor for maximizing biodiesel yield. Regression analysis showed a good fit of the experimental data to the second-order polynomial model. Higher cetane number (74.92) and low iodine value (58.81 g I_2/100 g) crude biodiesel produced from SCM were found in compliance with the European standard (EN 14214). The SCW and SCM experimental data were fitted with three models, namely first-order kinetic model, second-order kinetic model and Fick's law kinetic model. A comparison between SCW and SCM in terms of mass flow and energy consumption is provided through the LCA study. In terms of energy requirements, SCM has a lower energy demand than SCW. The use of subcritical technology for high-grade algal biodiesel production is expected to be promising and will result in a positive outlook for commercially viable production of high-quality biodiesel.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PROSES PENGEKSTRAKAN AIR SUBKRITIKAL UNTUK PENGELUARAN BIODIESEL MICROALGAL

Oleh

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Microalga telah digunakan sebagai substrat untuk pengeluaran biodiesel kerana banyak kelebihannya, termasuk kadar pertumbuhan yang cepat, tidak dapat dipertahankan, dan keupayaan untuk mengumpul sejumlah besar karbohidrat, lipid, dan protein. Walau bagaimanapun, teknologi pengekstrakan semasa yang digunakan untuk menghasilkan minyak daripada biojisim mikro adalah mahal, tidak lestari, melibatkan langkah pemprosesan yang panjang dan menghasilkan hasil produk yang lebih rendah. Salah satu teknik pengekstrakan yang lebih baru adalah teknik pengekstrakan subkritikal yang menawarkan kos pengeluaran yang lebih rendah, keadaan operasi yang lebih ringan, dan tempoh pengeluaran yang lebih pendek berbanding dengan kaedah konvensional yang lain, seperti pengekstrakan kimia dan biologi. Teknik pengekstrakan subkritikal air (SCW) untuk penghasilan biodiesel melibatkan dua langkah iaitu: pengekstrakan dan transesterifikasi. Dua langkah ini boleh digabungkan menjadi satu langkah seperti yang dicadangkan daripada proses pengekstrakan subkritikal methanol (SCM) untuk penghasilan biodiesel daripada mikroalga.

Dalam kajian ini, SCW dan SCM digunakan untuk merawat *Chlorella pyrenoidosa*. Faktor-faktor operasi seperti suhu tindak balas, masa tindak balas dan pemuatan biomas mempengaruhi hasil minyak semasa proses pengekstrakan. Dalam kajian ini, metodologi permukaan tindak balas digunakan untuk mengenal pasti keadaan pengekstrakan yang dikehendaki bagi hasil pengekstrakan maksimum. Eksperimen SCW dilakukan dalam reaktor batch sebagai satu reka bentuk komposit pusat dengan tiga faktor bebas termasuk suhu tindak balas (170 hingga 370 °C), masa tindak balas (1 hingga 20 min) dan pemuatan biomas (1 hingga 15%). Hasil minyak maksimum sebanyak 12.89 wt% diperoleh pada 320 °C dan 15 min, dengan 3% biomass loading. Ujian model urutan menunjukkan kesesuaian data eksperimen dengan model kuadrat urutan kedua. Minyak yang diekstrak dari SCW ditukarkan kepada biodiesel

melalui langkah kedua, transesterifikasi. Perkembangan terbaru dalam kajian subkritikal menggunakan pelarut alkohol subkritikal sebagai satu proses langkah untuk menghasilkan biodiesel dari alga. Di sini, biomas alga tertakluk kepada SCM dalam fasa kedua kajian ini. Kesan tiga faktor operasi: suhu tindak balas (140 hingga 220 °C), masa tindak balas (1 hingga 15 min) dan metanol kepada nisbah alga (1 hingga 9%) telah disiasat. Hasil maksimum biodiesel mentah sebanyak 7.1% diperolehi pada 160 °C, masa reaksi 3 min dan 7% methanol kepada nisbah alga. Analisis varians mendedahkan bahawa nisbah metanol kepada alga adalah faktor paling penting untuk memaksimumkan hasil biodiesel. Analisis regresi menunjukkan kesesuaian data eksperimen untuk model polinomial pesanan kedua. Bilangan cetane yang lebih tinggi (74.92) dan nilai iodin yang rendah (58.81 g I_2/100 g) oleh biodiesel mentah yang dihasilkan dari SCM didapati mematuhi piawaian Eropah (EN 14214). Data eksperimen SCW dan SCM diuji dengan menggunakan tiga model, iaitu model kinetik pertama, model kinetik kedua dan model kinetik berdasarkan undang-undang Fick. Perbandingan antara SCW dan SCM dari segi aliran masa dan penggunaan tenaga disediakan melalui kajian LCA. Dari segi keperluan tenaga, tenaga yang diperlukan oleh proses SCM adalah lebih rendah daripada SCW. Model matematik telah dicadangkan berdasarkan baki pemindahan massa semasa proses pengekstrakan subkritikal. Penggunaan teknologi subkritikal bagi pengeluaran biodiesel alga gred tinggi dijangka menjanjikan dan akan menghasilkan tinjauan positif untuk menghasilkan biodiesel berkualiti tinggi secara komersial.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in the Universiti Putra Malaysia (Graduate Studies) Rules 2003 (Revision 2012-2013) are adhered to.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ANOVA	Analysis of variance
CHF	Catalytic hydrothermal gasification
EROI	Energy return on investment
FAME	Fatty acid methyl ester
FCCCD	Face-centered central composite design
FFA	Free fatty acids
HHV	Higher heating value
LCA	Life cycle assessment
LC-GHG	Life-cycle greenhouse gas
LE	Lipid extraction
LEA	Lipid-extracted algae
LHV	Lower heating value
MUFA	Monounsaturated fatty acid
PUFA	Polyunsaturated fatty acid
RSM	Response surface methodology
SCM	Subcritical methanol extraction
SCW	Subcritical water extraction
SEM	Scanning electron microscopy
SEQSCW	Sequential subcritical water
TGA	Thermo-gravimetric analyzer
UAE	Ultrasound-assisted extraction
UCAS	Utility-connected algae system
WWTP	Wastewater treatment plant

CHAPTER 1

INTRODUCTION

This chapter briefly introduces the background and context of this thesis work. The motivation for this research has been established in the problem statement. Also, the objectives and scope of the study are further outlined in this chapter.

1.1 Research Background

Subcritical water has been utilized for solid waste resource recovery and is gaining interest as a potential solvent and catalyst for organic reactions. Among the different media used for the reaction, water is attractive because of its safety and low cost. Subcritical states of water are described at temperatures between its boiling point (100 °C) and its critical point (374 °C) and at pressures high enough to maintain the liquid state of water. At such conditions, the dielectric constant of water decreases, thereby lowering its polarity. Secondly, the magnitude of the ionic product of water increases three orders higher around 250 °C compared to room temperature. These properties are advantageous for the hydrolysis and decomposition of organic compounds including polymeric materials (Tavakoli & Yoshida, 2006a). Extensive studies led by Yoshida and co-workers have concluded that valuable and useful substances, such as organic acids, amino acids, proteins, fatty acids, oils, and nutrition were made recoverable by utilizing the subcritical extraction technique for waste treatment. For instance, fish waste was easily liquefied by hydrolysis with subcritical extraction, which enabled the recovery of organic acids, amino acids and the extraction of fatty acids (Yoshida, Terashima, & Takahashi, 1999). Similar results were also obtained with squid waste where free fatty acids (FFA) containing eicosapentaenoic acid and docosahexaenoic acid were produced during subcritical extraction (Tavakoli & Yoshida, 2006b).

The rapid depletion of fossil fuels, together with the uncertain global climate in the past decade, has inevitably led to an increased commercial interest in renewable fuels. Biodiesel and bioethanol are viewed as attractive potential solutions to alleviate the existing dependency on petroleum-based fuels (Lang, Dalai, Bakhshi, Reaney, & Hertz, 2001). The current production of biodiesel involves methanolic transesterification of extracted plant lipids, while bioethanol is presently synthesized via anaerobic yeast fermentation of sugar molecules found in the biomass of different food crops (Harun, Danquah, & Forde, 2010). Due to its high biomass productivity, perceived rapid lipid accumulation, and the suitability of its carbohydrate biochemistry for the fermentation process, microalgae are identified as a promising alternative feedstock for both biofuels (Chisti, 2007; Halim, Gladman, Danquah, & Webley, 2011; Sheehan, Dunahay, Benemann, & Roessler, 1998). Additionally, unlike other fuel-producing crops, most marine microalgae can be grown with saline water in non-agricultural lands, thereby exempting their large-scale cultivation from placing additional demands on precious freshwater and arable lands required for food production (Sheehan et al., 1998). Since the biochemical products used in the synthesis of either biofuel (neutral lipids for biodiesel and simple sugars for bioethanol) are encapsulated within the microalgal cellular structures, disintegrating the cells to liberate these intracellular products will render them more readily accessible and subsequently enhance production yield.

A body of work has been reported on the application of the subcritical technique for the extraction of essential oils from coriander seeds (Eikani, Golmohammad, & Rowshanzamir, 2007), citrus fruit Yuzu (Ueno, Tanaka, Hosino, Sasaki, & Goto, 2008), and herb zaatar (Ozel, Gogus, & Lewis, 2003); proteins and amino acids from de-oiled rice bran (Sereewatthanawut et al., 2008); antioxidant compounds from canola meal (Hassas-Roudsari, Chang, Pegg, & Tyler, 2009), and winery waste (Aliakbarian, Fathi, Perego, & Dehghani, 2012); phenolic compounds from bitter melon (Budrat & Shotipruk, 2009), and pomegranate (He et al., 2012). The high moisture content of algal feedstock has made this technique a promising technology to produce biocrude with minimal dewatering requirements. Numerous methods for the extraction of biochemical products from microalgae have been applied; but most common methods are expeller/oil press, solvent extraction, supercritical fluid extraction, and ultrasound techniques (Popoola & Yangomodou, 2006). The cost of these extraction methods for commercial applications could be high. One of the techniques to overcome the existing problem is employing a subcritical extraction technique.

Life-cycle assessment (LCA) is a standardized tool for evaluating the environmental impact of a product. The international standard for life-cycle assessment, ISO 14040:2006, which was reviewed and confirmed in 2016, states that “LCA addresses the environmental aspects and potential environmental impacts (e.g., use of resources and the environmental consequences of releases) throughout a product’s life-cycle from raw material acquisition through production, use, end-of-life treatment, recycling, and final disposal (i.e., cradle-to-grave)”. All life-cycle stages of the algae-to-biodiesel process via subcritical extraction are thoroughly studied during LCA analysis. The cradle-to-gate assessment provides complete information from the start to the end of the product’s life, comprising all processes from the supply of raw materials to the production of the final product.

1.2 Problem Statement

Algae are a unique biomass feedstock for the sustainable production of biofuels. Algae, one of the fastest-growing photosynthetic organisms on earth, have biomass productivity rates higher than terrestrial plants (Alba, Torri, Fabbri, Kersten, & Brilman, 2013). Benefits of algae over food crops include fast growth rates, less water intake, adaptation to various water sources (fresh, seawater, saline/brackish and wastewater), high photosynthetic efficiency, carbon dioxide (CO_2) bio-sequestration, phytoremediation, inexpensive cultivation techniques using non-arable land and short harvesting periods. Notwithstanding these benefits, algal biofuel development faces a few drawbacks which include low biomass densities and high operating costs for biomass generation and conversion (Harun et al., 2014). Although algal-based biofuels generate approximately 13% CO_2 lower emissions from combustion relative to CO_2 emissions from petroleum diesel, in terms of absolute emission levels, algal biofuels can be significantly high for full-scale applications (Nair & Paulose, 2014). The development of biofuels from algal biomass has been significantly successful under lab-scale conditions (Hannon, Gimpel, Tran, Rasala, & Mayfield, 2010). However, opportunities for commercial-scale applications should focus on addressing related environmental, technological, and economic drawbacks (Khan, Shin, & Kim, 2018).

A body of work has been reported on algae extraction using alkaline treatment (Harun, Jason, Cherrington, & Danquah, 2011), enzymatic treatment (Harun & Danquah, 2011a), acidic treatment (Harun & Danquah, 2011b). Though these methods were found to be effective in the extraction process, the use of toxic organic solvents, expensive enzymes and treatment conditions makes the process non-commercially feasible. In view of the economic and environmental needs, it is desirable to explore the use of subcritical water extraction (SCW) as fundamental research in recovering valuable materials from microalgal biomass.

The SCW technique is simpler, more environmentally friendly and can reach high extraction in a very short time (Kumar, Yadav, Kumar, Vyas, & Dhaliwal, 2017). In general, this technique is the most promising technology that can be the first step to the fractionation and obtaining high-value products according to the biorefinery concept (Alba et al., 2011). Depending on the operational conditions (temperature, residence time, particle size, moisture, and reactor configuration), subcritical extraction can cause several effects over the product yield and its quality. The conventional method for biodiesel production from algae via SCW is a two-step process, i.e., extraction of oil from algae via SCW and catalyst-mediated transesterification of extracted oil to biodiesel. Hence, the conventional process has many disadvantages, including expensive and complicated downstream processing steps (Bi, He, & McDonald, 2015). Therefore, to circumvent these disadvantages, this research study proposes a one-step, *in-situ* algal biodiesel production using subcritical methanol extraction (SCM).

This research work will unite oil extraction and transesterification as a single process for producing high-quality biodiesel from algae, a potential and promising feedstock. High capital costs due to low lipid productivity of microalgae is a major bottleneck, hindering the commercial production of microalgal oil-derived biodiesel (Dahmani, Zerrouki, Ramanna, Rawat, & Bux, 2016). *Chlorella pyrenoidosa* was selected for conducting the feasibility study of high biomass productivity low-lipid algal strain for maximum oil extraction. Reaction temperature, reaction time and biomass loading were identified as major influencing factors from previous literature on subcritical studies (Edeh, Overton, & Bowra, 2019; Ravber, Knez, & Škerget, 2015). The batch experimental setup in this research project limits the consideration of these three variables as independent variables as these variables can be systematically manipulated during the experimental run. Therefore, this study aims to evaluate the crude biodiesel production from *C. pyrenoidosa* under two-step SCW and one-step SCM along with three independent variables.

Response surface methodology (RSM) is used to assess the importance of independent variables and their interactions; hence, it is applied in the optimization of independent variables (Bai, Saren, & Huo, 2015). In this work, RSM was applied to assess the oil yield from SCW and SCW of *C. pyrenoidosa* from the optimization of three independent variables – reaction temperature, reaction time and biomass loading. Thus, RSM allows understanding the interactions among independent variables over oil yield. Kinetic studies on SCM of algae remains unexplored. The extraction rate of oil is an important parameter for constructing large-scale extraction units (Saxena, Sharma, & Sambi, 2011). Three kinetic models were evaluated to fit the experimental data of SCW and SCM. LCA is an important tool for evaluating new technologies and it helps to identify the technical bottlenecks and therefore encourages the eco-design of an effective and sustainable production chain (Lardon, Hélias, Sialve, Steyer, & Bernard, 2009). Hence, the economic and environmental impacts of the subcritical extraction systems were investigated through the LCA analysis.

1.3 Objectives

1.3.1 Overall Objective

To develop a one-step algal crude biodiesel production process to eliminate expensive and complicated downstream processing steps associated with conventional two-step approaches.

1.3.2 Specific Objectives

The following are the specific objectives:

a. To evaluate the effects of process parameters via RSM for the two-step SCW and one-step SCM of algal crude biodiesel production processes.
b. To evaluate three kinetic models for SCW and SCM of *C. pyrenoidosa* for the algal biodiesel production process.
c. To analyze the LCA of the algae-to-biodiesel process via subcritical extraction.

1.4 Scope of the Study

The scope of the study is summarized based on the thesis objectives as below:

a. Evaluation of the effects of process parameters

First, standard methods were implemented to characterize the algae, *C. pyrenoidosa*, including proximate and ultimate analyses. Secondly, SCW experiments were carried out as per RSM with three independent factors: reaction temperature (170 to 370 °C), reaction time (1 to 20 min) and biomass loading (1 to 15%). Thirdly, SCM experiments were carried out as per RSM with three independent factors: reaction temperature (140 to 220 °C), reaction time (1 to 15 min) and methanol to algae ratio (1 to 9 wt.%). The effects of process parameters are evaluated and the optimum conditions for maximum oil yield from each subcritical extraction process were achieved.

b. Investigation of the kinetic and thermodynamic parameters

The experimental data of SCW and SCM were fitted with three kinetic models, namely, first-order rate law kinetic model, second-order rate law kinetic model and Fick's law kinetic model— to presume the extraction mechanism parameters.

c. Evaluation of LCA analysis of the algae-to-biodiesel process via subcritical extraction

Mass and energy balances were evaluated to perform LCA analysis of the algae-to-biodiesel process. This study also compared the energy requirements of subcritical water and subcritical methanol processes.

1.5 Significance of the Study

The purpose of this thesis was to compare SCW and SCM techniques on the production of biodiesel from *C. pyrenoidosa*. The emphasis is put on the extraction of maximum oil yield which is a basis for such extraction techniques. To compare the effects of process parameters, RSM is utilized to optimize the reaction conditions. The commercial application of the subcritical technique is limited due to high operating and investment costs. Kinetics data are crucial in understanding the extraction process in detail. LCA studies provide a better insight into operating costs between these two extraction techniques. The goal of this study is to generate a major interest in utilizing subcritical extraction in a wide-scale commercial biofuel production facility exploiting algae as a renewable source.

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LIST OF PUBLICATIONS

Thiruvenkadam, S., Izhar, S., Hiroyuki, Y., & Harun, R. (2019). One-step microalgal biodiesel production from *Chlorella pyrenoidosa* using subcritical methanol extraction (SCM) technology. *Biomass and Bioenergy*, *120*, 265-272.

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