



## Full Length Article

# The response surface optimization of steryl glucosides removal in palm biodiesel using silica adsorption



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## HIGHLIGHTS

- The cause of commercial biodiesel precipitates was identified and solved in this study.
- Steryl glucosides (SGs) containing in biodiesel induced precipitation along with mono- and diglycerides.
- Silica adsorption was proposed for precipitates removal and the optimum conditions were suggested by response surface methodology.
- The optimal conditions could remove 100% of SGs.

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## ABSTRACT

A critical disadvantage of palm biodiesel is the presence of precipitates above the cloud point temperature. Gas chromatography with flame ionization detector (GC-FID) and Fourier transform infrared spectroscopy (FTIR) were employed to identify the composition of the precipitates. The results showed that steryl glucosides (SGs), mono-, and diglycerides were the major precipitates, even when contamination by mono- and diglycerides in biodiesel was in accordance with the ASTM D 6751 and EN 14214 standards. Therefore, this research investigated the optimal removal conditions for SGs in palm biodiesel through response surface design. Three independent parameters were studied: silica concentration, adsorption temperature and adsorption time. The optimal conditions for SGs removal was 3 wt% silica concentration, 112 °C adsorption temperature and 72 min adsorption time. Under these removal conditions, it was found that SGs were completely removed using GC-FID and FTIR analysis. Moreover, this removal treatment provided a higher quality of biodiesel, comprising 99.72% fatty acid methyl ester, 0.38% monoglycerides, 0.09% diglycerides and 0.14% triglycerides.

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## 1. Introduction

Biodiesel is a renewable energy produced from vegetable oils, animal fats or waste cooking oils using transesterification or esterification reactions. The performance of biodiesel is close to that of diesel, so biodiesel may be used directly or blended with diesel in diesel engines [1]. Although the ASTM D 6751 or EN 14214 standards are applied to control biodiesel quality, precipitates above the cloud point temperature of biodiesel can occur during storage and transportation [2]. This causes engine filter clogging or depositing on vehicle injectors [3,4], resulting in increased maintenance costs to clean biodiesel facilities, transportation vessels, storage containers and engine fuel filters [5].

It has been reported that biodiesel precipitates are either steryl glucosides (SGs) or a combination of SGs and other components,

such as intermediate glycerides (monoglycerides, diglycerides and triglycerides), acylated steryl glucosides (ASGs), soaps, antioxidants, free fatty acids, and water. Formation of precipitates depends on types of raw materials, raw material pretreatments, and biodiesel production steps, as well as production processes. The concentration of SGs found in biodiesel produced from soybean or palm oil was 0–158 ppm and 57–276 ppm, respectively [6]. Similarly, Na-Ranong and Kitchaiya [7] reported that palm biodiesel contained 110 ppm of SGs. Additionally, Tang et al. [4] analyzed precipitates from cotton seed, soybean and poultry fat biodiesels. They found both SGs and monoglycerides in precipitates of cotton seed biodiesels, while only SGs were detected in precipitates of soybean biodiesel. An aggregation in poultry fat biodiesel was from monoglyceride contamination. Moreau et al. [8] reported that the solid residues collected at different steps of soybean biodiesel production from commercial plants were SGs and a mixture of SGs with biodiesel intermediates.

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However, contradictory results have also been reported. Researchers have suggested that biodiesel precipitates could result from monoglycerides instead of SGs. Chupka et al. [9–11] mentioned that soy biodiesel containing saturated monoglycerides above a eutectic value markedly raised its cloud point, final melting temperature, and cold soak filtration time. This may promote precipitates in biodiesel above cloud point temperature. In addition, they found that saturated monoglyceride polymorph became more stable and less soluble after measuring by a differential scanning calorimetry (DSC) and observing under a microscope. Its melting point was also increased during a slow heating rate of 1.5 °C/min. Moreover, it was revealed that monoglycerides, glycerine and soap in canola biodiesel increased cold soak filtration time [12], which indicated a risk of filter clogging.

SGs in biodiesel can be removed by several techniques, including adsorption, hydrolysis, cold filtration, centrifugation and vacuum distillation. Na-Ranong et al. [2] compared efficiency of commercial grade magnesium silicate (Magnesol®) and bleaching earth to remove SGs from palm biodiesel. The process was performed at 65–80 °C for 10 min. They found that magnesium silicate had a higher removal efficiency (80% removal) than bleaching earth (60% removal). Aguirre et al. [13] reported that LacS (thermo stable water soluble  $\beta$ -glycosidase enzyme) found in *Sulfolobus solfataricus* P2 reduced SGs concentration in soybean biodiesel from 100 ppm to as low as 20 ppm. The process was carried out under pH of 5.5 and 87 °C for 7 h in the presence of 0.9% of the emulsifier polyglycerol polyricinoleate to promote SGs diffusion to LacS in water-in-oil emulsion. During hydrolysis, SGs were broken down into sterols, which are soluble in biodiesel, and sugars, which can be removed during a washing step. The disadvantage of this method is that polyglycerol polyricinoleate may remain in biodiesel as an impurity. Brask and Nielsen [14] also mentioned that lipase enzyme could convert 10–95% SGs to ASGs, the acylated form of SGs. This can be soluble in biodiesel. However, the process required a long reaction time, as much as 22–43 h. Danzer et al. [15] proposed to use a winterization technology that could separate minor impurities including SGs from biodiesel. Biodiesel was cooled to 4 °C for 1–1.5 h in order to allow impurities to solidify. From 0.1 to 0.25% of diatomaceous earth was then added to form a slurry and was subsequently separated out by a leaf filter. However, major disadvantages were high viscosity of biodiesel at a cold temperature, resisting filtration flowability [16,17], discontinuous operation due to cleaning or changing of the filters after 4–12 h operation, and loss of biodiesel yield because of filter cakes. Lee et al. [18] reported that 70% of SGs in biodiesel might be reduced by filtering it through diatomaceous earth. Silica is an adsorbent generally used in a biodiesel dry washing process in order to eliminate methanol, soap, free glycerol, mono- and diglycerides. Mazzieri et al. [19] proposed that silica efficiently and robustly removed free glycerol and monoglycerides from soybean biodiesel. However, the adsorption efficiency of monoglycerides was lower than that of free glycerol due to higher numbers of hydroxyl groups of glycerol. Faccini et al. [20] reported that 2% of silica concentration was used as an adsorbent to remove certain soap, potassium, water, methanol, free glycerol and bonded glycerides (mono-, di-, and triglycerides) in crude soybean biodiesel. Moreover, Yori et al. [21] mentioned that 4 times of bed volumes of methanol following by drying in nitrogen stream for 1 h may regenerate the silica and methanol can be recycled to transesterification process with no waste.

Therefore, the objectives of this research were to evaluate the optimal removal conditions of SGs and to study the effects of silica concentrations, adsorption temperatures and adsorption times on %SGs removal in palm biodiesel using the Box–Behnken response surface design.

## 2. Materials and methods

### 2.1. Materials

Biodiesel based on a refined bleached deodorized palm oil (RBD biodiesel) was produced by a commercial biodiesel plant in Thailand. The biodiesel was kept in a light-protected container at room temperature. Silica was purchased from Vertical Chromatography Co., Ltd. (Thailand) with 60 Å of pore size, 450–600 m<sup>2</sup>/g of specific surface area, 0.7–0.9 ml/g of pore volume, and 40–63  $\mu$ m of particle size. Before using, the silica was dried at 105 °C for 12 h and placed in a desiccator for 1 h. All chemicals used in this experiment were analytical reagent grade and purchased from Fluka (Switzerland) and Sigma-Aldrich (Switzerland).

### 2.2. Identification of precipitates by gas chromatography with flame ionization detector (GC-FID) and Fourier transform infrared spectroscopy (FTIR)

#### 2.2.1. Precipitate preparation

To identify precipitate composition of RBD and treated biodiesels, the precipitates were prepared. Prior to analysis, 30 mL of RBD biodiesels were stored at room temperature (30–35 °C) while treated biodiesels were refrigerated at 4 °C for 24 h to accelerate precipitation then allowed to return to room temperature. The biodiesels were subsequently centrifuged at 4000 rpm for 10 min (Kubota 7780 centrifuge, Japan). Supernatants were decanted, while precipitates were washed with isoctane three times and dried in a hot air oven (Mettler UF55, German) at 80 °C for 30 min. Samples were then identified mono-, di- and triglycerides, and SGs.

#### 2.2.2. GC-FID identification

The precipitate samples from the RBD biodiesels were identified for mono-, di- and triglycerides by the EN 14105 method. Tricaprin, mono-, di- and trionadecanoate were used as standards. Prior to injection, pyridine and *n*-methyl-*n*-(trimethylsilyl) trifluoroacetamide (MSTFA) were added to the samples as a solvent and a silylation agent, respectively. The analysis was performed by GC-FID (Shimadzu 2010, Japan), equipped with a DB-5HT capillary column (15 m  $\times$  0.320 mm  $\times$  0.10  $\mu$ m, Agilent, USA).

To identify the SGs, the precipitate sample was mixed with pyridine (50 mg), an internal standard, tricaprin solution (50 mg), and MSTFA (100 mg) as a silylation agent. The mixture was silylated at room temperature for 30 min. Heptane (300 mg) was then added. The mixture (1  $\mu$ L) was injected into the GC-FID (Shimadzu 2010, Japan). The temperature program of the GC-FID system was maintained in the oven at 80 °C, 25 °C/min, 250 °C, 15 °C/min, 305 °C (hold 5 min) and 30 °C/min, 345 °C (hold 3 min). The FID temperature was set at 380 °C.

#### 2.2.3. FTIR identification

Precipitates were characterized using FTIR (Bruker tensor 27, USA). The spectrum was carried out in the wavenumber range of 4000–400 cm<sup>-1</sup> with 64 scans and run air as a background.

### 2.3. Experimental design for the maximum percentage of SGs removal using RSM

A three-level three-factor Box–Behnken design was applied to find the optimal performance of SGs removal and to investigate the impact of independent parameters, namely silica concentration (1.0–5.0 wt%), adsorption temperature (80–120 °C), and adsorption time (10–90 min), on the percentage of SGs removal (%SGs removal). The range of three independent factors was based on a

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