

FAME Filterability: Understanding and Solutions

Stephanie Camerlynck and John Chandler
Infineum USA LP

Ben Hornby and Isabel van Zuylen
Infineum UK Ltd

ABSTRACT

The introduction of fatty acid methyl ester (FAME) into the diesel pool has led to an increase in the incidence of diesel fuel filter blocking. In contrast to conventional diesel, filter blocking events can occur above a fuel's Cloud Point (CP). It has been shown that this phenomenon is due to trace levels of impurities carried over from the original oil source into the final fuel. The two species identified as being the main cause of the filtration problems are saturated monoglycerides (sMG) and sterol glucosides (SG).

Reported in this paper is an extensive study completed to understand the impact that these impurities have on the filterability of FAME and FAME containing fuels. This has been investigated using laboratory based filterability tests that incorporate a specific cold soak and the critical contaminant levels causing failure have been determined. In addition to this, the appearance of the crystals formed and their coverage of the fuel filter surface have been studied using scanning electron microscopy (SEM).

These two techniques have also been used to identify and select additive technology that can positively impact filterability when sMG and SG precipitate from either FAME or fossil fuel containing a portion of FAME.

CITATION: Camerlynck, S., Chandler, J., Hornby, B. and van Zuylen, I., "FAME Filterability: Understanding and Solutions," *SAE Int. J. Fuels Lubr.* 5(3):2012, doi:10.4271/2012-01-1589.

INTRODUCTION

Filter Blocking in the Presence of Biodiesel

Field problems with vehicle and fuel dispenser filters have been occurring more frequently as filters become less porous to meet the requirements of advanced fuel injection systems designed to deliver improved fuel economy and reduce exhaust emissions. These filter blocking problems can result in poor vehicle performance or even complete vehicle failure, as well as problems at fuel dispensers and terminals.

The use of biodiesel has been identified as one factor that causes these filters to block at temperatures above the cloud point of the fuel. As early as in the winter of 2004/5 there were incidents in both Minnesota [1,2,3] and Sweden [4,5,6] where filters were blocked by saturated monoglycerides (sMG). In the literature sterol glucosides (SG) [7, 8], carboxylates (soaps) [9], and bacterial/fungal growth [10] are also discussed as possible causes. However, in the industry, the causes of above cloud point precipitation most often cited are from impurities such as sMG and SG in FAME.[11]

Monoglycerides are a side product of the transesterification reaction. Their total amount is limited to 0.8% by the current EN 14214 specification for FAME in Europe. Depending on the fatty acid distribution, a share of the monoglycerides will be saturated; in rapeseed methyl ester this will be ~7%, in soy methyl ester ~15% and in palm methyl ester ~45%. SGs, depicted in [Figure 1](#), originate from bio membranes in plants. In their acylated form they are soluble in vegetable oil; however, during transesterification they are deacylated and lose solubility. Most of the SG is removed during processing but the finished biodiesel can still contain up to 60 ppm.

In the industry it has been proposed to add limits to the fuel specifications for sMG and SG. The latest revision of the EN 14214 specification currently under consideration by CEN introduces categories for FAME blending components according to the cloud point / CFPP and to the total monoglyceride content. This effectively limits the amount of sMG, and is a first step aimed at preventing field issues. SG and other contaminants are more difficult to limit in this way as they are an order of magnitude lower in concentration and more difficult to quantify accurately. To combat this it is the



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aspiration of the CEN standardisation body to introduce a performance based test.

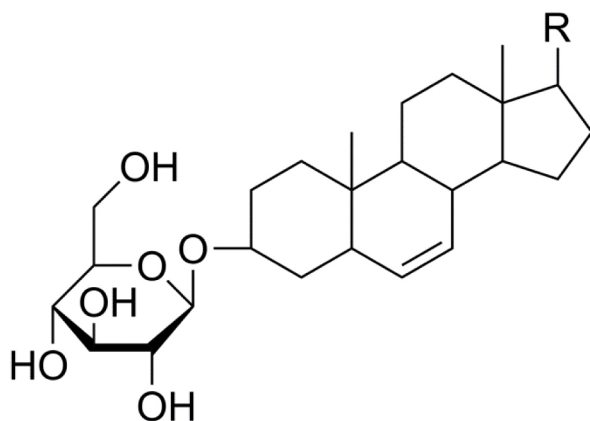


Figure 1. Chemical structure of sterol glucoside. *R* represents a branched alkyl chain.

Filtration Tests Developed in the Industry

Performance tests to evaluate the filtration behaviour of biodiesel in blends have been developed in the industry with the aim of protecting vehicle fuel systems. These tests work by pumping fuel through a filter membrane at a constant rate while measuring the filter pressure. The three main tests developed are the Cold Soak Filtration Test (CSFT, ASTM D7501), the Canadian Cold Soak Filter Blocking Tendency test (CSFBT) and the European Cold Soak test (CS IP387). The CSFT test was developed in the US specifically with soy methyl ester (SME) samples. It is run using 100% FAME and as such does not evaluate the effect of solvency change when blending with diesel. The other two tests are run with B20 and B10 respectively, where the number represents the volume percentage of FAME. In order to ensure that the most severe diesel component is represented a diluent with low aromatic content, Isopar L, is used. This is a paraffinic solvent produced to a defined specification to eliminate the potential variability seen with different diesel samples.

The advantage of this approach, compared to limiting individual causes of filter blocking, is that a performance test captures the impact of FAME on the finished Bx filterability independent of identifying and quantifying all possible causes for poor filtration. The challenge here is to set the pass/fail level that protects vehicle and fuel dispensers whilst balancing additional processing cost.

Initial investigations at Infineum showed significant variation in the CS IP387 test between samples taken from the same original FAME, despite great care being taken to homogenise the FAME prior to sampling. Therefore the investigation reported here followed an approach similar to that previously reported [12]: controlled levels of sMG and SG were added to distilled FAME to study their impact on filtration tests, with results confirmed in field FAME samples. Distilled FAME was used, as this processing step removes all impurities. To gain insight into how sMG and SG

impacted the filterability, differential scanning calorimetry (DSC) and SEM analyses were conducted. Finally the results were validated by a vehicle test.

EXPERIMENTAL

Filtration Tests and Analysis

The published method for CSFBT[13] and CS IP387[14] were followed. Both tests use the same test rig (see Figure 2). They only differ in the sample preparation; in particular the level of FAME blended with Isopar L and the temperature of the cold soak. See also Table 1.

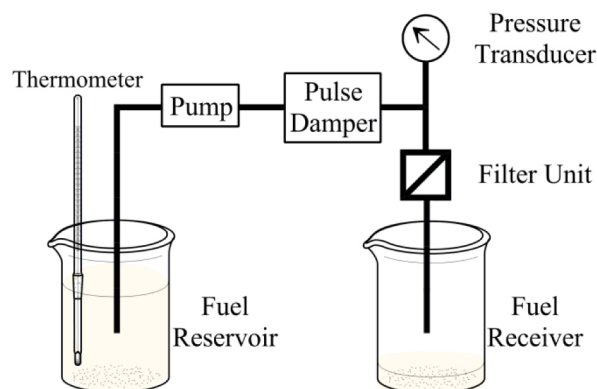


Figure 2. Schematic of the rig setup for filterability tests.

Table 1. Test conditions for CS IP387 and CSFBT.

	CS IP387	CSFBT
B100 concentration / vol%	10	20
Diluent	Isopar L	Isopar L
Conditioning temperature / °C	+ 60	+ 60
Soak temperature / °C	+ 5	+ 1
Soak time / hours	16	16
Filter porosity / µm	1.6 (GF/A)	1.6 (GF/A)
Filter diameter / cm	1.3	1.3
Test time / mins	15 max	15 max
Test volume / ml	300	300

300ml fuel is pumped at a rate of 20ml/min through a 1.6µm glass fibre filter (Whatman). The rig pressure is monitored. The test finishes after 15 min with all fuel pumped through and the final pressure is recorded (Equation 1a) or, if the pressure exceeds 105kPa the test is stopped and the time/pumped volume recorded (Equation 1b). The test result is expressed as a numeric filter blocking tendency (FBT), calculated as in Equation 1. FBT values of less than 1.41 represent excellent filterability, whereas values higher than this indicate a blocking tendency that may be unacceptable.

$$(a) FBT = \sqrt{1 + \left(\frac{P}{105}\right)^2} \quad (\text{values between 1 and 1.41})$$

$$(b) FBT = \sqrt{1 + \left(\frac{300}{v}\right)^2} \quad (\text{values between 1.41 and 15})$$

Equation 1 - Equations to calculate the FBT for (a) tests passing the sample volume through the filter and (b) tests where the pressure maximum of 105 kPa is exceeded. P = maximum pressure obtained (kPa), v = volume of fuel passed (ml).

The impact of sMG and SG in the CSFBT and CS IP387 were studied by adding known levels of each to distilled tallow methyl ester (TME). This FAME was chosen as the commercial distillation step, as part of its manufacture, renders it free of contaminants.

The samples were prepared as follows: For both tests distilled TME was conditioned by warming to 60°C for a total of 3h. After the first hour sMG or SG were added as a 10m/v% solution in tetrahydrofuran (THF) and a 1m/v% solution in pyridine, respectively, as required. Pyridine was used in these experiments to introduce SG into the FAME, because it is one of the few solvents that will dissolve SG. After another hour the additive was added as a 10m/v% solution in Solvesso 150 where required. This was followed by the last hour of warming to 60°C.

The B20 or B10 blend was then prepared by adding the FAME to the required amount of Isopar L at room temperature (v/v). This blend was cold soaked and tested as described in the test methods.

DSC analysis was performed on a TA Instruments DSC Q20. Ramp rates were as in the figure description, with programs incorporating a 5 min isotherm at both the maximum and minimum temperatures of each program.

SEM analysis was performed on a Hitachi TM-1000 equipped with a cold stage (5°C).

Solvents were obtained from commercial suppliers. SG was purified from rape seed methyl ester extractor residue. sMG was obtained as 90% saturated MG derived from palm oil from ASG Analytische Service Gesellschaft and used without further purification.

Engine Test Procedure

Engine testing was carried out on an Isuzu NPR light-duty diesel truck on a Cold Chamber Chassis Dynamometer (CCCD). The vehicle fuel system was modified by taking out the "last chance" filter and feeding the fuel from an external supply line rather than the vehicle tank. This "last chance" filter is made of a coarse mesh and is intended to capture large particles, such as machining swarf, when new upstream fuel system components are fitted. Temperature probes and pressure sensors were fitted in the fuel line before and after the fuel filter. Fuel was supplied from a 200l drum. The return line was connected to a separate drum; no fuel was returned to the original drum.

The fuel was prepared from SME doped with sMG or SG and additive as required and homogenised by hot boxing at 60°C and mixing on a drum roller. The FAME was added to Swedish Class 1 low aromatic diesel fuel to make a B20 blend and homogenised by rolling of the drum both when blended and again just before starting the overnight cold soak (−7°C (+/−1)). The following morning the drum was stored at ambient and rolled to homogenise till the fuel reached a temperature of 0°C.

The cold chamber was held at 2°C, the fuel drum was connected to the vehicle and fitted with an overhead paddle stirrer. The fuel was stirred throughout the test. The vehicle was started and accelerated to 80km/h. The pressure difference measured before and after the fuel filter was monitored as well as the vehicle speed and fuel temperature. After the test the fuel filter was removed, the system flushed and a new filter fitted.

RESULTS AND DISCUSSION

Filterability Impact of Sterol Glucoside and Saturated Monoglyceride

The level of SG and sMG that leads to filter blocking in the CSFBT and CS IP387 was studied by increasing the amount of each contaminant added to distilled FAME.

The impact of sterol glucoside

In the CSFBT, as little as 10 ppm SG in FAME was found to lead to high filtration pressure. The test was stopped after 7.4 minutes - this gives an FBT of 2.3. The pressure increase over time is shown in [Figure 3a](#). Higher levels of SG lead to an even shorter time till the pressure limit is reached.

In the CS IP387 test, the threshold between a pass and a fail is around 25 ppm SG in FAME ([Figure 3b](#)). This higher level of SG compared to the CSFBT is expected: the B20 blend used in the CSFBT contains double the absolute amount of SG than the B10 blend of the CS IP387 and the cold soak conditions (+1°C versus +5°C) further increase the severity of the CSFBT test.

These levels of impurity shown to cause filter blocking problems in CSFBT and CS IP387 testing are not unusually high when compared with commercial fuels. Biodiesel made from crude soybean oil was reported to contain 272 ppm SG while biodiesel from refined-bleached soybean oil contained 64 ppm SG [15]. Processing steps reduce the SG content and commercial biodiesel samples typically contain less than 25ppm SG, but occasionally up to 60 ppm can be found.[16]