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ORIGINAL PAPER

Comparing Process Efficiency in Reducing Steryl Glucosides in Biodiesel

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Abstract A significant obstacle to the commercial acceptance of biodiesel is the potential for filter plugging due to precipitates in the fuel. The majority of these precipitates can be attributed to either steryl glucosides (SGs) or monoacylglycerols in biodiesel. A GC–FID method to quantify minor components content in biodiesel is presented. The effectiveness of room temperature and cold soak filtration, adsorbent treatment, centrifuge, and vacuum distillation processes for SG removal was studied. The vacuum distillation process is the most effective method of removing the SG from biodiesel.

Keywords Biodiesel · Biofuels (energy)

Introduction

Biodiesel is a renewable and environmentally friendly alternative fuel. However, filter plugging, deposits on injectors and on other critical fuel system components can occur in vehicles using biodiesel blends due to precipitate formation at low-temperatures. Our previous study [1] showed that the formation of precipitates during cold temperature storage depended on the feedstock, blend concentration, and storage time. Moreover, more precipitates were formed in soybean oil (SBO-) based biodiesel blends at 4 °C than cottonseed (CSO-), poultry fat (PF-), and yellow grease (YG-) based biodiesel. In addition, the solvency effects of biodiesel blends were more pronounced at low temperatures than at room temperature leading to a higher amount of precipitate formed. Most of precipitate formation in soybean oil based biodiesel can be attributed to steryl glucoside (SG), while the precipitates formed in poultry fat (PF-) based biodiesel are due to monoacylglycerols; moreover, the precipitates from cottonseed (CSO-) and palm oil (PO-) based biodiesel are due to both SG and monoacylglycerols [2]. These dispersed SG particles, even at relatively low concentration (35 ppm or higher), can result in filter plugging [3].

Typical plant sterol contents are 3,600, 11,800, 4,300, 2,600, and 6,100 ppm for commercial soybean oil, corn oil, cottonseed oil, palm oil, and rapeseed oil, respectively [4]. Plant sterols include four types: free sterols, steryl esters, SG, and acyl steryl glucoside (acyl SG). Approximately 9–37% of the total sterols in foods are glycosidic sterols [4]. The acyl SG concentration is two to tenfold greater than those of the free form of SG. Previous studies reported that crude soybean oil and palm oil may contain about 2,300 ppm SG, while corn oil has 500 ppm SG [3]. Little information exists on SG content in finished biodiesel. One study found that the SG contents ranged from 25 to 270 ppm in SBO-based biodiesel, 8 to 22 ppm in CSO-based biodiesel, 480 ppm in corn oil-based biodiesel, and 140 ppm in PO-based biodiesel [5]. The different levels of SG may be caused by the processing method for vegetable oil and the biodiesel production process [3]. Verleyen et al. [6] found that the neutralization process during the vegetable oil refining significantly reduced the content of the sterols, and the free sterols were distilled from the oil during deodorization. Kochhar [7] reported that the plant sterols were reduced from 10 to 70% after complete refining of vegetable oils. Moreover, the acyl SG can be hydrolyzed to the free form of SG by an alkali-catalyzed transesterification process of the oil to produce biodiesel [8]. However, little literature on the removal of SG in

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post-processing has been published. Lee et al. [3] found that the SG level in biodiesel can be reduced from 68 to 20 ppm by filtering it through diatomaceous earth.

This paper reports on efforts to develop a cost-effective processing technique to reduce SG and acylglycerols in biodiesel, as well as more effective analytical techniques for their determination [3].

Materials and Methods

Materials

SBO-I-based and CSO-based biodiesel was obtained from Biodiesel Industries (Denton, TX), SBO-II-based biodiesel was bought from G. E. Wacker Inc. (Manchester, MI), and SBO-III-based biodiesel was obtained from NextDiesel (Adrian, MI). Certification #2 ultra low sulfur diesel (ULSD) was purchased from Haltermann Products (Channelview, TX). The blends were made on a volume basis and stored in glass bottles at room temperature.

A SG standard was purchased from Matreya LLC (Pleasant Gap, PA). *N*-Methyl-*N*-trimethylsilytrifluoroacetamide (MSTFA), heptane (>99% capillary GC), pyridine (>99%), and α-tocopherol (1,000 IU/g) were purchased from Sigma–Aldrich Inc. (St. Louis, MO). 1, 2, 4 butanetriol (1 mg/mL, internal standard 1 (ISTD1)), tricaprin (8 mg/mL, internal standard 2 (ISTD2)) in pyridine, monoacylglycerols, diacylglycerols and triacylglycerols standards were obtained from Supelco (Bellefonte, PA). Filter aids, including PURIFIDE 200, FW 6, and FW 12 of Diatomaceous earth (DE) and cellulose blend were obtained from EP Minerals, LLC. (Reno, NV). B600 and B800 of ARBOCEL cellulose fibers, and EFC250C, EFC250C +, EFC950, and EFC950C + of filtracel cellulose of silica gel encapsulated fibers were obtained from J. RETTENMAIER & SÖHNE (JRS, Germany).

Analytical Procedures

Composition

The fatty acid methyl ester (FAME) composition of untreated and treated biodiesel samples were analyzed using a PerkinElmer Clarus 500 gas chromatograph mass spectrometer (GC–MS) with a split automatic injector and an Rtx-WAX (Restek, Bellefonte, PA) column (length: 60 m; ID: 0.25 mm, coating: 0.25 μm). The column was held at 120 °C for 1 min and ramped to 240 °C at 20 °C/min, and it was then held at 240 °C for 13 min. The transfer line between GC and MS was kept at 240 °C.

Kinematic Viscosity, Acid Number, and Oxidative Stability

The viscosity of biodiesel at 40 °C was determined following ASTM D 445 [9] using a Rheotek AKV8000 automated kinematic viscometer (Poulten Selfe & Lee Ltd., Essex, England). The acid number was determined according to ASTM D 664 [10] using a Brinkmann/Metrohm 809 Titrando (Westbury, NY). Oxidative stability was determined as induction period (IP) according to EN14112 [11] using a Metrohm 743 Rancimat instrument (Herisau, Switzerland).

Cold Flow Properties

The cloud point (CP), pour point (PP), and cloud filter plugging point (CFPP) measurements were done as per ASTM standards, D 2500-05 [12], D 97-96a [13], and D 6371-05 [14], respectively. A Lawler model DR-34H automated cold properties analyzer (Lawler Manufacturing Corporation, Edison, NJ) was used to measure the cold flow properties.

Minor Components Contents

The content of SG, free and total glycerin, and α-tocopherols were analyzed with a PerkinElmer Clarus 500 GC–FID. Free glycerin and total glycerin were determined according to ASTM D 6584 [15]. The absolute difference between two independent single test results did not exceed the repeatability limit of ASTM D 6584 method. A standard solution of SG was prepared with pyridine, while a standard solution of α-tocopherol was prepared in heptane. The biodiesel sample (~100 mg) was dissolved in 200 μL of pyridine. The standard solution or the biodiesel solution and then was mixed with 20 μL of ISTD2, and 100 μL of MSTFA in a vial, and allowed to sit for 30 min at room temperature. Finally, 2 mL of heptane was added to the vial. A PE-5HT column (15 m in length, with a 0.32 mm internal diameter, and a 0.1 μm film thickness) was obtained from PerkinElmer (Shelton, CT). It was held at 50 °C for 1 min and then ramped to 180 °C at 15 °C/min, 230 °C at 7 °C/min, and 380 °C at 30 °C/min. Finally, it was held at 380 °C for 10 min. Hydrogen (99.9999%, Cryogenic Gases, Detroit, MI) was used as the carrier gas with a flow rate of 3 mL/min.

Process Treatments

Room Temperature (RT) and Cold Soak Filtration

One-hundred milliliter of fuel in 250-mL media bottles with fluoropolymer resin-lined caps were stored at room

temperature or in a refrigerator at 4 °C for 24 h before filtering process. After the cold soak was completed, the sample was removed and allowed to come to room temperature without external heating before filtering. The biodiesel (B100) was filtered using the filtration apparatus according to the Annex A.1 of D6751-08 [16]. One membrane filter was placed on the filter support, and then the filter funnel was clamped to the support. One hundred milliliter of the fuel was poured into the funnel and filtered into a clean 500-mL glass suction flask, maintained at 68 kPa by a KNF Laboport filtration pump (KNF Neuberger INC. Trenton, NJ). The filtration time was recorded. If the filtration of 100 mL was not completed after 1,800 s, the volume filtered was recorded and the filtration stopped. Different pore sizes (0.7, 2.6, 25 μm) of paper and glass fiber filter materials (Whatman) were used.

Adsorbent Treatment

Adsorbent (ca. 5 wt.%) was added in 100 mL of CSO-based biodiesel samples, and then mixed at 200 rpm for 2 h at 4 °C, followed by filtering through a 0.7-μm GF/F glass fiber filter using the filtration apparatus. 1% of PURIFIDE, 1% of EFC 250C+, or the combination of 0.5% of PURIFIDE and 0.1% EFC 250C+ were added to SBO-based biodiesel and mixed at 200 rpm at 24 h, then the treated samples were filtered.

Centrifugation

One-hundred milliliter of biodiesel was centrifuged at 4,000 rpm (Eppendorf centrifuge 5804R, Germany) for 10 min; the upper layer of fuel was removed and analyzed.

Vacuum Distillation

One-hundred milliliter of biodiesel samples was distilled under reduced pressure (3×10^{-3} torr) and a temperature range of 130–150 °C using a Koehler (Bohemia, NY, USA) K80200 vacuum distillation apparatus.

Results and Discussion

Quantification of SG and α-Tocopherol Contents

Figure 1 shows the GC chromatograph for standard reference SG (from 15 to 150 ppm) and corresponding calibration curve (which was forced through zero). Peaks at 18.85, 20.61, 20.65, and 20.74 min are due to tricaprin (ISTD2), campesterol glucoside, stigmasterol glucoside, and β-sitosterol glucoside, respectively [1]. A calibration curve over a range of 15–150 μg SG was constructed using

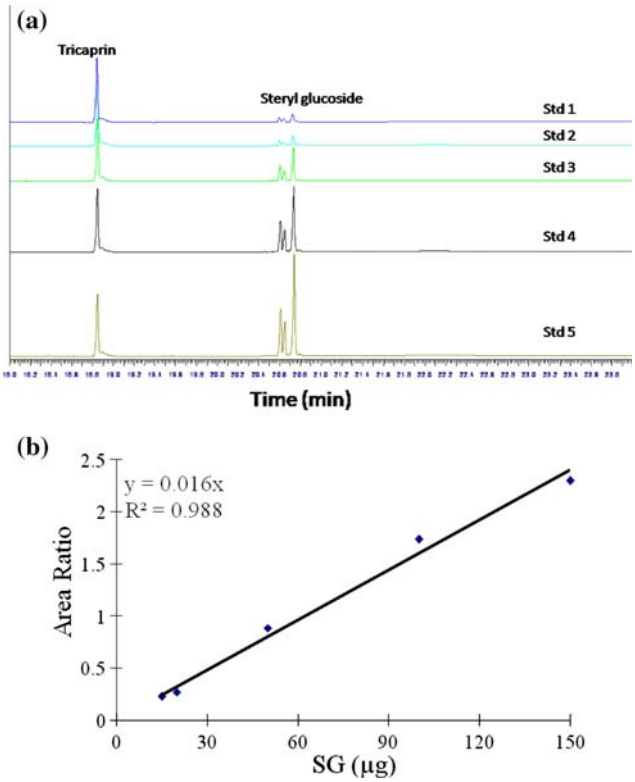

Fig. 1 **a** Representative GC–FID chromatograms of reference standard SG at different level of content, **b** calibration of response area ratio (SG area/tricaprin area) versus mass of SG

the mass versus chromatography response area ratio (SG/ISTD2). The GC chromatograph of standard reference α-tocopherol (from 20 to 200 ppm) and corresponding calibration curve are shown in Fig. 2. Peaks at 17.42 and 18.62 min are attributed to α-tocopherol and tricaprin (ISTD2). A calibration curve with a range of 40–400 μg tocopherols was constructed using the mass versus chromatography response area ratio (tocopherols/ISTD2). The recovery and repeatability tests were carried out by mixing a solution of standard reference SG in pyridine or α-tocopherol in heptane with distilled biodiesel. The final SG and α-tocopherol concentration in biodiesel were approximately 80 and 400 ppm, respectively. The average SG and α-tocopherol recovery rates were 97.9 and 98.1%, respectively (Table 1). Figure 3 shows the chromatograms of the lower layer of the SBO-II-based biodiesel and of that by vacuum distillation. For SBO-II-based biodiesel, typical peaks of mono-glycerides, α-tocopherol, free sterols, ISTD2, di-glycerides, SG, and tri-glycerides are observed in Fig. 3a (based on reference chromatograms [2]), while for the vacuum-distilled sample only a trace of mono-glycerides was found (Fig. 3b). These results demonstrate that SG and tocopherols in biodiesel can be successfully and directly quantified using GC–FID.

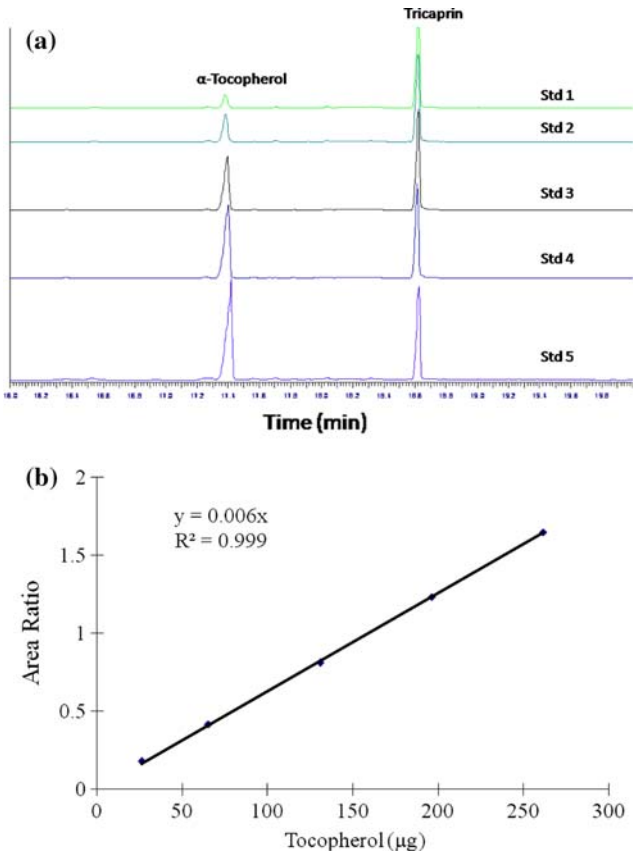

Fig. 2 **a** Representative GC–FID chromatograms of reference standard α-tocopherol at different levels of content, **b** calibration of response area ratio (α-tocopherol area/tricaprin area) versus mass of α-tocopherol

Table 1 Recovery tests of SG and α-tocopherol dissolved in distilled biodiesel

	Test no.			Average value	SD (%)
	1	2	3		
SG (ppm)	69	87	79	78	9.0 (11.5)
Recovery (%)	86.3	108.8	98.8	97.9	0.11 (11.5)
α-Tocopherol (ppm)	415	350	412	392	36.7 (9.4)
Recovery (%)	103.8	87.5	103.0	98.1	0.09 (9.4)

Theoretical SG and α-tocopherol concentration are 80 and 400 ppm, respectively

Influence of Filtration

Filtering is the most simple and direct approach to removing SG and/or other particulate contaminants. The influence of RT soak filtration and cold soak filtration using different type of membrane filter on SG content and filtration time of SBO-I-based biodiesel is represented in Table 2. The untreated SBO-I-based biodiesel contained 55 ppm SG and no precipitate was observed at room temperature. After RT soak filtration, a slight reduction in SG content of SBO-based biodiesel was observed with different pore size of paper and glass fiber membrane filters (from 0.7 to 25 μm). However, there is no significant difference in SG removal with difference pore size and type of membrane filter. The cold soak filtration decreased the SG content of SBO-I-based biodiesel from 55 to 40 ppm, slightly more than RT soak filtration. This is consistent with previous findings that the measured mass of precipitates for RT stored SBO-B100 was about 5 ppm, while there was about 10 ppm for the SBO-B100 sample stored at 4 °C [1]. It should be noted that the type and pore size of the membrane filter had an effect on the flow rate of filtration; however, the flow rate of filtration had no influence on the quantity of SG removed.

CSO-based biodiesel possessed 182 ppm of SG and precipitates were not seen at room temperature. The higher level of SG content in CSO-based biodiesel made the sample flow slower compared to SBO-I-based biodiesel. Similarly, RT and cold soak filtration can reduce the SG content from 182 ppm to 145–157 ppm for CSO-based biodiesel (Table 3). The nature of the precipitate from CSO-based biodiesel is attributed to SG and monoglycerides.

Influence of Adsorbents

The effect of various adsorbents on SG content of CSO-based biodiesel after treatment is shown in Table 4. The largest decrease in SG content of CSO-based biodiesel is from 182 to 157 ppm with EFC250C+, followed by FW 12, EFC 950 C+, EFC 250C, while the lowest efficiency of SG removal is with PURIFIDE. The EFC 950, FW 6, B800, and B600 had a similar influence on reducing the SG. It indicated that the adsorbent treatment had no extra effect on reducing SG content in CSO-based biodiesel, as compared to cold soak filtration. Moreover, reduced filtration time with adsorbent treatment was observed as compared to cold soak filtration. This shows that the adsorbent treatment significantly improved filtration performance. This can be attributed to the high porosity of the adsorbent, the intricate and porous structures of which creates networks of void spaces that result in buoyant filtration media particles that have densities apparently similar to those of the fluids in which they are suspended [17].

Influence of Process Strategies

Table 5 shows the influence of process treatments with RT soak filtration, cold soak filtration, adsorbent treatment (AT), centrifugation, and vacuum distillation on SG content, total glycerin, and α-tocopherol content of two of

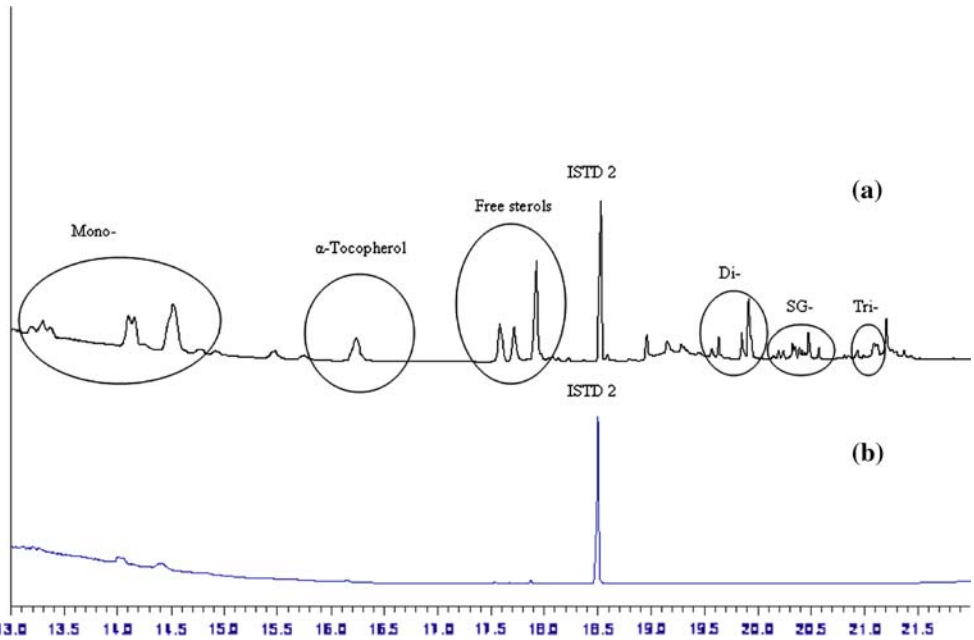

Fig. 3 Representative GC–FID chromatograms of **a** SBO-II-based biodiesel at the lower layer, **b** treated SBO-II-based biodiesel by vacuum distillation

Table 2 Influence of membrane filter on filtration time and steryl glucosides (SG) content for SBO-based biodiesel at 4 and 23 °C

SBO-based biodiesel	Type of membrane filter	Filter pore size (μm)	Storage temperature (°C)	Filtration time (s)	SG content (ppm)[a]
Blank	–	–	–		55 ± 3
1	Paper	20–25	23	72	48 ± 5
2	Paper	2.6	23	133	47 ± 7
3	Glass	2.6	23	18	49 ± 3
4	Glass	0.7	23	63	49 ± 3
5	Glass	2.6	4	53	40 ± 5
6	Glass	0.7	4	129	40 ± 3

[a] Three sets of experiments were conducted and data presented are the averages of SG ± standard deviation

Table 3 Influence of filter on filtration time and SG content for CSO-based biodiesel at 4 and 23 °C

CSO-based biodiesel	Type of membrane filter	Filter pore size (μm)	Storage temperature (°C)	Filtration time (s)	Left volume (mL)	SG content (ppm)[a]
Blank	–	–	–			182 ± 1
1	Paper	20–25	23	36		145 ± 6
2	Paper	2.6	23	>1,800	48	152 ± 3
3	Glass	2.6	23	>1,800	36	147 ± 2
4	Glass	0.7	23	>1,800	89	154 ± 2
5	Glass	2.6	4	>1,800	44	156 ± 4
6	Glass	0.7	4	>1,800	74	157 ± 4

[a] Three sets of experiments were conducted and data presented are the averages of SG ± standard deviation

SBO-II-based sample. Two of the samples were obtained from different positions in the storage tank. One of the SBO-II-based samples was obtained from the bottom layer of the tank and contained 161 ppm of SG, 0.078% total glycerin, and 36 ppm of tocopherol, the other was obtained from the upper layer of the tank and contained 18 ppm of SG, 0.038% of total glycerin, and 30 ppm of tocopherol. Natural settling led to different SG content in SBO-II-based biodiesel. For higher levels of SG content of SBO-II-based biodiesel, the precipitates were observed at room temperature. A significant reduction from 161 ppm to 15–19 ppm of SG content was found after RT and cold soak filtration. A similar reduction in SG content was observed during both adsorbent treatment with different types of compounds and centrifuge treatment, while the vacuum distillation process decreased the SG content to

Table 4 Influence of adsorbents (5% wt) on filtration time and SG content for CSO-based biodiesel after adsorbent treatment at 4 °C for 2 h

Type of absorbent	Filtration time (s)	SG content (ppm)[a]
Blank	>1,800	182 ± 1
PURIFIDE	410	176 ± 2
FW6	221	167
FW12	150	159 ± 3
B600	619	170 ± 2
B800	577	169 ± 4
EFC250C	161	163 ± 2
EFC250C+	270	157 ± 2
EFC950	137	166 ± 4
EFC950C+	256	161 ± 2

[a] Three sets of experiments were conducted and data presented are the averages of SG ± standard deviation

non-deductible level. For low SG content of sample, no insoluble matter was observed at room temperature. SG was completely removed after the distillation process, while no significant change in SG content was observed after RT and cold soak filtration, adsorbent treatment and centrifuge process. These results suggest that the vacuum distillation process is the most effective method of reducing SG in biodiesel and can completely remove SG even at the lower concentrations. The RT and cold filtration, adsorbent treatment, and centrifuge treatment can significantly reduce SG content by removing the precipitates. However, there is a threshold SG content in biodiesel (about 20 ppm) below which the SG content could not be reduced further for the RT and cold filtration, adsorbent treatment, and centrifuge treatment. A similar study reported that 117 ppm of SG content in SBO-based biodiesel was reduced to 20 ppm when passed through a bed of DE [18].

During RT and cold soak filtration, 84–87% of SG in the higher level SG content of SBO-II-based biodiesel decreased (Table 5), while only 11–27% of SG in SBO-I-based biodiesel was reduced (Table 2), and 14–15% of SG in CSO-based biodiesel were removed (Table 3). The significantly different reduction for SBO-based biodiesel samples may due to the fact that SBO-I-based biodiesel has a higher viscosity (4.50 mm^2/s) than that of SBO-II-based biodiesel (4.06 mm^2/s), and the precipitates were seen in SBO-II-based biodiesel at room temperature. Similarly, the higher viscosity with no precipitates observed at room temperature for CSO-based biodiesel may result in lower efficiency in reducing SG content. This indicates that the higher viscosity of the sample has a negative impact on removing SG during the filtration process.

The total glycerin was reduced from 0.078% to zero after the vacuum distillation process, while the centrifugation process decreased the total glycerin to 0.038%. There was no significant change of total glycerin after RT and cold soak filtration, and adsorbent treatment. For the other sample (0.038% of total glycerin), the total glycerin decreased to zero during the vacuum distillation process. However, the other methods had no influence on total glycerin content in biodiesel. Lee et al. [18] found that the total glycerin of SBO-based biodiesel was reduced from 0.8154 to 0.7911% with DE through a deep bed. This is in good agreement with our finding that adsorbent treatment with DE has no significant effect on reducing the total glycerin of SBO-based biodiesel. These results indicate vacuum distillation is the most effective process for removing the acylglycerols.

The natural antioxidant content is one of the important factors for determining the oxidative stability in biodiesel [19]. The α-tocopherol is one of the most common natural antioxidants in vegetable oils. The tocopherol content of

Table 5 Influences of room temperature soak filtration (RT soak filtration), cold filtration, adsorbent treatment, centrifugation, and vacuum distillation process on SG, free and total glycerin, and α-tocopherol content in two of SBO-based biodiesel samples

Process	Condition	SG (ppm)[a]		Total glycerin (mass %)		Tocopherol (ppm)	
		Bottom layer	Upper layer	Bottom layer	Upper layer	Bottom layer	Upper layer
–	–	161 ± 4	18 ± 2	0.078	0.038	36	30
RT soak filtration	23 °C	18 ± 2	15 ± 1	0.078	0.036	23	23
Cold soak filtration	4 °C for 24 h	17 ± 3	15 ± 3	0.079	0.038	25	27
AT, 1% DE	23 °C for 24 h	17 ± 1	12 ± 2	0.076	0.031	18	23
AT, 1% DE	4 °C for 24 h	16 ± 2	16 ± 1	0.08	0.04	17	23
AT, 1% EFC 250C+ (filter aid)	4 °C for 24 h	15 ± 1	16 ± 1	0.077	0.04	17	25
AT, 0.5% DE + 0.1% EFC250C+	4 °C for 24 h	17 ± 2	13 ± 2	0.078	0.034	17	25
Centrifuge	23 °C	19 ± 2	14 ± 2	0.038	0.04	24	23
Vacuum distillation		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. Not detectable, *DE* diatomaceous earth

[a] Three sets of experiments were conducted and data presented are the averages of SG ± standard deviation

biodiesel was completed removed by the distillation process, while the tocopherol content was decreased to a similar extent with RT and cold soak filtration, adsorbent treatment, and the centrifugation processes. A significant reduction in tocopherol content resulted in poor oxidative stability of the biodiesel.

FAME Composition and Physical Properties of Treated Biodiesel

Table 6 shows the FAME composition, SG, free glycerol, mono-, di, and tri-glycerides, and α-tocopherol content in three of the vacuum-distilled SBO (DSBO-) based biodiesel samples and one of the vacuum-distilled CSO- (DCSO-) based biodiesel, as compared to untreated samples. For all of untreated SBO-based biodiesel samples, the similar FAME compositions were observed: methyl linoleate (C18:2) is the predominant FAME (48.7–55.4%); methyl oleate (C18:1) is the next most abundant FAME (22.6–25.3%), followed by methyl palmitate (C16:0, 10.2–14.1%). CSO-based biodiesel was predominantly methyl linoleate (53.4%), with methyl palmitate having the second greatest abundance (23.2%), followed by methyl oleate (20.8%). There was no significant change in FAME composition for all distilled biodiesel samples as compared to untreated ones. However, SG, free and total glycerin were almost completely removed from all of the distilled biodiesel samples, the natural tocopherol content of DSBO-based and DCSO-based biodiesel was significant decreased. These results indicate that the vacuum distillation process will not affect the FAME

Table 6 Influence of distillation process on fatty acid methyl ester (FAME) composition, SG, total glycerin, and α-tocopherol of three of SBO-based biodiesel and CSO-based biodiesel from different sources

	FAME and minor components compositions							
	SBO-I	SBO-II	SBO-III	CSO	DSBO-I	DSBO-II	DSBO-III	DCSO
C14:0 (%)	0	0	0	0.6	0	0	0	0.5
C16:0 (%)	14.1	11	10.2	23.2	14.9	10.6	11.9	23.2
C16:1 (%)	0.7	0	0	0	0.5	0	0	0
C18:0 (%)	5.2	4.2	4.3	1.6	5.3	4.1	4.0	2.5
C18:1 (%)	25.3	22.6	22.6	20.8	27.2	24.0	22.9	20.0
C18:2 (%)	48.7	55	55.4	53.4	46.9	54.1	54	53.2
C18:3 (%)	6	7.2	7.5	0.5	5.2	7.2	7.2	0.4
∑SFA (%)	19.3	15.2	14.5	25.4	20.2	14.7	15.9	26.2
∑UFA (%)	80.7	84.8	85.5	74.6	79.8	85.3	84.1	73.8
Free glycerin (mass %)	0.006	0	0.002	0.001	0	0	0	0.001
Mono-glycerides (mass %)	0.145	0.061	0.128	0.154	0	0	0	0.002
Di-glycerides (mass %)	0.023	0.014	0.026	0.024	0	0	0	0
Tri-glycerides (mass %)	0.003	0.003	0.007	0.008	0	0	0	0
Total glycerin (mass %)	0.177	0.078	0.164	0.186	0	0	0	0.003
Tocopherol (ppm)	733	36	167	970	37	0	40	47
SG (ppm)	55	161	18	182	n.d.	n.d.	n.d.	n.d.

n.d. Not detectable

Table 7 Influence of distillation process on the physical properties of three of SBO-based biodiesel from different sources and CSO-based biodiesel

Properties	ASTM method	ASTM specification[a]	Untreated samples				Distilled sample			
			SBO-I	SBO-II	SBO-III	CSO	DSBO-I	DSBO-II	DSBO-III	DCSO
Viscosity, 40 °C (mm^2/s)	D 445	1.9–6.0	4.5	4.06	4.14	4.39	4.05	3.98	3.99	4.1
Acid number (mg KOH/g)	D 664	0.5	0.44	0.21	0.46	0.49	0.18	0.2	0.31	0.1
Oxidative stability, IP (h)	EN14112	3 minimum	<1	7.2	2.8	<1	<1	1.43	<1	<1
CP (°C)	D 2500	Report	3	0	3	6	4	−1	−1	5
PP (°C)	D 97		0	0	−3	5	0	0	0	6
CFPP (°C)	D 6371		−1	−3	−3	7	0	−1	−2	5

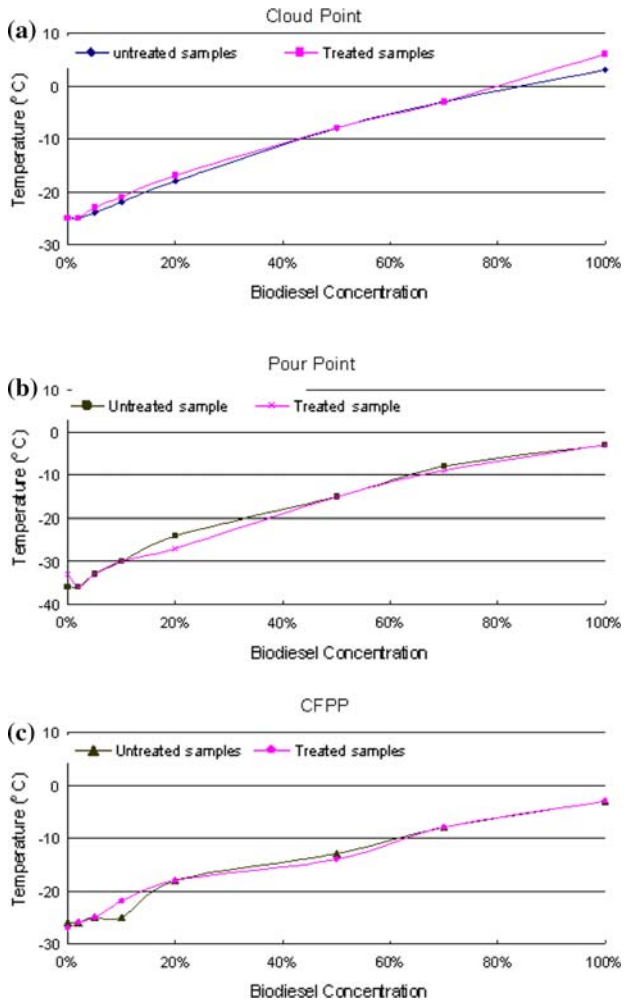

Fig. 4 Comparisons of cold flow properties of SBO-biodiesel blends (from B2 to B100) treated by a cold soak filtration process with untreated ones: **a** cloud point, **b** Pour point, and **c** cold filter plugging point (CFPP)

composition, while significantly reducing the SG, total glycerin, and α-tocopherol content in biodiesel.

Table 7 shows the physical properties of vacuum-distilled biodiesel samples as compared to the untreated ones. All except induction period (IP) were found to be within ASTM D6751-08 specifications. The data show that IP, the viscosity, and acid number significantly decrease for vacuum-distilled samples as compared to untreated ones. The CP, PP, and CFPP remaining relatively constant within experimental error were found for distilled samples. The significantly decreasing IP, viscosity, and acid number can attributed to the removal of minor contents of tocopherol, acids, aldehydes, and dimers formed by oxidation [20, 21]. Moreover, the unchanged cold flow properties suggested that SG content and glycerin content at the tested levels would not affect the CP, PP, and CFPP and the unchanged FAME composition of distilled biodiesel led to the relatively constant CP, PP, and CFPP. This finding is consistent with Pfalzgraf et al. [21] that SG at 40 ppm did not have a negative effect on CP.

Influence of Filtration on Cold Flow Properties for Biodiesel Blends

Figure 4 shows CP, PP, and CFPP of SBO-I-based biodiesel blends with ULSD (from B2 to B100) before and after cold soak filtration treatment. The CP, PP, and CFPP at different concentrations in biodiesel were not significantly changed after the filtration treatment, as compared to untreated samples. This suggested that the tested level of SG (55 ppm or lower) for biodiesel blend has no effect on cold flow properties.

Conclusion

The effect of RT and cold soak filtration, adsorbent treatment, centrifugation, and vacuum distillation on SG, total glycerin, natural antioxidant, FAME, and physical properties of biodiesel were investigated. The following conclusions can be made

1. GC–FID can be used to quantify SG, total glycerin, and α-tocopherol content in biodiesel. The detection limit for SG was below 15 ppm, while below 20 ppm for α-tocopherol.
2. The RT and cold soak filtration, adsorbent treatment, and centrifugation methods can all significantly reduce SG content by removing the precipitates; however, they have no impact on the soluble SG content in biodiesel (about 20 ppm) below which the SG content could not be reduced further, except by vacuum distillation.
3. Vacuum distillation was the most effective method for removing the SG and acylglycerols content in biodiesel in this study; however, it resulted in a significant decrease in the natural antioxidant content reducing the oxidative stability of the biodiesel.

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