Determining the Acid Number of Biodiesel

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ABSTRACT: Commercial biodiesel is composed of FAME. It may also contain small amounts of FA, which are quantified by an acid number, expressed as milligrams of potassium hydroxide required to neutralize 1 g of sample. In 2006, the ASTM D 6751 biodiesel acid-number limit was harmonized with the European biodiesel value of 0.50. ASTM D 664 is the standard reference method for measuring the acid number of both ASTM biodiesel and petroleum-derived diesel. This potentiometric method cites acceptable repeatability and mediocre reproducibility, but no information on accuracy. ASTM D 974 is a non-aqueous colorimetric titration that uses potassium hydroxide in isopropanol as the titrant and *p*-naphtholbenzein as indicator. It was designed for petroleum products and is suitable for colored samples. It has been tested on nine palmitic acid/soybean oil standards in the acid-number range of 0.198 to 1.17. All accuracies were within 3.3%. The repeatability was approximately 6% at an acid number of 0.5. The reproducibility appears to be only slightly greater than the repeatability at an acid number of 0.5. It is concluded that ASTM D 974 is a good method for evaluating the acid-number compliance of biodiesel samples.

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KEY WORDS: Acid number measurement, biodiesel standards, fatty acid methyl esters.

Biodiesel fuel in the form of vegetable oil methyl esters was first used commercially in Austria about 25 years ago (1). In 1991, the first Austrian standard for rapeseed methyl ester (RME) set many quality parameters including limitations on the acidity. Other European countries then developed standards for RME. In 2001, an American Society of Testing of Materials (ASTM) standard, D 6751, was set for biodiesel in the form of the lower alkyl esters of FA (2). This was followed soon by a European standard, EN 14214 (3). One of the most critical quality parameters of biodiesel, particularly from the viewpoint of producers, is the acid number, which is the number of milligrams of potassium hydroxide that is required to neutralize a 1-g sample. In the case of biodiesel, the acid number derives almost exclusively from the FA content. This is because FA can be formed by the hydrolysis of ester linkages in both the TG feedstock and the biodiesel during its manufacture. The ASTM Task Force on Biodiesel recently lowered the ASTM D 6751-allowed acid number of biodiesel from 0.80 to 0.50 to harmonize with the European standard (4). The setting of the acid number limit at such a low level (0.50), which corresponds to a FA content of approximately 0.25 wt%, is arguably overly cautious. Concerns focus around the possibility that FA may cause engine deposits, particularly in fuel injectors, by catalyzing polymerization in hot recycling fuel loops.

The ASTM standard for biodiesel includes specific analytical reference methods, which are to be used in the case of disputes. ASTM D 664 (hereafter referred to as D 664) is the reference method for the acid number, and it is the same as that used for petroleum diesel (5). At first sight, this appears to be a sensible choice. Most of the general methods for measuring acid number are based on titrations with standardized base, the end point being identified by the color change of an indicator. D 664 is a potentiometric method, which has certain advantages. It is useful when samples are colored, in which case indicator color changes may not be visible. In addition, the titration may be automated. D 664 self-cites acceptable repeatability, but only mediocre reproducibility. This is undoubtedly due to the many problems associated with the variability of electrodes. The method also cites no information on accuracy. This is because there is no reasonable way to make up relevant standards for petroleum oils, particularly as no one class of acids can be identified as contributing to the acid number of petrodiesel. Acid number is seldom a problem in unused fossil fuel products. This is primarily because they are hydrocarbons and therefore unreactive, and secondarily, because the products usually have been distilled. The standard for petrodiesel is set at 0.10 (6). Products either easily meet this standard or fail badly. Therefore, the accuracy and reproducibility of the supporting method do not appear to be a major issue for petroleum products. In fact, the cited reproducibility of this method cannot support the stated precision of the standard.

Fats and oils have FA ester linkages as does biodiesel, so a method for measuring acid number as developed by the American Oil Chemists Society (AOCS) seems appropriate for biodiesel. This would be AOCS Official Method Cd 3d 63 (Revision 1987) in which samples are titrated with aqueous potassium hydroxide using phenolphthalein as the indicator (7). This method only has problems if the samples are highly colored. The European biodiesel fuel standard for acid number is supported by analytical method EN 14104, which also uses aqueous base titration and phenolphthalein as indicator. Although the aqueous titrations appear to work well, there is always the possibility that some ester bonds would be hydrolyzed by the aqueous base, leading to consumption of base and elevated measurements. ASTM D 974 (hereafter referred

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to as D 974) is a method for measuring the acid number of petroleum oils (8). It uses *p*-naphtholbenzein as the indicator in an isopropanol/toluene mixture. The change of this indicator from orange to green at the end point can be seen even in colored samples.

Recently, we were involved, together with two other laboratories, in the measurement of acid numbers of biodiesel samples produced at a test facility. All three laboratories used D 974, whereas one certified analytical laboratory ran parallel determinations using D 664. It was clear that, whereas all three laboratories obtained similar results when using D 974, the values measured by D 664 were erratic and seldom agreed with those measured by D 974. This is consistent with the cited mediocre reproducibility of D 664 and creates doubt about its suitability as the standard reference method for measuring the acid number of biodiesel. D 974 is easy to perform and duplicate in laboratories because it involves only glassware, solutions, and an indicator. D 664 uses electrodes, which often differ in their characteristics, thereby introducing another level of uncertainty. In this study we focused on validating D 974 as a method for measuring the acid number of both biodiesel and vegetable oils, rather than confirming the deficiencies of D 664.

This study quantifies the accuracy and repeatability of D 974 with respect to the titration of FA in FA esters such as vegetable oils and biodiesel. Data from three laboratories were also compared to estimate (but not determine) reproducibility of the method. It was beyond the resources of this study to access six different laboratories as required by ASTM to establish reproducibility. The acidic contaminants of biodiesel are invariably FA. Therefore, unlike petroleum oil, representative standards can be made in order to evaluate a method. Standards that had acid numbers in the range of 0.198 to 1.167 were made by using palmitic acid in soybean oil. A refined vegetable oil rather than a biodiesel sample was used as the solvent for the palmitic acid, because biodiesel with a sufficiently low acid number was not available. Vegetable oils contain FA ester bonds, so any undesirable reaction of the hydroxide ion in the titrant with ester bonds could still be identified.

EXPERIMENTAL PROCEDURES

Materials. The soybean oil that was used as the solvent was a food-grade President's Choice product, purchased from Loblaws Inc. (Toronto, Canada). The following chemicals were supplied by Sigma-Aldrich Chemical Company (Milwaukee, WI): palmitic acid (99%), 2-propanol (anhydrous, 99.5%), toluene (HPLC grade, 99.8%), *p*-naphtholbenzein (indicator grade), sulfuric acid (volumetric standard, 0.0995 N solution in water). BDH Analar solid KOH was supplied by VWR International (Mississauga, Ontario, Canada).

Method. The volumetric standard KOH, the titration solvent, and indicator solution were prepared as detailed in ASTM D 974 (8). Nine standards were prepared (not by the operator) by dissolving measured weights of palmitic acid in measured weights of soybean oil. The range of the standards was restricted to the acid numbers commonly found in biodiesel samples.

For determining the acid number, 2 g (measured to four decimal places) of a sample was collected in an Erlenmeyer flask (125 mL). Ten milliliters of titration solvent and 8 drops of the indicator solution were added to each sample. The sample was then titrated against the 0.02 M KOH solution. The titration was deemed complete when a color change from orange to green that held for at least 15 s was observed in the titration mixture. The acid number was calculated as follows:

$$\text{acid value}\left(\frac{\text{mg KOH}}{\text{g sample}}\right)=\left[\frac{\text{volume KOH(mL)}\times\text{N KOH(mmol/mL)}*56.1(\text{mg/mmol})}{\text{sample weight (g)}}\right] \quad [1]$$

Each standard was titrated at least six times by the operator, who only knew the acid number range encompassed by all the standards. Seven solvent determinations were also made. The accepted analytical procedures of delivering partial drops from the burette and reading partial divisions were employed.

RESULTS AND DISCUSSION

The results for determination of the acid number of the solvent (soybean oil) are shown in Table 1. Each standard was titrated at least six times; the means, SD, repeatabilities, and accuracies are also shown in Table 1. Blind determinations were also made on five biodiesel samples that had acid numbers close to the biodiesel standard of 0.50. The measurements were made in three different laboratories. Two of the determinations were made independently by two operators in the same laboratory. The means and repeatabilities are shown in Table 2.

Any suitable method can be used to measure the acid number of the solvent when the value is significantly lower than that of the standards. Therefore, we also used D 974 for the solvent. From Table 1 one can see that the mean acid number of the solvent was 0.062 with a SD of 0.004. This uncertainty is incorporated in the calculated values of the standards and was deemed acceptable, which the final results of this study confirm. The contribution to the uncertainty from the solvent measurement is obviously greater for the lower acid number standards.

The mean acid number values for all nine standards, except for one, were within 2.1% of the calculated values (Table 1). The one exception was standard 5 (0.615), for which the mean value was 3.3% lower. There also did not appear to be an overall positive or negative bias on the accuracy.

Repeatability of a method is defined according to ASTM as "the difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions and on identical test materials, which would in the long run in the normal and constant operation of the test method be exceeded only in one case in twenty" (9). If sufficient measurements are made on a sample, then repeatability has a value of 2.77 multiplied by the SD. The repeatability for the nine standards, expressed as percentages of the means, is shown in Table 1. D 974 as applied to petroleum

TABLE 1
Calculated and D 974 Acid Numbers of Standards

Stand. #	Acid number by D 974 (mg KOH·g^{-1}	Mean	SD	Repeatability[a]	Real acid number[b]	Accuracy[c]
Solvent	0.057, 0.068, 0.057, 0.057, 0.063, 0.060, 0.060,	0.060	0.0041	18.7%	—	—
1	0.177, 0.205, 0.183, 0.194, 0.199, 0.205	0.194	0.0116	16.6%	0.198	98.0%
2	0.286, 0.302, 0.307, 0.313, 0.263, 0.287	0.293	0.0182	17.2%	0.289	101.4%
3	0.371, 0.372, 0.349, 0.372, 0.349, 0.338, 0.349, 0.333, 0.372	0.356	0.0158	12.3%	0.363	98.1%
4	0.448, 0.448, 0.443, 0.464, 0.437, 0.441	0.447	0.0094	5.8%	0.438	102.1%
5	0.585, 0.607, 0.601, 0.595, 0.608, 0.614, 0.583, 0.595, 0.572	0.595	0.0136	6.36%	0.615	96.7%
6	0.774, 0.746, 0.782, 0.752, 0.787, 0.765	0.768	0.0164	5.9%	0.757	101.5%
7	0.843, 0.841, 0.837, 0.866, 0.876, 0.846, 0.848, 0.849, 0.846	0.850	0.0126	4.1%	0.865	98.3%
8	0.897, 0.899, 0.902, 0.900, 0.895, 0.891	0.897	0.0039	1.21%	0.894	100.3%
9	1.142, 1.137, 1.136, 1.135, 1.137, 1.140, 1.157, 1.155, 1.141	1.142	0.0082	1.98%	1.167	97.9%

[a]Repeatability expressed as a percentage of the experimental mean.
[b]Real acid numbers are based on the acid number of the solvent and the weights of palmitic acid and soybean oil in the standards.
[c]Accuracy = (experimental mean/real acid number) × 100.

oils cites repeatability of 0.05 in the acid number range of 0.1 to 0.5 for 20-g samples of petroleum oils. This corresponds to 50% of the value at 0.1 and 10% of the value at 0.5. These values were obtained using 20-g samples for the determinations because D 974 recommends such sample sizes when acid numbers lie between 0 and 3.0. In this study, the repeatability on the standards decreased from 17 to 6% (of the means) in the range 0.198 to 0.438 (Table 1). It is surprising that D 974, as applied to the palmitic acid/soybean oil standards, has better repeatability than for its application to petroleum samples, particularly given that sample sizes were one-tenth as large. In another comparison, D 664, the potentiometric method, cites a repeatability of 7% when manually titrating fresh oils and additive concentrates and using inflection points to determine end points, and of 5% for used oils using buffer end point. However, no ranges are given for these quoted repeatabilities.

The definition of reproducibility is similar to that for repeatability but takes into account measurements made in different laboratories on the same test material. Therefore, reproducibility for a method should be higher than repeatability. D 974, as applied to petroleum oils, cites reproducibility of 0.08 over the acid number range of 0.1 to 0.5. This corresponds to 16% of the actual value at 0.5, as compared to the repeatability of 10%. This is consistent with a method that is "wet chemical" in nature and easily duplicated. In contrast, D 664 quotes reproducibility as 20% of the mean for the manual titration of fresh oils and additive concentrates, and 28% using an automated system. The stated reproducibility increases to 39% when buffers are used to determine the end points manually for used oils. This increases further to 44% in automated systems. However, no ranges are given for which these values apply. The use of electrodes obviously contributes to the mediocre reproducibility of D 664.

TABLE 2
Acid Numbers of Biodiesel Samples (mg KOH·g^{-1}) and Their Repeatability

Sample #	Lab 1	Lab 2	Lab 3a	Lab 3b	Mean	SD	Repeatability[a]
1	0.580	0.594	0.586	0.592	0.588	0.0063	3.0%
2	0.460	0.498	0.486	0.479	0.481	0.0159	9.2%
3	0.480	0.498	0.496	0.491	0.491	0.0081	4.5%
4	0.450	0.449	0.463	0.480	0.461	0.0145	8.7%
5	0.430	0.468	0.451	0.463	0.453	0.0169	10.3%

[a]Repeatability expressed as percentage of the experimental mean.

ASTM requires the involvement of at least six laboratories, each making a minimum of three measurements on the same test material, when determining the reproducibility of a method. From the data on petroleum oils, it was anticipated that the reproducibility of D 974 as applied to the standards would not be much greater than the repeatability. Although insufficient data were available from this study to calculate the true reproducibility, it was possible to calculate repeatabilities on each of the five samples, as determined in three laboratories by four operators. The five samples have similar acid numbers, so the repeatability should be similar for all samples. Only four measurements were made on each sample, so there is a significant scatter in the SD (see Table 2). However, the mean of the five repeatabilities should provide an estimate of the true reproducibility for an acid number of approximately 0.5.This mean is 7.2%, which is not statistically different from the repeatability obtained from samples having acid numbers in the same range. This suggests that the true reproducibility of D 974 as applied to the standards is not much greater than the repeatability at values around 0.5.

Thus, it is difficult to support the use of D 664 as the standard reference method for measuring the acid number of biodiesel, given its mediocre reproducibility. D 974 shows good accuracy and repeatability with all indications that the reproducibility is acceptable. It is recommended that the appropriate organizations officially prove D 974 as an acceptable method for measuring the acid number of ASTM biodiesel, perhaps with a view to adopting it as the standard reference method. In addition it should be confirmed that the second decimal place in the standard (0.50) can be supported by the reference method.

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