**A Simple Standardization Method for the Biodiesel Cold Soak Filtration Apparatus**

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**KEY WORDS:** ASTM D6751, ASTM D7501, Biodiesel, Cold Soak Filtration Test

**Abbreviations:** CSFT: Cold Soak Filtration Test

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**Abstract**

Commercially available refined vegetable oils were investigated as calibration standards for the filtration device and filtration protocol used in conducting ASTM D7501 (Standard Test Method for Determination of Fuel Filter Blocking Potential of Biodiesel [B100] Blend Stock by Cold Soak Filtration). Filtration time was determined to be a function of the amount of vacuum applied during filtration , with an 8% change in the filtration time of soybean oil occurring across the 21 to 25 in. Hg range specified as acceptable by ASTM D7501. Using a test volume of 150 ml and a vacuum of 22.5 in. Hg the mean filtration time of replicate samples of seven commercial brands of edible refined soybean oil was 396 s with a Minimum Significant Difference of 28 s. Filtration times of seven of eight tested brands of soybean oil fell within this Minimum Significant Difference. Filtration time was independent of operator, device, oil manufacturer and lot number. Refined edible corn, canola, peanut, safflower and sunflower oils gave reliable filtration times and may also be suitable for use in validating performance of the filtration device, though each exhibited a characteristic filtration time greater than that for soy oil. The filtration times of the oils were a linear function of their kinematic viscosities, as predicted by Darcy’s Law. The results indicate that edible vegetable oils may serve as reliable, affordable, consistent, and generally available materials for confirming the operability of the filtration device used in conducting the biodiesel cold soak filtration test.

**Introduction**

The development and application of quality specifications are essential to the reliability and thus the adoption of a commercial product. In the case of biodiesel, quality standards are specified by ASTM D6751 (1). As with all useful standards this specification is flexible and dynamic, expanding in depth and breadth as field experiences indicate necessary new quality parameters.

Soon after the implementation of statewide mandatory biodiesel addition to petroleum diesel fuel in the state of Minnesota in the fall of 2005 instances of engine inoperability due to fuel starvation resulting from clogged fuel filters were experienced. It was subsequently found that in many instances the filters were plugged by solids that had formed post-production in the biodiesel component of the fuels, that the solids had formed at temperatures above those at which they were expected based on the Cloud Point test applied to diesel fuel, and that they were composed largely of saturated monoacylglycerols and sterol glucosides (2, 3). An empirically developed test, the Cold Soak Filtration Test (CSFT), was found to be a reliable predictor of the tendency of a biodiesel to form solids at temperatures above the Cloud Point. An official protocol for the CSFT was developed, approved as ASTM D7501 (4) and became a component of ASTM D6751. In combination with other advances, the implementation by the industry of technologies to ensure that biodiesel passed the CSFT has led to a steady improvement in the quality and reliability of biodiesel (5, 6).

The CSFT consists of three successive actions: (A) incubation of 300 mL of fuel at 4.5 oC, the ‘cold soak’; (B) a slow rewarming to 25 oC; and (C) filtration under defined conditions. The accumulation of fuel-borne solids on the filter reduces the flow rate, increasing the filtration time, which is the measured parameter. The original Standard called for a maximum acceptable filtration time of 360 s. Fuel meeting this specification is now termed grade ‘No. 2-B’. To further ensure low temperature operability a second grade, ‘No. 1-B’, intended for cold weather use and characterized by a maximum 200 s filtration time, was specified by ASTM D6751 in 2012. Longer filtration times are associated with increased risk of fuel filter plugging during real world use.

The filtration step involves passage of the fuel sample, under specified vacuum, through a defined filter medium in a defined physical setup (Fig. 1). Filtration rate will be affected not only by the presence of solids by also by system features such as the constancy of the vacuum, the accuracy of the vacuum gauge by which it is measured, the vacuum integrity of the several fittings and couplers in the system, the quality of the filter and of its seal to the filtration device, and by operator awareness and skill. Other factors, such as whether the low temperature incubation and the subsequent reheating are conducted properly, will also influence the filtration rate.

The integrity of the CSFT and the reliability of its results can dictate whether a batch or lot of biodiesel will enter commerce. Standardization or ‘control assay’ protocols are typically developed to assure the reliability of quantitative assays. However, we are not aware of such a protocol being described to date for the CSFT, and have sought to develop one. Our goal was to identify a readily available solution that gave reproducible filtration times when filtered across the CSFT apparatus.

The use of a reference solution whose filtration rate was based on the presence of solids could be difficult, with poor performance and reproducibility due to variations in the formation, morphology, stability and mixing of the crystals. The filtration rate of a solution is a function not only of its solids content but also of its viscosity, as described by Darcy’s Law (7):

R = k P/U (Eqn 1)

Where R = filtration rate, P = pressure drop across the filter, U= viscosity, k = constant

A homogeneous liquid could be a useful and desirable standardization solution since it lacks the difficulties noted above for solutions containing solids. We therefore explored the possibility that a liquid of appropriate viscosity, in this case vegetable oil, could serve as an acceptable filtration standard in the CSFT.

**Materials and Methods**

Materials

Commercial edible refined vegetable oils (Table 1) were obtained from local food stores and used before their listed ‘Best By’ dates. Oils of the same type and brand were segregated by production date code or Best By date (referred to here as ‘lot’). Analysis of acylglycerol contents by HPLC (7) showed that all oils contained at least 97% triacylglycerols, with the balance primarily diacylglycerols. Alkaline transesterification and GC analysis (8) indicated fatty acid compositions consistent with the labeled contents of each oil (9). The sunflower oil was of the mid oleic type, with oleic and linoleic acid contents of 64% and 26%, respectively. The safflower oil was a high oleic variety, containing 74% oleic acid, 16% linoleic acid.

Biodiesel produced from soybean oil and meeting ASTM D6751-13 was generously provided by Renewable Energy Group Inc., Ames, IA. Glass microfiber filters (47 mm diam.) were Whatman Brand (GE Healthcare UK Limited, Little Chalfont, UK).

Filtration System and Use

Vacuum filtration devices were assembled as specified by ASTM D7501-12 (Fig. 1). Vacuum was provided either by a laboratory benchtop vaccum pump or by house vacuum. Vacuum was measured with a recently calibrated VWR Model 23609-222 Traceable Pressure Meter (VWR International, vwr.com). Volumes of 150 mL of vegetable oil were studied since this gave filtration times of 300-400 s, the amount of time that a filter would be under vacuum with a sample that failed the biodiesel CSFT test. Oil samples were poured into the filtration device with vacuum already applied. Filtration time was recorded as the time from addition of the last drops of sample to the filtration device to the moment when portions of the filter became noticeably brighter upon going dry due to the passage of all the test liquid. Work was conducted at room temperature (23 + 1 oC).

Viscosity Measurement

Kinematic viscosities of commercial vegetable oils were determined at 40 oC with a size 150 (range: 7 – 35 centiStokes) Cannon-Ubbeholde viscometer (A.H. Thomas, Philadelphia) as per manufacturer’s instructions.

Data Analysis

Replicate filtrations were conducted. Results are presented as mean + standard deviation. Differences in mean filtration times were assessed at p = 0.05 using the general linear models procedure (GLM) of the SAS/STAT statistical analysis package (SAS Institute, Inc., Cary, NC, USA).

**Results and Discussion**

Validation of System Operation

When subjected to the full cold soak protocol as per ASTM D7501-12, 300 mL of biodiesel had a filtration time of 91 + 5 s (4 replications) on the filtration systems employed here. This is comparable to the CSFT value of 82 s reported for this biodiesel by its manufacturer, suggesting that the test devices were functioning correctly.

Relationship between Applied Vacuum and Filtration Time

ASTM D-7501 specifies the application of a vacuum of between 21 and 25 in. mercury during filtration of a biodiesel sample. We explored the effect on filtration time of vacuum variation within this range and found a substantial effect (Fig. 2). As would be expected, higher applied vacuum caused faster filtration, resulting in a negative linear relationship between filtration time and applied vacuum (Fig. 2). Over the range of vacuums tested the filtration times of soy oil fell by 8% as vacuum increased. It is possible that the filtration times for biodiesel samples could exhibit a similar dependence on applied vacuum. ASTM D6751 specifies a single acceptable maximum filtration time, not a range of times. A fuel with a failing (i.e. long) filtration time under minimum acceptable vacuum may pass the test when filtered at a higher, though still acceptable, vacuum. It is unclear if such a fuel would subsequently cause filter blockage in the field. A reduction in the range of allowed vacuums may eliminate such difficulties should they occur. All subsequent filtration times reported here were collected at a vacuum of 22.5 + 0.5 in. mercury, the midpoint in the range specified by ASTM D7501.

Dependence of Filtration Time on Operator and System Variation

Two separate filtration units were constructed as per Fig. 1 and used by two different operators to conduct the filtration of a single lot of soybean oil (Table 1, ‘A’). Each operator filtered ten 150 mL aliquots of oil over one of the filtration units. Mean filtration times for data obtained by the two operators were not significantly different: 404 + 6 and 404 + 11 s. Exchanging the units between the two operators and conducting another series of filtrations gave similar results. Thus, refined soybean oil gave highly reproducible filtration times irrespective of operator and filtration apparatus.

Lot-Dependent Impacts on Soybean Oil Filtration Time

To examine the effects on filtration rate of lot-to-lot variations within a brand of soybean oil, duplicate samples from eight lots of one brand of soybean oil (Table 1, Samples B through I). The average of the mean observed filtration times for the eight lots was 394 s with a Minimum Significant Difference (MSD) of 21 s. The difference between the largest and smallest average filtration times was 22 s, one second greater than the MSD, indicating a lot-based impact on filtration rate. However, for an assay such as the CSFT a one second difference is essentially irrelevant. For all practical purposes it can be said that filtration time was independent of production lot for soybean oil.

Brand Dependence of Soybean Oil Filtration Time

Filtration times were measured on duplicate samples of seven brands (Table 1, Samples J - P) of edible refined soybean oil. The average of the resulting mean filtration times was 396 s with a Minimum Significant Difference (MSD) of 28 s. Filtration times for six of these seven brands, as well as for the brand studied above in the lot-to-lot work, were within the MSD. An eighth brand, however, (Table 1, Sample J) had a mean filtration time of only 311 s, 100 s below that of the others tested. The reason for its much faster filtration is not known. With the exception of this brand it appears that refined soybean oils can serve as effective standards for calibration of the CSFT filtration apparatus.

Potential of Other Vegetable Oils to Serve as Filtration Standards

Soybean oil is the least expensive vegetable oil and would seem to be the most probable choice for use as a filtration standard. We explored the possibility that other affordable and widely available vegetable oils would exhibit filtration behaviors similar to that of soy oil, allowing the use of virtually any refined vegetable oil as the standard. Table 2 lists the mean filtration times of duplicate 150 mL aliquots of peanut, safflower, canola corn and sunflower oils, as well as the average filtration time for 8 lots of one brand of soy oil. For each oil the filtration time was highly reproducible, with replicates differing by 3% or less. Filtration times were generally unique to each oil, although the mean filtration time of corn oil was essentially identical to that of soy oil. Further studies may show that some or all of these oils display sufficient uniformity of filtration time across brand and lot to serve as calibration fluids for the filtration device.

Relationship Between Oil Viscosity and Filtration Time

Kinematic viscosities of the test oils were determined and plotted against the corresponding filtration times (Fig. 3a). In accord with Darcy’s Law (Eqn. 1) a linear relationship (R2 = 0.83) existed between filtration time and kinematic viscosity. Thus the differences seen above in the filtration times of the oils can be understood in light of differences in their kinematic viscosities.

One data point, for safflower oil, appears to deviate substantially from the best-fit line depicting the relationship between filtration time and viscosity for the oils tested (Fig. 3a). A best-fit line through the other five data points results in a much better fit of the raw data to the resulting line, with an R2 = 0.96 (Fig. 3b). It is unclear why the safflower oil sample diverged so noticeably from the filtration times - kinematic viscosity relationship established by the other oils. The sample was clear and bright, suggesting that it did not contain fine particles that would have increased its filtration time. GC and HPLC indicated a typical safflower oil composition. Further work may indicate whether this is a typical feature of safflower oil or perhaps only a trait of the particular sample studied here. Its aberrant performance suggests that safflower oil may not be a reliable general filtration standard. Notwithstanding this observation, vegetable oils other than soy oil may also be suitable for use as filtration standards, with the filtration times being unique for each oil.

The standardization protocol developed here does not require the time-consuming ‘cold soak’ and warmup steps of ASTM D7501, and the vegetable oils used as test fluid are inexpensive, widely available, consistent over time and space, nontoxic and readily disposed of. An attractive additional feature of vegetable oils is that rather than requiring the expense and effort of disposal as chemical waste, if desired they can be recovered and transesterified to yield biodiesel. They cannot, however, be reliably recovered and reused in repeated standardizations: the filtration times of reused samples were as much as 25% lower than obtained on first filtration (data not shown).

In searching for a material suitable for use as a filtration standard, automotive products such brake fluid, power steering fluid, antifreeze, and various viscosities of engine oil were also tested. For various reasons all were inferior to vegetable oil. Aqueous dilutions of commercial edible corn syrup were also tested, since disposal of an aqueous standard would be straightforward and inexpensive. However, the reproducibility of filtration times was poor with corn syrups.

**Conclusions**

- Filtration time in the CSFT apparatus is dependent on the value of the applied vacuum, with substantial variations in filtration time being observed across the range of vacuum values designated by ASTM D6751 as acceptable.

 - The filtration time of commercial refined edible soybean oil over a properly functioning filtration device designed for use in the cold soak test for biodiesel quality is constant throughout variations in unit, operator, brand and lot.

- Soybean oil may thus be an acceptable reference material for validation of correct functioning of a filtration device intended for use in ASTM D6751.

- It is possible that other refined vegetable oils may also be suitable reference filtration standards.

**References**

 1. American Society for Testing and Materials (2012) Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, designation D6751-12. ASTM, West Conshohocken, PA.

2. Pfalzgraf LM, Lee I, Foster J, Poppe G (2007) Effect of minor components in soy biodiesel on cloud point and filterability. Biorenewable Resources No. 4; a special supplement to *inform*. AOCS Press, Champaign, IL. 17-21.

 3. Chupka GM, Fouts L, McCormick RL (2012) [Effect of low-level impurities on low-temperature performance properties of biodiesel](http://pubs.rsc.org/EN/content/articlehtml/2012/ee/c2ee22565d). Energy & Env. Sci. 5:8734-8742

 4. American Society for Testing and Materials (2012) Standard Test Method for Determination of Fuel Filter Blocking Potential of Biodiesel (B100) Blend Stock by Cold Soak Filtration Test (CSFT), designation D7501-12. ASTM, West Conshohocken, PA.

 5. Alleman TL, McCormick RL, Deutch S (2007) 2006 B100 Quality Survey Results: Milestone Report.. Golden, CO: National Renewable Energy Laboratory, Golden, CO. Technical Report NREL TP-540-41549

 6. Alleman TL, Fouts L, Chupka G (2013) Quality Parameters and Chemical Analysis for Biodiesel Produced in the United States in 2011. National Renewable Energy Laboratory, Golden, CO. Technical Report NREL/TP-5400-57662

 7. Anonymous. (2014) Darcy’s Law. <http://hlsweb.dmu.ac.uk/ahs/elearning/RITA/Filtration/Darcy.html>, accessed 7/15/2014

 8. Haas MJ, Cichowicz DJ, Jun W, Scott K (1995) The enzymatic hydrolysis of triglyceride-phosphoglyceride mixtures in an organic solvent. J. Am. Oil Chem. Soc. 74:519-525

 9. will be added.

10. Hammond, E.W. (1993) Chromatography for the Analysis of Lipids, CRC Press Inc., Boca Raton, FL. ISBN 0-8493-4255-4. p. 174