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Characterization of insoluble material isolated from Colombian palm oil biodiesel

Vladimir Plata [a,*], Paola Gauthier-Maradei [b], Arnold R. Romero-Bohórquez [c], Viatcheslav Kafarov [a], Edgar Castillo [d]

[a] Research Center for Sustainable Development in Industry and Energy, Industrial University of Santander, Carrera 27 calle 9, Bucaramanga, Colombia
[b] INTERFASE, Industrial University of Santander, Carrera 27 calle 9, Bucaramanga, Colombia
[c] Organic and Biomolecular Chemistry Laboratory, Industrial University of Santander, Carrera 27 calle 9, Bucaramanga, Colombia
[d] Colombian Petroleum Institute ICP-Ecopetrol, Autopista Bucaramanga-Piedecuesta kilómetro 7, Piedecuesta, Colombia

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ABSTRACT

Palm oil biodiesel (POB) is characterized by a very high precipitate content. Precipitate has caused potential customers to view POB unfavorably, thereby putting the suitability of this biofuel at risk. Therefore, precipitates isolated from POB were characterized in this study. The precipitates were fractionated by column chromatography, and then characterized using thin layer chromatography, FTIR, GC-FID, differential scanning calorimetry, and thermogravimetric analysis. Characterization revealed the preponderant presence of monopalmitin and free steryl glucosides (FSG) in the precipitates. FTIR suggested the presence of acylated steryl glucosides and fatty acid soaps, and thermal analysis revealed the presence of trace contaminants that may have coeluted with the monopalmitin and FSG during fractionation. All these findings should result in the development of techniques to prevent precipitate formation not only focused on the removal of FSG from POB.

1. Introduction

During the last two decades, biodiesel has emerged as a promising alternative to traditional diesel. It offers the advantage that is renewable, biodegradable, and non-toxic; it also improves lubricity when blended with diesel fuel and reduces greenhouse gas emissions [1]. However, precipitate formation well above the cloud point temperature has limited biodiesel acceptance. Precipitate induces a number of undesired consequences: it may affect process equipment upstream of the tank farm in biodiesel facilities; it may also settle at the bottom of tanks where biodiesel is stored. As a consequence, frequent maintenance is necessary in biodiesel facilities [2]. More important, precipitate has also caused

* *Corresponding author*. Escuela de Ingeniería Química, Universidad Industrial de Santander, Apartado Aéreo 678, Bucaramanga, Colombia. Tel.: +57 7 6344000; fax: +57 7 6344684.
E-mail address: vladimirplata@gmail.com (V. Plata).
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plugging of fuel filters in engine fuel delivery systems and formation of deposits on engine injectors [3].

Currently, there are seven palm oil biodiesel (POB) plants in Colombia with an annual capacity of 550,000 t, making Colombia one of the leaders of biodiesel production in Latin America [4]. These plants are the centerpiece of the Colombian Biofuel National Program. The Colombian Biofuel National Program was designed to develop the agricultural sector, generate permanents job, improve the air quality, and replace illicit crops. However, the viability of this program will be put at risk if precipitate formation is not prevented.

Most techniques developed so far to prevent precipitate formation have focused on either the removal of free steryl glucosides (FSG) present in biodiesel by physical means such as adsorption [5] or the chemical modification of FSG by enzymatic acylation or hydrolysis [6,7]. FSG are glycosylated steryl derivatives naturally present in vegetable oils [8]. Because of their low solubility in biodiesel, researchers have reported that FSG are the main cause of precipitate formation [2,8,9]. However, trace contaminants different from FSG have been identified in biodiesel precipitate (Table 1).

Most of papers regarding the isolation, purification, and characterization of biodiesel precipitate published so far have focused on soybean oil biodiesel (Table 1), and papers focused on POB have been contradictory. Van Hoed et al. [2] found that FSG were the major constituent of the cake collected after filtration of biodiesel between storage tanks in a POB facility. Analogous results were reported by Bondioli et al. [9] and Bondioli [16] for the solid material isolated from a centrifuge in the water washing stage of a POB facility. In contrast, Tang et al. [12] identified only monoglycerides in the precipitate isolated from turbid POB. Therefore, the objective of this study was to characterize precipitates isolated from POB. The precipitates were purified by successive washes with hexane, then fractionated by column chromatography, and then characterized using thin layer chromatography (TLC), FTIR, GC-FID, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Materials

POB was supplied by Ecodiesel Colombia S.A. (Barrancabermeja, Colombia). Distilled palm oil biodiesel (DPOB) was provided by the Colombian Petroleum Institute (ICP-Ecopetrol, Piedecuesta, Colombia). The POB was prepared from degummed, bleached, and deodorized palm oil and was obtained dynamically from a sampling loop in a distribution line in the processing facility. The DPOB was produced in accordance with the ASTM D5236 Standard Test Method. Two types of precipitate were characterized in this study. The first was collected from the bottom of glass containers in which POB was stored at 20 °C for 1 month; the second was collected from the bottom of storage tanks in which POB was stored at ambient temperature (35 °C–40 °C) for 6 months. All solvents were Carlo Erba Reagents (Milan, Italy) and Honeywell International Inc. (Morris Township, NJ) ACS reagent grade. Monopalmitin standard was obtained from Sigma Aldrich Co. LLC. (St. Louis, MO) and was reported to be >99% pure. FSG and acylated steryl glucosides (ASG) standards mixtures were obtained from Matreya LLC. (Pleasant Gap, PA) and were reported to be >98% pure. The composition (mass fraction) of the standard mixtures was 56, 25, and 18%, β sitosteryl, campesteryl, and stigmasteryl glucoside, respectively.

2.2. Biodiesel analysis

Fatty acid composition of the as-received POB was determined by the Chromatography and Mass Spectrometry Laboratory at the Industrial University of Santander (Bucaramanga, Colombia) in accordance with the ISO 5508:1990 and 5509:2000 Standards. Free and total glycerin content (mass fraction) of the POB was provided by Ecodiesel Colombia S.A. FSG content (mass fraction) was determined by the Chromatography Laboratory at ICP-Ecopetrol using a GC-FID method (ICP CLR-CRO-I-

Table 1 – Identity of precipitate originated at various locations.

Feedstock oil	Origin	Analysis	Precipitate identity	Ref.
Soybean Cotton seed Poultry fat	Turbid biodiesel	FTIR, GC-FID	FSG FSG, monoglycerides, free and acylated sterols Monoglycerides	[2].
Soybean	Turbid biodiesel, solid or semisolid material: polish filter cake, transit pipe residue, storage tank bottoms	HPLC-ELSD, HPLC-MS	FSG	[9].
Soybean Palm	Turbid biodiesel	FTIR, GC-FID	FSG Monoglycerides	[10].
Soybean Palm	Solid material: washing centrifuge residue	FTIR, GC-FID	FSG FSG	[11].
Soybean Palm	Turbid biodiesel, solid material: polish filter cake	GC-FID, NMR	FSG FSG	[12].
Soybean	Turbid biodiesel/ultra low sulfur diesel B20 blend	GC-FID, GC-MS	FSG, monoglycerides, unsaturated esters oxidation byproducts	[13].
Canola	Semisolid material: storage tank bottoms	FTIR	Fatty acid soaps, glycerin	[14].
Beef tallow	Turbid biodiesel	GC-FID, TGA	Saturated monoglycerides	[15].