Transesterification of Refined Bleached Deodorized Palm Oil (RBD PO) Using Homogeneous Base Catalyst and Methanol and Investigation of Factors Filter Blocking Issue in Palm Based Biodiesel

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Abstract. The aim of this study is to investigate the major properties of biodiesel causing filter-blocking issue in biodiesel especially for palm oil based, to identify the suitable solution to reduce or eliminate these factors for improving the filter properties of the palm based biodiesel by control the specific parameter (mono-glycerides during intermediate process and minimize or eliminate the Steryl Glycoside after post treatment. This study may give significant impact especially to local industry of biodiesel producer which operated with normal transesterification process and using palm base feedstock to conform international biodiesel specification such as ASTM D D7501 (Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels). In this paper the Filter Blocking Tendency (FBT) testing and Cold Soak Filterability Test (CSFT) testing procedure and result will be presented.

1. Introduction
The filter blocking issue in biodiesel or blend biodiesel is a norm issue especially originated from palm based has been involved many researcher to further investigation. Biodiesel is generally produced by transesterification of the lipid with a short-chain monohydric alcohol. This process may leave behind very small (trace) concentrations of minor constituents such as saturated monoglyceride (MG) or steryl glucosides (SG). These materials have high melting points and very low solubilities allowing them to form solid residues when stored during cold weather. Several researchers were made conclusion the blocking issues caused by minor (trace) contaminants i.e. monoglycerides and or steryl glycoside [1-3]. There are several parameters can be determined the blocking in filter such as The Filter Blocking
Tendency (FBT)-, Cold Soak Filtration Test (CSFT), Cold Filter Plugging Point (CFPP) and etc. In this study, the focus on two parameters i.e. FBT Test Method IP 387 and CSFT Test method ASTM D7510 as to address the proposal made by Malaysian Biodiesel Association (MBA) to include either one of this parameter in MS 2008 specification. The Filter Blocking Tendency (FBT) is the relation between the fuel volume flowing through a standardized filter and the pressure drop across the filter reached during the test at ambient temperature (standard ASTM 2068 considers the range 15–25 °C as acceptable) [4-6]. Biodiesel blended into petroleum refined diesel fuel is increasing the incidence fuel filter clogging. Diesel fuels blended with biodiesel are at risk for potential filter blockage. Sterol glucosides and saturated monoglyceride in the fuel can cause the filter blockage [5, 6]. Biodiesel fuel filter blockage problems occur even though the biodiesel’s CFPP do not predict the likelihood of filter clogging problems. The presence of sterol glucosides at problematic double-digit ppm levels can lead to the formation of a cloudy haze in biodiesel even at room temperature [9]. Biodiesel has an affinity for water and easily absorbs moisture from the atmosphere. This water then supports microbiological growth in fuel storage tanks. At low levels microbes usually don’t make a major impact on fuel functionality, but if left unchecked, bacteria growth can block fuel filters. Biodiesel is a form of diesel fuel manufactured from vegetable oils, animal fats, or waste cooking oil [19,20]. Biodiesel is an alternative fuel for diesel engines that has receiving great attention worldwide. It is renewable, it can be also used either pure or in blends with diesel fuel in unmodified diesel engines, and it reduces some exhaust pollutants. Biodiesel i.e. Palm Methyl Ester (PME) is produced through the transesterification process using RBD Palm Oil as feedstock which reacts through methanol in the presence of sodium methylate as catalyst [21,22]. The PME is meets the EN 14214 and ASTM 2008 specifications are shown in table 1.

Table 1. Typical Results of several parameters of Industry’s palm biodiesel

| Test Parameter | Unit | Method | Specification | Result |
|----------------|------|--------|---------------|--------|
| FAME content   | % (m/m) | EN 14103 | 96.5 min     | 98.3   |
| Monoglyceride  | % (m/m) | EN 14105 | 0.70 max     | 0.52   |
| Water content  | Mg/kg | ISO 12937 | 500 max      | 186    |

2. Process
There are some improvement have approached by improving contact between the oil and alcohol phases, either chemically or mechanically, heterogeneous and enzymatic catalysts, simultaneous extraction and reaction, reaction with simultaneous removal of the product and microwave irradiation.

2.1 Biodiesel Properties, Cold flow properties and method for improving

Many researcher encounter cold flow properties of biodiesel with high saturated fatty acids content is lead to precipitation, clogging and blocking issue in diesel engine. The cold flow properties discussed in this literature review are cloud point (CP), pour point (PP), cold filter plugging point (CFPP), cold soak filterability test (CSFT) and filter blocking tendency (FBT). Biodiesel made from oilseeds with high contents of saturated fatty acids like palm oil shown higher oxidation stability and high heating value but they have cold flow properties worse than other biodiesels due to solidification of the fatty acids at high temperatures [10, 11]. Due to this behaviour, among alternatives for improve cold flow properties in the biodiesel can be finding mixture’s oils with a high content of unsaturated fatty acids, oil fractionation, Alkyl esters structure modification and additive use.

There are two major problems before using biodiesel as a substitute for engine fuel i.e. “cold flow property of biodiesel” and “stability of biodiesel”. Some of the cold flow properties such as a cloud point, pour point and cold filter plugging point are causing solidification of fuel lead to fuel line filter blockage [12]. He also mentioned that crystallization of fatty acid during cold weathers causes fuel starvation and operability problem due to solidified material clogs the fuel lines and filters. More solid is formed with decreasing of temperature and material approaches the pour point which is the lowest temperature at which it will stop to flow.
Dunn, 2009 states the transesterification of the lipid with short-chain monohydric alcohol may leave behind very trace amount of impurities such as saturated moacylglycerols (MAGs) or free steryl glucosides (FSG) which contributed to solid residue formation when stored during cold weather. These settling solid residues were found to clog the fuel filters in fuel dispensers and vehicles. Reference to this clogging problems the biodiesel industry in the United States collaborated with American Society of Testing and Materials (ASTM) to develop cold soak filterability performance test (CSFT) that will help identify fuels may have a tendency to clog filters if exposed to long-term storage and in cold weather.

According to Magin et al., 2018 filter plugging problems caused by some biodiesel components have recently discouraged biodiesel users and suppliers, and triggered normalization actions to limit operability problems in diesel engines. Bioalcohols such as methanol and ethanol have proven to be a sustainable alternative as diesel component and potential to improve the cold flow properties of diesel and biodiesel fuels as far as they remain within the miscible range. The ethanol and n-butanol were blended with diesel and biodiesel fuels showing benefits in cold filter plugging point, cloud point, pour point, freezing point and filterability from certain concentrations. The Filter Blocking Tendency (FBT) is the relation between the fuel volume flowing through a standardized filter and the pressure drop across the filter reached during the test at ambient temperature (standard ASTM 2068 considers the range 15–25 °C as acceptable). The minimum FBT value is 1, which indicates good filterability while higher values of FBT indicate worse filterability, with 2.52 representing a higher limit in some local standards such as UK or Australia. For all the tests carried out in their study, ambient temperature remained between 21 and 25 °C (at which the unstable region for ethanol-diesel blends ranges between 20 and 70% v/v). Pure biodiesel fuel led to the highest FBT values, while pure diesel fuel and pure alcohols have no filterability problems, small alcohols contents improve the filterability of biodiesel. Biodiesels, composed of saturated fatty acid alkyl esters (FAAE), have relatively high cloud points (CP), which limit their commercial application [14,16] above the cloud point issue in biodiesel due to main factor i.e. minor contaminants such as saturated monoglycerides (SMG) and steryl glucoside (SG) [16]. Their focuses on understanding the correlation between cold soak filtration test results and presence of contaminants such as sterol glucosides and saturated monoglycerides in biodiesel fuels.

Other researchers were concluded that minor contaminant such as Steryl glucosides (SG), mono-, and diglycerides in biodiesel causing major precipitates. SG causes accumulation in downstream production line, storage stability of biodiesel and filter clogging in diesel engine. These statement also supported by other researcher mentioned that even though the biodiesel is compliance to ASTM D 6751 and EN 14214 standards, these minor contaminant causing precipitates above the cloud point [15,16]. Other researchers reported these minor contaminants also may interact with moisture, intensifying precipitate formation. Their studies concluded that SG affecting Cold Soak Filterability Test (CSFT)[5].

Another study concluded CSFT was found to be influenced only by Free Steryl Glycoside (FSG) whereas the precipitate content was found to be influenced by FSG, MG, and moisture. Increasing FSG increased precipitation at low levels of moisture; in contrast, when MG increased, the precipitate content decreased. Interaction with moisture worsened precipitation. [16].

The effective method to reduce the amount SG is by using adsorption of magnesium silicate (MS) compared to bleaching earth (BE) for the post-treatment. were investigated the biodiesel fuel consisting of fatty acid methyl esters and made from lipid feedstocks, has presented persistent cold weather operability problems that are not predicted using the standards tests common in the petroleum refining industry [16]. These problems have been referred to as “precipitate formation above cloud point” and are known to be caused by minor impurities such as steryl glucosides (SG), and saturated monoglycerides (SMGs). Steryl glucosides (SG), and saturated monoglycerides (SMGs) were spiked into 100% biodiesel (B100) from various feedstock sources [17]. Only SMGs were found to have a significant effect on the cloud point (CP) and final melting temperature (FMT) in four B100 samples with a range of CP. A large difference between FMT and CP indicates that a metastable phase of SMG forms initially and can transform into a more stable, less SMGs at concentrations above 0.24 wt% caused
failure of the cold soak filtration test (ASTM D7501); however, at higher water concentrations (~1200 ppm), the effect of SMGs was significantly reduced. Addition of SGs had no effect on cold soak filterability [13,17].

Lin, H et al in 2011 had investigated effect of trace contaminants (Saturated monoglycerides (SMG), soap and glycerin) on coal soak filterability of canola biodiesel. The study was found that saturated monoglycerides (SMG) gave significant impact on filtration time after spiked 0.28% in canola biodiesel. Filtration time still passed the ASTM D6751 limit of 360s when biodiesel was spiked to 0.26% SMG. With the further increasing amount of SMG to 0.28%, the filtration time failed to meet the ATSM limit. Refer to figure 1, the contour plots, when soap and glycerin concentration was held at the lowest level, increasing SMG had minor negative impact on filtration time (figure 2) because the value was lower than the estimated SMG solubility (0.28%) in canola biodiesel [4].

Figure 1. Graph of filtration time versus SMG concentration in biodiesel

Figure 2 show the contour plots of cold soak filtration time of canola biodiesel. (A) the effect of glycerin and SMG; (B) the effect of soap and SMG; (C) the effect of soap and glycerine [4].

Figure 2. The graph of cold soak filtration time

When SMG level was held at the lowest level, increasing glycerine and soap concentration increased filtration time from less than 50s to more than 110s (figure 2C) as glycerin forms emulsion in biodiesel which increases the dynamic viscosity and consequently the filtration time. The addition of soap has a more significant effect on filtration compared with glycerine as it is insoluble in biodiesel and could form gels in biodiesel and interact with glycerin to generate a colloidal which obstructs filtration.

Plata et al, in 2015 found the precipitate formation of biodiesel due to presence of free steryl glucosides (FSG) and monoglycerides (MG). These minor components may interact with moisture, worsening precipitate formation [6, 7]. Therefore, the effect of FSG, MG, and moisture content on precipitate formation and filterability of palm oil biodiesel (POB) was investigated. Blends of distilled palm oil biodiesel spiked with the minor components were prepared following a three-factor, five-level
center composite design and tested for the cold soak filtration time (CSFT) and the precipitate content. CSFT was found to be influenced only by FSG whereas the precipitate content was found to be influenced by FSG, MG, and moisture. Increasing FSG increased precipitation at low levels of moisture; in contrast, when MG increased, the precipitate content decreased. CSFT increased with increasing FST content and reached a maximum value at a certain point, regardless of moisture content due to increase the precipitate content. Beyond this point, CSFT slightly decreased as in figure 4, response surface of the combined effect of MG and moisture on the precipitate content of palm oil biodiesel.

![Figure 3](image)

**Figure 3.** Response surface of the combined effect of (a) FSG and moisture on CFST, (b) MG and moisture on the precipitate content and (c) FSG and moisture on the precipitate content of biodiesel.

The precipitate content decreased with increasing MG content. Smaller-sized precipitate may have been formed at high level of MG and less retained on the glass microfiber filter. But not at high level of moisture as it contributed to increase precipitate formation. MG is amphiphilic in nature and interact with moisture to form larger precipitate may be easier to retain on the glass microfiber filter.

3. **Methodology**

3.1 **Pre-treatment**

Sample was treated using filtration apparatus using 0.7μm filter paper. The filtrate of early stage is prepared to proceed for FBT and CSFT testing. The filtration apparatus and the assembly of filter A as shown in figure 4 and figure 5 respectively.

![Figure 4](image)

**Figure 4.** Filtration Apparatus

![Figure 5](image)

**Figure 5.** Assembly of Filter A
3.2 Determination of Filter Blocking Tendency (FBT), IP 387

Table 2 show the procedure of determination filter blocking tendency (FBT) based on IP 387.

Table 2. Determination of Filter Blocking Tendency (FBT) test procedure

| Step | Procedure |
|------|-----------|
| i    | Filtration Media and assemblies using Procedure A |
| ii   | Filtration housing- stainless steel 13 mm with Luer fitting at the top with it connect with the filtration Apparatus |
| iii  | Filtration media- glass fibre GF/A, 1.6 μm nominal pore diameter, 13 mm diameter and with an effective filtration area of 63.6 mm² |
| iv   | Sample preparation- As general, test fuel having an extremely high blocking tendency may cause the pressure reading to rise so rapidly at the beginning of the test that initial pressure requirement cannot be met. |
| v    | Obtain 00 ml of representative of sample to be tested an epoxy lined can of at least 500 ml capacity |
| vi   | Measure the temperature of sample in container and adjust to 25°C |
| vii  | Shake the bottle vigorously for 120 s and allow to stand on vibration free surface for 300 s. |
| viii | Place 350 ml of the sample into reservoir beaker and check the temperature is still maintained to 25°C |
| ix   | Place the pump suction pipe into the reservoir beaker and run the pump. Flush the system through with the sample by allowing 20 ml of the sample to flow into the receiver. Stop the pump and discard any sample from the fuel receiver |
| x    | Calculation the filter blocking tendency (FBT) using equation below. Equation 1 applies when 300 ml of sample have passed through the filter medium at pressure below 105 kPa and equation 2 applies when the test has been discontinued when the pressure reached to 105 kPa. |

\[
FBT = \sqrt{1 + \left( \frac{P}{105} \right)^2} \quad [1]
\]

\[
FBT = \sqrt{1 + \left( \frac{300}{V} \right)^2} \quad [2]
\]

Where, \( P \) is the maximum pressure reading obtained for 300 ml of sample to pass filter, in kPa and \( V \) is the volume of sample in ml, passed prior to the pressure rising to 105 kPa.

3.3 Cold Soak Filterability Test (CSFT)- ASTM D 7501

The procedure of CSFT consist several step based on ASTN D 7501 as listed in Table 3 below.
Table 3. Cold Soak Filterability Test (CSFT) test procedure

| Step | Procedure |
|------|-----------|
| i    | Prepare the filtration apparatus (Figure 4) |
| ii   | 300mL of test sample is chilled to 4.5°C ±0.5°C for 16hrs (as shown in figure 6 (a) and (b)) |
| iii  | After 16hrs, remove sample from batch and place in circulating water bath with temperature set to 25°C ± 0.5°C for 2 ± 0.25 h. (as shown in figure 6(c)) |
| iv   | Verify the sample is at 25°C ± 0.5°C by dipping with digital thermometer |
| V    | Filter the sample as quickly as possible upon removal from water bath. |
| Vi   | Record the vacuum in the system within 1 min of starting the filtration. The vacuum shall be between 70 and 85 kPa (21 and 25 in. of Hg) |
| Vii  | When the filtration is complete, as evidenced by no sample remaining on the filter paper, immediately turn off the vacuum system and record the duration of the filtration, rounding to the nearest second. Currently, Less than 360 sec. is required to pass. |
| viii | If filtration is not complete when 70 s (12 min) has elapsed, turn off the vacuum system and record the duration of the filtration to the nearest second. Record the pressure in the system and the volume filtered just before the termination of the filtration. |

![Figure 6](image)

Figure 6. (a) Sample before incubate at 4°C (b) Incubate the sample at 4°C in incubator (c) Incubate the sample at 25°C

4. Result

Table 4 show the result of filtration. After done treatment of the sample using filtration apparatus, the result of CSFT and FBT passed the specification.

Table 4. Result of testing

| Test Parameter                      | Unit | Method      | Specification | Result |
|-------------------------------------|------|-------------|---------------|--------|
| Cold Soak Filterability Test (CSFT) | second | ASTM D 7501 | 360 max       | 340    |
| Filter Blocking Tendency (FBT)      | -    | IP 387      | 2 max         | 1.05   |
| Initial Pressure                    | kPa  |             |               | 18     |
| Test Temperature                    | °C   |             |               | 24     |
| Volume Passed                       | mL   |             |               | 300    |
| Final Pressure                      | kPa  |             |               | 35     |
5. Conclusion
The aim of the study is to investigate the major properties of biodiesel causing filter-blocking issue in biodiesel especially for palm oil based, to identify the suitable solution to reduce or eliminate these factors for improving the filter properties of the palm based biodiesel by control the specific parameter mono-glycerides during intermediate process and minimize or eliminate the steryl glycoside after post treatment. After done the treatment of the sample using filtration apparatus, the result found that the CSFT and FBT passed the specification.

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