Fuel 122 (2014) 287–293

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Precipitation above cloud point in palm oil based biodiesel during production and storage

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HIGHLIGHTS

- Precipitation above cloud point occurred in PO-B100 meeting EN-14214.
- Precipitates from a storage tank, a filter bag and after cold-soak were identified.
- Precipitation in PO-B100 was resulted from steryl glucosides, not monoglycerides.
- Reduction of SG from 110 to 20 ppm significantly improved stability of PO-B100.
- Temperature did not affect the composition of precipitates.

ARTICLE INFO

Article history:
Received 12 October 2013
Received in revised form 15 December 2013
Accepted 4 January 2014
Available online 23 January 2014

Keywords:
Steryl glucosides
Palm oil
Biodiesel
Precipitation

ABSTRACT

Precipitation of a white solid in palm oil based biodiesel (PO-B100) can be found even in PO-B100 that contains minor contaminants (i.e. mono-, di- and triglycerides) within the limitation according to EN-14214 and Thailand's regulation. To identify compounds causing this precipitation, the precipitates collected at the temperature near cloud point and at room temperature were characterized using a gas chromatograph-flame ionization detector, gas chromatograph-mass spectrometry and fourier transform-infrared. The result indicated that the compounds causing the precipitation were steryl glucosides, not glycerides, regardless of temperature. Therefore, effect of steryl glucosides on precipitation time was further investigated using PO-B100s with different amounts of steryl glucosides, mono-, di- and triglycerides. The result revealed that precipitation time of the PO-B100 with high concentration of steryl glucosides was much less than the one without steryl glucosides and decreasing steryl glucosides concentration to 20 ppm significantly improved storage stability of PO-B100. In addition, the precipitation time was not influenced by concentration of mono-, di- and triglycerides.

1. Introduction

Biodiesel or fatty acid methyl ester (FAME) has become a promising green and renewable fuel. It is synthesized from vegetable oils, wasted cooking oils and animal fats. To increase income of farmers in rural area and to decrease country's dependency on petroleum fuel, several countries in South East Asia have set their policies on increasing plantation area of oil palm for biodiesel production. Research and development have been focusing on how to enhance overall process efficiency for obtaining high quality biodiesel; including strain development, plantation, harvest, palm oil production, biodiesel production and by-product and waste utilization. Recently, palm oil and by-products from palm oil refinery process have been mainly used as a raw material for production of biodiesel, called palm oil based-biodiesel (PO-B100), in these countries. Unfortunately, there have been troubles in production line and controlling quality of products due to white precipitate formation. The white precipitate accumulates in pipeline, pumps and downstream equipments hence laborious maintenance is required. Moreover, the precipitation gradually occurs during storage even at room temperature and even in PO-B100 that meets the specification of widely used standards such as ASTM D 6751 and EN-14214. The use of PO-B100 or diesel blends, which may further have the white precipitate, will cause deposition or plugging in an engine system, especially a modern model. To avoid these problems, biodiesel producers have to store their products in a large vessel for several days and pump PO-B100 only from the top layer of the storage tank through a filter bag to eliminate fine particles suspending in the biodiesel before transferring to their

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http://dx.doi.org/10.1016/j.fuel.2014.01.003
0016-2361/

Nomenclature

W_{SG}	weight of steryl glucosides (μg)
A_{SG}	area under the peaks of steryl glucosides (μV s)
A_{ISTD2}	area under the peak of tricaprin (μV s)

customers. In Thailand, even biodiesel producers have included this procedure in their processes and the government also set the goal to commercialize B10, petroleum diesel blending with 10% of PO-B100, over the whole country within 2012, this goal was not successfully implemented. This is resulted from the occurrence of gradual formation of this precipitate. Therefore, the regulation used at present controls the amount of PO-B100 that can be blended with petroleum diesel to be not more than 5%. To overcome this limitation, it is necessary to develop an economical process for preventing this precipitate formation. The main component that causes this problem under Thailand's climate condition has to be clarified to accomplish this goal.

Precipitation in B100 meeting ASTM D 6751 and B20 made from biodiesel meeting ASTM D 6751 has been reported since 2006 in North America, where soybean oil is mainly used as a feedstock for biodiesel production [1]. This precipitation occurs above cloud point (CP) of B100 leading to filter plugging in vehicle engines. Moreover, precipitation occurrence cannot be predicted by cold flow properties of B100 or B20. Archer Daniels Midland Co. (ADM) found that this phenomenon closely related to the presence of steryl glucosides (SG) in biodiesel [1]. Steryl glucosides gradually agglomerated and formed cloud like small particles, due to its low solubility in biodiesel, even in B100 with SG concentration as low as 35 ppm.

Naturally, plant oils contain several types of steryl glucoside (SG) and acylated steryl glucoside (ASG) with different amounts [2]. During transesterification in biodiesel production, ASG is converted to SG. Therefore, the amount of SG in biodiesel increases and may be higher than that of the originated oil. Depending on plant oil, oil refinery process and biodiesel production process, the amount of SG varies from several ppm to several thousands ppm [3,4].

Monoglycerides (MG) and diglycerides (DG) may cause precipitation in biodiesel from other sources such as soybean oil, canola oil and cotton seed oil [5–10]. Moreau et al. [5] analysed the precipitates collected from various equipments in biodiesel supply chain and found that some samples consisted of monoglycerides and diglycerides without steryl glucosides. They claimed that the samples used in their study were likely from soybean oil derived biodiesel. Tang et al. [6] indicated that the precipitate from poultry fat based biodiesel mainly consisted of monoglycerids while the one from cottonseed oil based biodiesel contained both steryl glucosides and monoglycerides.

Some recent studies showed that saturated monoglycerides (SMG) had negative effect on low-temperature performance of biodiesel (i.e. cloud point, final melting temperature and cold soak filtration time) and potentially contributed to the precipitate formation above cloud point in biodiesels from canola oil and soybean oil [7–10]. X-ray powder diffraction and differential scanning calorimetry results showed that phase transformation, from metastable SMG into the more stable but less soluble one, occurred when concentration of SMG was above the eutectic point and the effect on low-temperature performance became more significant [8].

In literature, there are few works focusing on the precipitation in PO-B100 and diesel blends derived from palm oil. Hoed et al. [3] measured the amount of SG in hazy biodiesel produced from refined bleached deodorized palm oil (RBD-PO) and reported that industrial grade RBD-PO-B100 samples contained SG with the amount varying from 55 to 275 ppm. They also identified the main components of the filter cake obtained from filtering biodiesel in a storage tank and of the washed filter cake using nuclear magnetic resonance and mass spectroscopy techniques. The results indicated that the precipitation related to the presence of SG in biodiesel. Bondioli et al. also identified SG as the main component causing precipitation in biodiesel produced from palm oil [4]. However, Tang et al. found that the precipitate formed in PO-B100 after cold soaking at 4 °C for 24 h consisted of monopalmitin, monosterin and monoolein and concluded that the precipitations in PO-B100 and in diesel blends derived from palm oil was resulted from these monoglycerides, not SG [11].

In commercial biodiesel plants located in Thailand, the precipitation in PO-B100 was found in wide range of temperature. It may gradually occur even at 32 °C which is much higher than the cloud point of PO-B100 ($CP_{PO\text{-}B100}$ = 17 ± 1 °C, [12]). To design an economical process for preventing this precipitation, it is necessary to clarify the compound leading to the precipitation which may not be the same at different regions of temperature. Although there are many works focusing on precipitation above cloud point in biodiesel from different sources in literature, predicting the precipitation in PO-B100 from these published results is difficult. This is because the phenomenon is complicated and sensitively influenced by several factors including composition of fatty acid methyl esters, the presence of other impurities and the temperature range. In addition, biodiesels used in these works had cloud point much lower than the cloud point of PO-B100. No comparative study on the precipitation at different temperatures, near cloud point and higher, was reported for PO-B100 in literature. In this study, the precipitation in PO-B100 meeting EN-14214, similar to the specification regulated in Thailand, has been investigated. The objectives of this work were to identify the compounds causing the precipitation near cloud point and room temperature and to investigate how their concentrations affect the precipitation.

2. Materials and methods

2.1. Materials

2.1.1. Samples

To identify the compounds causing the precipitation, PO-B100, P-Cake, Washed-P, Bag-Res, CSP-23 and CSP-32 were characterized. All the samples were obtained from a commercial scale biodiesel production plant in Thailand. Palm oil based biodiesel (PO-B100) was clear light yellowish liquid and was used as received. A mixture of precipitate and biodiesel in the bottom layer of the PO-B100 storage tank was filtered to separate biodiesel from the precipitate. The obtained cake was named as "P-Cake". To remove all biodiesel remained in the cake, P-Cake was washed several times by hexane. Acetone and methanol were also used to wash other polar contaminants that might remain in P-Cake. After washing and subsequent drying at room temperature, the obtained solid was light gray powder and named as "Washed-P". Residue from the filter bag obtained from final filtration step, filtration of the biodiesel pumped from the upper layer of the PO-B100 storage tank through the filter bag before transferring to transportation trucks, was used as received and named as "Bag-Res". Cold-soaking method for