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Removal of steryl glucosides in palm oil based biodiesel using magnesium silicate and bleaching earth

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HIGHLIGHTS

- Post-treatment to remove steryl glucosides (SG) from biodiesel (B100) was proposed.
- SG was effectively removed by using magnesium silicate and bleaching earth at 65–80 °C.
- Magnesium silicate had overall performance in SG removal higher than bleaching earth.
- The proposed method could reduce SG to below 20 mg kg^{-1} within 10 min.

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ABSTRACT

Steryl glucosides (SG) may cause problems including accumulation in downstream equipment in production line, storage stability of biodiesel and filter plugging in a diesel engine. In this study, adsorption was used as a post-treatment method to reduce the amount of SG in biodiesel. Commercial grade magnesium silicate (MS) and bleaching earth (BE) were selected as potential adsorbents for SG removal and their performances were evaluated comparatively. To investigate effects of important operating parameters (adsorption time, adsorbent loading and temperature), batch adsorption experiment was performed using palm oil based biodiesel containing 97.6 mg kg^{-1} of SG as a feedstock. The results revealed that efficiency in SG removal of MS was higher than that of BE. In the tested range of 65–80 °C, by treating with 1 wt% of adsorbent, MS could reduce about 81.4–82.5% of SG, whereas BE could reduce only about 48.6–58.9% of SG. Only at low adsorbent loading, the efficiencies of both MS and BE were significantly affected by temperature and then reached the maximum values at temperatures around 70–75 °C. Due to the adsorption treatment, mono-, di- and triglycerides were simultaneously removed and the maximum selectivities towards SG adsorption of MS and BE were 11.8% and 13.5%, respectively. In addition, this adsorption treatment provides the higher efficiency in reduction of the concentration of SG (approx. 20 mg kg^{-1} within 10 min), comparing to a conventional method.

1. Introduction

Generally, biodiesel is commercialized as diesel blends, i.e., B2–B20, which is a mixture of petroleum diesel and 2–20 vol% of biodiesel. Although the quality of biodiesel to be blended with petroleum diesel is controlled by stringent ASTM D 6751 or EN-14214, white solid precipitates were found in biodiesel and diesel blends during storage, especially at relatively low temperature [1]. The use of biodiesel containing the white precipitates or biodiesel, in which white precipitates will further form, may cause filter plugging in engine systems [2,3].

Depending on type of raw material, raw material treatment and biodiesel production process, steryl glucosides (SG) and glycerides (monoglycerides; MG and diglycerides; DG) are two main groups of chemicals that have been considered as a cause of this precipitation [1–10]. Steryl glucosides naturally present in plant oils as free steryl glucosides (SG) and acylated steryl glucoside (ASG) at different amounts. For examples, crude palm oils from Malaysia contain 8–81 mg kg^{-1} of SG and 173–352 mg kg^{-1} of ASG, while the one from India contains much higher SG and ASG; 686 mg kg^{-1} of SG and 2,212 mg kg^{-1} of ASG [11,12]. In addition, the concentration of SG in biodiesel may be higher than that of raw materials since the bond between glucose and fatty acid in molecule of ASG is easily broken under alkaline condition during transesterification [3]. MG and DG are formed from incomplete transesterification of triglycerides (TG) and remain in biodiesel.

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Nomenclature

$C_{SG,0}$	initial concentration of SG in biodiesel (mg kg^{-1})	S_{SG}	selectivity towards SG adsorption (%)
$C_{SG,t}$	concentration of SG in biodiesel at time "t" (mg kg^{-1})	t_{ads}	adsorption time (min)
q_i	amount of component "i" adsorbed on an adsorbent ($mg_i\ g_{ads}^{-1}$)	W_{ads}	mass of adsorbent (g)
		W_{B100}	mass of biodiesel (kg)
R_i	reduction amount of component "i" (%)		

The precipitation in soybean-derived biodiesel related to the presence of SG and might occur even in biodiesel containing SG with the concentration as low as 35 ppm [1]. The precipitation in biodiesel produced from palm oil also related to the presence of SG [3–5]. Moreau et al. [2] reported that the precipitates collected from equipment in supply chain of soybean-derived biodiesel consisted of MG and DG. Tang et al. [6,7] investigated the precipitation at low temperature in biodiesel produced from various raw materials. They found that the precipitates in biodiesel from soybean oil was SG, from poultry fat and palm oil mainly consisted of MG and from cottonseed oil was a mixture of SG and MG. Some recent publications indicated that saturated MG led to precipitation in biodiesels produced from canola oil and/or soybean oil and influenced cold flow properties of these biodiesels [8–10].

In Thailand, biodiesel is mainly produced from palm oil and by-products from palm oil refinery process [13]. White precipitation was observed over a wide range of temperature in many commercial plants and hence additional maintenance is required to maintain high processing efficiency. Furthermore, even the quality of biodiesel fulfilled the requirements of Thailand's regulation, which is similar to EN-14214, fine particles suspending in biodiesel have been occasionally found after storing the biodiesel for several days. In such a case, biodiesel must be reprocessed. The previous work focusing on precipitation in palm oil-based biodiesel (PO-B100) revealed that the precipitates formed in PO-B100 were SG and their compositions were not influenced by storage temperature (20–32 °C) [5]. Therefore, a process to remove SG with reasonable cost is necessary.

Few works focusing on the removal of SG from biodiesel were reported in literature [14–20]. Lee et al. [14] disclosed that filtering crude biodiesel through a bed of sugar, NaCl, citric acid, or diatomaceous earth could reduce SG from 174 ppm to 22–39 ppm. Tang et al. [15] applied cold-soak filtration, adsorption, centrifugation and vacuum distillation to the reduction of SG in biodiesel produced from soybean oil and cottonseed oil. Among these four methods, only vacuum distillation could completely remove SG from biodiesel, while the others could reduce the concentration of SG to as low as 20 ppm but could not further reduce the concentration of SG to below this soluble content. However, vacuum distillation reduced the oxidation stability of biodiesel due to losing of tocopherol, natural antioxidant. Other available approaches are based on enzymatic transformation of insoluble SG into soluble forms, i.e., ASG and free sterols. Enzyme with capable of acylating SG could transform SG in fatty acid alkyl esters (FAAE) into ASG and could reduce at least 20–80% of SG presenting in FAAE [16]. Enzymatic hydrolysis of SG into glucose and sterols could reduce SG up to 81% [17]. SG in biodiesel was also successfully removed by using at least one of enzymes that can acylate and/or hydrolyze SG [18,19].

In order to remove SG from biodiesel by vacuum distillation, biodiesel must be heated to 130–150 °C and vaporized under high vacuum condition (3×10^{-3} torr) [15]. In the case of cold-soak filtration, biodiesel must be refrigerated at 4 °C for 24 h [15]. To apply this cold-soak filtration condition to reduce SG in PO-B100, which has cloud point around 17 ± 1 °C [21], cold-soak temperature cannot be set to be as low as 4 °C and cold-soak time must be prolonged to obtain filterable size of particles. Enzymatic transformation of SG into ASG at 50 °C requires at least 22–43 h of reaction time [16]. To remove SG by enzymatic hydrolysis, an emulsifier is required and must be removed after the reaction [17]. Moreover, a mixture of biodiesel, water, emulsifier and enzyme must be heated to 87 °C for 7 h and pH of the mixture must be carefully controlled at 5.5. Among these techniques, adsorption provides the highest feasibility for industrial scale application, especially when the selected adsorbent has high efficiency and is inexpensive. Magnesol®, a commercial synthetic magnesium silicate, showed good performance in biodiesel dry washing process [22–26]. Berrios and Skelton [24] reported that 0.75 wt% of Magnesol® was enough to reduce soap and glycerol in biodiesel produced from refined and used cooking oils to fulfill standard EN-14214 and removal of methanol by preheating crude biodiesel enhanced performance of Magnesol®. Faccini et al. [25] demonstrated that using 1 wt% of Magnesol® significantly reduced acid value, soap, potassium, water and methanol but slightly reduced free glycerol, MG, DG and TG in crude biodiesel produced from soybean oil. Bleaching earth, mainly consisting of silica, is commonly used in industrial process to purify vegetable oils [27]. It has high removal efficiencies for color materials and can also remove pigments, soap, trace metals, phospholipids, oxidation products and polyaromatics from palm oil [28–30].

In this study, adsorption was used as a post-treatment to reduce SG in high quality biodiesel. Magnesol® and commercial bleaching earth were considered as adsorbents with potential to selectively adsorb SG in biodiesel. The main objectives were to demonstrate the feasibility of using these adsorbents to remove SG from biodiesel and to investigate the effects of important operating parameters, including adsorption time, adsorbent loading and temperature, on performance of these selected adsorbents.

2. Materials and methods

2.1. Materials

PO-B100 was taken from the outlet stream of the vacuum drying unit, where water remaining in biodiesel after wet washing was removed. The temperature of as received PO-B100 was 75 °C and was carefully kept above 70 °C to prevent solid formation in PO-B100 before adsorption experiments.

Magnesium silicate (MS) or Magnesol® obtained from The Dallas Group of America and local bleaching earth (BE), synthesized from Montmorillonite, provided by Bornnet Corporation were used. MS and BE were dried at 110 °C in an oven for 24 h and stored in a desiccator before being used in adsorption experiments.

Heptadecanoic acid methyl ester, 1,2,4-butanetriol, tricaprin, *N*-Methyl-*N*-trimethylsilytrifluoroacetamide (MSTFA; GC derivatization grade), glycerol, monoolein, 1,3-diolein and triolein supplied from Sigma–Aldrich Inc., steryl glucosides (⩾98%) supplied