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# Reactive extraction of after-stripping sterilized palm fruit to biodiesel

Ponsak Jairurob [a,b], Chantaraporn Phalakornkule [a,b,*], Anamai Na-udom [c], Anurak Petiraksakul [a,b]

[a] Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand
[b] The Research Center for Renewable Energy and Product, Science and Technology Research Institute, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand
[c] Department of Mathematics, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand

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ABSTRACT

Biodiesel from crude palm oil (CPO) is conventionally produced via a two-step method: oil extraction followed by an esterification/transesterification reaction of oil to fatty acid methyl esters (FAME). In this study, a single-step *in situ* extraction and transesterification method (collectively known as reactive extraction) of CPO in palm fruit fiber from mesocarp to biodiesel was investigated. The reaction parameters studied include catalyst loadings (1–4% KOH w/v), reaction time (8–11 h) and mole ratios of methanol to oil (147:1–225:1). An optimum biodiesel yield of 97.25% w/w was obtained under the following reaction conditions: catalyst loading of 3.85% w/v of KOH, reaction period of 9 h and 36 min, methanol to oil mole ratio of 225:1 and reaction temperature of 60 °C. The biodiesel yield based on palm fresh fruit bunch (FFB) was found to be 272 and 175 g biodiesel per kg FFB by the single-step reactive extraction method and the conventional two-step extraction followed by reaction method, respectively.



## 1. Introduction

Biodiesel for transportation has been one of the options being promoted worldwide for sustainable energy. For tropical and subtropical countries such as Malaysia, Indonesia or Thailand, there are many kinds of plant oils which can be used as the feedstock for biodiesel production. These include palm, coconut and jatropha oils. Nevertheless, CPO is found to be the most attractive feedstock for industrial production of biodiesel [1]. The production of biodiesel from CPO in Thailand has increased steadily for the past 4 years; from 0.35 million tons in 2008 to 0.654 million tons in 2011. The attractiveness of palm lies in its high yield of oil, which by far exceeds that of other vegetable oils, and its lower production cost [2].

Conventional methods for producing biodiesel from palm oil involve various stages: oil extraction, purification and subsequent esterification/transesterification. If refined palm oil is used as the feedstock, these multiple biodiesel processing stages constitute more than 70% of the total biodiesel production cost [3,4]. Therefore, CPO is more commonly used for biodiesel production than refined palm oil. In the conventional biodiesel production process, extraction of oil can be performed by both physical and chemical methods. A typical physical method is to sterilize FFB by steam under pressure and subsequently to extract oil by means of screw presses. The main disadvantage of the screw pressing is that approximately 5–8% of the oil in the FFB cannot be extracted by this process. An alternative chemical extraction method involves the use of solvents, especially hexane, to dissolve oil from palm fruits at high temperatures. However, even though this solvent extraction method recovers almost all the oils from the palm fruits, it is relatively costly due to additional equipment and solvent costs.

In an attempt to reduce the costs associated with this solvent extraction process, an alternative single-step process has been investigated. This single step process involves *in situ* extraction and transesterification (collectively known as reactive extraction). In this reactive extraction process, extraction of oil and transesterification proceeds in a single step in which the alcohol reacts with the oil-bearing material directly instead of with previously extracted oil. In other words, in the single-step process, the alcohol acts both as an extraction solvent and as a transesterification reagent during the reactive extraction. As a result, a higher amount of alcohol is required. However, the reactive extraction eliminates the requirement for two separate processes of extraction and transesterification, and therefore the single-step *in situ* extraction and transesterification may reduce processing time and equipment cost [5]. Furthermore, in a previous study of the reactive extraction of soybeans, it has been demonstrated that the reactive extraction process can be scaled up without encountering problems that could arise from mass and heat transfer limitations [6].

* Corresponding author at: Department of Chemical Engineering, Faculty of Engineering, King Mongkut's University of Technology North Bangkok, Bangkok 10800, Thailand. Tel.: +66 (0) 8 9 135 3253; fax: +66 (0) 2 587 0024.
*E-mail addresses:* cpk@kmutnb.ac.th, cphalak21@yahoo.com (C. Phalakornkule).

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The main objective of this research was to investigate the reactive extraction process for biodiesel production from oil-bearing palm fiber. In particular, the aim was to find the reaction parameters that would maximize the biodiesel yield from the process. Both the one-factor-at-a-time method and a Taguchi experimental design were used to investigate the effects of catalyst loadings (1–4% KOH w/v), reaction time (8–11 h) and mole ratios of methanol to oil (147:1–225:1) on the biodiesel yield. The biodiesel properties, the reaction yield (g biodiesel/g reactant oils) and the total yield (g biodiesel/kg FFB) from this single-step reactive extraction process were then compared with those from the conventional two-step method for biodiesel production from CPO.

**Table 1**
Profiles of fatty acids in the oil extracted from A-sSPF.

| Fatty acid composition (% w/w) | Typical fatty acid composition of palm oil [21] | Oil extracted from A-sSPF |
|---|---|---|
| Lauric acid (C12:0) | 0.30 ± 0.12 | 0.25 |
| Myristic (C14:0) | 1.10 ± 0.08 | 1.01 |
| Palmitic (C16:0) | 43.5 ± 0.95 | 39.7 |
| Palmitoleic (C16:1) | 0.20 ± 0.05 | 0.21 |
| Stearic (C18:0) | 4.30 ± 0.18 | 4.41 |
| Oleic (C18:1) | 39.8 ± 0.94 | 42.2 |
| Linoleic (C18:2) | 10.2 ± 0.56 | 11.2 |
| Linolenic (C18:3) | 0.30 ± 0.07 | 0.22 |
| Arachidic (C20:0) | 0.20 ± 0.16 | 0.37 |
| Others | – | 0.37 |

## 2. Materials and methods

### 2.1. Materials and characterization

Palm fiber was kindly provided by Suksomboon Palm Oil Co., Ltd. (Chonburi, Thailand). The fiber supplied was mesocarp obtained from sterilized FFB by stripping out the nuts from the fruit (see Fig. 1). The sample will be called after-stripping sterilized palm fruit (A-sSPF) in this article. The fiber used in the study was 2.5–4.5 cm in length, which was the fiber length originally obtained from the factory.

As a preliminary step, the fiber was separated by hand. The oil content in the A-sSPF was measured by the oil and grease method using a Soxtec™ 2050 (Foss, Switzerland) with *n*-hexane as the oil-extraction solvent. In this method, the samples to be analyzed were dried at 105 °C for 1 h and then transferred into thimbles. The sample-containing thimbles were placed in an extraction unit connected to a chamber containing 80 ml of hexane. The three-step extraction procedure consisted of boiling at 185 °C for 20 min, rinsing for 35 min and solvent recovery for 10 min. The oil content was calculated from the ratio of the amount of the extracted oil to the sample weight. This value was used as 'total weight of oil in the sample' in the calculation of reaction yield [5].

Methanol (99.8% purity) was purchased from Merck, Germany. Potassium hydroxide (KOH) was purchased from Ajax Finechem, New Zealand. Pure methyl ester standard compounds (methyl heptadecanoate, methyl palmitate, methyl stearate, methyl oleate, methyl linoleate) were purchased from Sigma–Aldrich, USA.

### 2.2. Reactive extraction

The reactive extraction of A-sSPF was carried out in a duran bottle equipped with an agitator and a heater. Initially, 55 g of A-sSPF was loaded into a 1000 ml Duran bottle. KOH was used as the catalyst of the transesterification. The reaction variables studied were catalyst loadings (0.3–1.2 g of KOH per 30 ml of oil in A-sSPF; equivalent to 1–4% w/v), reaction time (8–11 h), and mole ratios of methanol to oil (147:1–225:1). The molar oil content in the fiber was calculated as the weight of the oil in the fiber divided by its average molecular weight. The average molecular weight of oil was calculated from the average of the individual molecular weights of the triglycerides of fatty acids in the oil extracted from A-sSPF (Table 1). The ranges of the variables were chosen based on a preliminary investigation (data not shown). The mixture was heated to the desired reaction temperature of 60 °C under an agitation speed of 300 rpm. Upon completion of the reaction period, the mixture was cooled and then filtered through cellulose membrane with an 11 μm size particle retention. The solid residue was washed repeatedly with methanol, and the excess methanol in the filtrate was recovered using an evaporator. After evaporation, two layers of liquid were formed. The upper layer was yellow–orange in color containing crude biodiesel, whereas the bottom layer was dark brown in color containing glycerol. Then, the upper layer was washed with water several times until the pH became neutral. After washing, the upper layer was dehydrated by heating at 105 °C for 45 min. The volume of the upper layer was recorded. The heating step was necessary to remove water from the product before the final volume was recorded. However, heating biodiesel at high temperatures may cause oxidation of unsaturated methyl esters, e.g. oleic and linoleic acid methyl esters, and may change cold properties especially the cloud point of the final product.

### 2.3. Chemical analysis

The properties of oil extracted from A-sSPF were evaluated according to standard methods as follows: (i) free fatty acid content (ASTM D5555-95), (ii) acid value (ASTM D974) and (iii) density at 15 °C (ASTM D4052-96). The analysis of fatty acid composition was performed according to AOAC 969.33 (2005).

The testing methods for biodiesel properties were evaluated according to the standard methods as follows: (i) density at 15 °C (ASTM D4052-96), (ii) viscosity at 40 °C (ASTM D445-06), (iii) flash

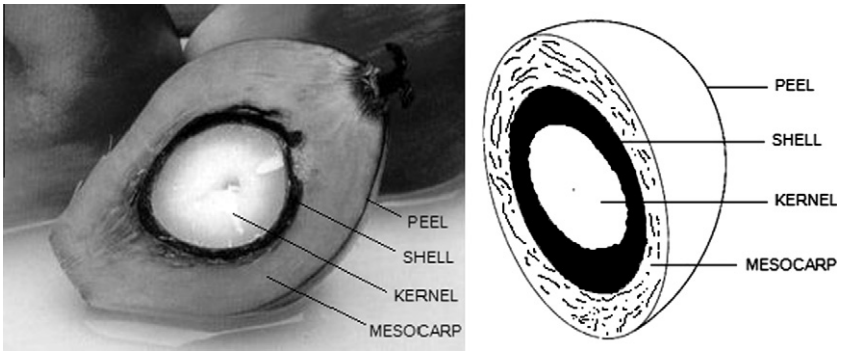


**Fig. 1.** Fresh oil palm fruit and its longitudinal section.