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Synthesis of biodiesel from vegetable oils wastewater sludge by *in-situ* subcritical methanol transesterification: Process evaluation and optimization

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ABSTRACT

Biodiesel are gaining increased public and scientific attention as an alternative to petroleum diesel fuel, driven by factors such as oil price spikes, energy security and environmental concerns. In this study, low grade wastewater sludge originated from wastewater treatment unit of vegetable oil factory as a viable alternative lipid source for biodiesel production was evaluated. The lipid mass fraction of the dry and ash-free sludge was 12.44 ± 0.87%, which mainly comprised of C16–C18 fatty acids. The *in-situ* transesterification process under subcritical water and methanol conditions was applied as a green pathway to convert lipids into fatty acid methyl esters (FAMEs). The reaction parameters investigated were temperatures (155–215 °C), pressures (5.5–6.5 MPa) and methanol to lipid mass ratios (1:1, 5:1 and 9:1). The highest FAME yield of 92.67 ± 3.23% was obtained at 215 °C, 6.5 MPa and methanol to lipid mass ratio of 5:1. Statistical analysis based on response surface methodology in 3-factor-3-level central composite designed experiments and analysis of variance were applied to examine the relation between input parameters and the response and to locate the optimum condition. Results showed that 98% of the variability in the response could be adequately explained by the second-order polynomial model. The optimum FAME yield (90.37%) was obtained at 215 °C, 6.5 MPa and methanol to lipid mass ratio of 5.12:1. Experimental validation ($N = 3$) demonstrated satisfactory agreement between the observed and predicted values with an error of at most 3.3%.

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1. Introduction

The development of sustainable biofuels is vitally crucial to global transportation and many industrial operations to generate electricity and heat. Such today's concern is driven by long-term supply issue associated with fossil fuels and their environmental impacts due to the release of carbon dioxide, SO_x and NO_x pollutants during fuel combustion. One of potential alternative and sustainable biofuels which have been extensively studied and now commercially produced is biodiesel. Although biodiesel produces less air pollutants and is fast becoming a currently recognized substitute and/or blending agent for petroleum diesel, yet it still possesses key limitations include a heavy price, life-cycle assessment and the necessity of a vast land to produce enough biofuel without threatening food supplies and biodiversity.

There are a number of factors affecting high variable costs in the production of biodiesel, limiting the fuel's widespread use. In this light, the cost of biodiesel feedstock is the most burdensome, which accounts for 70–85% of total cost of production [1]. Palm oil [2], soybean oil [3], corn oil [4], rapeseed oil [5], sunflower oil [6], sesame oil [7], rice bran oil [8] and a number of other food crops have all served as feedstock for biodiesel, however they all suffer from the same problems including threatening the food chain, increasing carbon emissions when planted outside traditional agricultural settings and intense growth requirements. Animal fats such as beef tallow [9], poultry fat [10], fish oil [11] and pork lard [12] have been investigated to produce biodiesel. Although much of animal fats are not considered edible by humans and their cost is substantially lower than the cost of vegetable oils, yet their applications can be challenging because they frequently contain contaminants (e.g., phospholipids and gums) that should be removed before the fuel is used in an engine and also animal fat-based biodiesel typically has higher viscosity and sulfur content. Therefore, it is necessary to gain a new perspective on the production of biodiesel by seeking an alternative feedstock, which is non-food crops and easily obtainable in large quantities. Recently, municipal wastewater sludge is being explored for its untapped potential as a cheap and readily available lipid feedstock for sustainable biodiesel production. The sewage sludge is a by-product generated after wastewater treatment and usually a blend of thickened primary and secondary sludges. This sludge contains considerable mass fraction of lipids (up to 30%) either as a composite organic matrix (oils, greases, sterols, fats and long-chain fatty acids) originated from direct adsorption of lipids in municipal and industrial wastewater or from phospholipids in the cell membrane of microorganisms, their metabolites and by-products of cell lysis [13]. The conventional technology to produce biodiesel from sewage sludge is by a two-step process involving lipid extraction using organic solvents and then alcoholysis of extracted lipids. However, this usual approach poses a great challenge for industrial practice. The lipid recovery process from sewage sludge is tedious and costly because it requires huge amounts of organic solvents and large vessels with stirring and heating systems. Also, most of organic solvents used for extracting lipids are not environmentally acceptable. In addition, the alcoholysis either by esterification or transesterification using liquid or solid catalysts often creates limitations in the catalyst recovery, yield and purity of biodiesel and treatment of wastewater. Kwon et al. [14] had demonstrated a thermochemical approach to transform lipids to biodiesel employing a catalyst-free, continuous flow system. However, non-catalytic thermochemical process suffers from the drawback of intense energy consumption due to the use of high temperatures (350–500 °C) although nearly complete conversion reaction is achieved within a short period of time.

Subcritical water (SubCW), that is, pressurized water at temperatures above the boiling point at ambient pressure and below critical point (T_C = 374 °C), is considered as a unique and green reaction medium for various applications including catalytic/non-catalytic reactions, biomass transformation to chemicals and materials and extraction of bioactive compounds from natural matrices. Several relevant properties of SubCW as a reaction medium are miscibility, ionic product, electrolytic solvent power, dielectric constant and transport properties (e.g., viscosity, diffusivity and ion mobility). The physicochemical properties of interest of SubCW can be tuned through changes in pressure and temperature. With the increase of temperature, there is a marked and systematic decrease in permittivity, viscosity and surface tension while the diffusion rate increases [15]. In the extraction of lipids by SubCW, the process is feasible at mild temperatures (typically 150–200 °C) due to reduced dielectric constant of water, making it capable to extract weakly polar to non-polar compounds. A successful implementation of SubCW as a green alternative solvent to recover lipids from wet algae [16] and dewatered activated sludge [17] has been reported and the possibility of producing biodiesel from wet activated sludge without any catalyst under subcritical water and methanol condition has been investigated by Huynh et al. [18]. In their recent paper, dried activated sludge was used instead of wet activated sludge as the lipid feedstock and water was added prior to methanolysis. Drying of wet activated sludge is a time-consuming as well labor- and energy-intensive process and for large-scale operation, this process is not economically feasible due to large fuel consumption in drying machine or huge land area for sun drying process.

To date, limited studies on the production of biodiesel from wet activated sludge can be found in literature. In most cases, transesterification is performed under catalytic action of acidic or base homogeneous/heterogeneous catalysts, either in single or two-step processes. In contrast to such method, the *in-situ* transesterification procedure under subcritical alcohol condition is an ongoing area of intense research. Therefore, the aims of this study are to evaluate *in-situ* transesterification of wet wastewater sludge to fatty esters under subcritical water and methanol conditions along with the influencing parameters (temperature, pressure and methanol to lipid mass ratio) and to determine the optimum reaction condition by employing response surface methodological approach (RSM) and analysis of variance (ANOVA). Several key properties of biodiesel is also investigated and compared to ASTM D6751 standard.