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Total Acid Number Determination of Biodiesel and Biodiesel Blends

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Abstract The repeatability and accuracy of the total acid number (TAN) measurement for soy oil-based biodiesel–diesel blends using the ASTM D664 method was studied. ASTM D664 is the standard reference method for measuring the acid number of both biodiesel and petroleum-derived diesel, which specifies procedures for the determination of acidic components in biodiesel and diesel, and claims good repeatability and mediocre reproducibility during application, but cites no information on accuracy. However, the accuracy of this method is very important for setting the specifications for biodiesel blends, especially for B20 (a mixture composed of 20% biodiesel with 80% diesel) because of its wide commercial production. The accuracy of ASTM D664 was measured to be within 4.13% for B20 in the acid number range of 0.123–0.332 mg KOH/g. The maximum repeatability was approximately 5.21% at an acid number of 0.123 mg KOH/g. Within the ASTM D6751-07b specification for TAN (0.5 mg KOH/g), good accuracy and repeatability were also obtained. Accuracy specification and electrode operation suggestions for ASTM D664 are also given.

Keywords Biodiesel · Total acid number (TAN) · ASTM D664

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Introduction

Biodiesel, defined as mono-alkyl (methyl or ethyl) esters produced from plant oils and animal fats [1] by transesterification reactions, plays a very important role as an alternative to conventional petroleum diesel. Transesterification, also called alcoholysis [2], has been widely used to reduce the viscosity of triglycerides and produce biodiesel. However, the relatively simple production process does not ensure high quality biodiesel. Small amounts of reactants and by-products during the transesterification reaction, including water, free glycerin, bonded glycerin, free fatty acids (FFAs), catalyst, residual alcohol, unsaponifiable matter (plant sterols, tocopherols and hydrocarbons), and soaps [3] may contaminate the final product. These minor components may cause severe operational problems, such as engine deposits, filter clogging, or fuel deterioration. Therefore, many American Society for Testing and Materials (ASTM) standards are in place to restrict the amount of most minor components that can affect biodiesel quality. One of the most important ASTM standards for biodiesel quality is ASTM D664, which is the reference method for the total acid number (TAN) [4]. The TAN, mainly an indication of the degree of oxidation and hydrolysis, is expressed as the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize the acids in one gram of sample [4]. In addition it is a facile method for monitoring fuel quality [5]. The maximum TAN value of biodiesel specified in ASTM D6751-07b [1] is 0.50 mg KOH/g. The free fatty acids are the major causes of the high TANs in biodiesel. Biodiesel with a low TAN is considered "safe" for storage and transportation, whereas those with TANs above the ASTM specification may not only result in the severe operational problems mentioned above, but also can cause corrosion during storage.

ASTM D664 is a widely used method for the TAN assessment not only because of its good repeatability, but also the advantages of being valid for deeply colored samples, and measuring both the strong acid number and the total acid number. For example, ASTM D 664 was employed to determine the TANs of deeply colored heavy oils and bitumens by Fuhr et al. [6]. However, there are still many problems related to this method, such as toxic aqueous calibration fluids (Toluene/2-Propanol), mediocre reproducibility, non-specified accuracy, and ester hydrolysis in the aqueous solution. In Fuhr et al.'s work [6], the reproducibility of ASTM D664 was improved from 21.3 to 3% without changing the basic procedures. Modifications to the toxic aqueous calibration fluids used in this method [7] were reported in 2004, which adopted the commercialized calibration fluids without compromising the repeatability and reproducibility of ASTM D664. Researchers in Canada [8] recommend ASTM D974 for TAN determination of biodiesel instead of ASTM D664, because it displayed better reproducibility in their three labs' results. The accuracy of ASTM D974 was evaluated in the study, but that of ASTM 664 was not tested for comparison. However, it was reported that the potentiometric method was more reliable compared with the color titrations [9]. There were also other studies [10–14] related to the acidity or basicity measurement of oil. However, the detection limit of ASTM D664 remains debatable. In our work, the accuracy of ASTM D664 in biodiesel and biodiesel blends was evaluated.

Biodiesel is commonly sold in blends with ultra low sulfur diesel (ULSD), of which B20 is one blend used for commercial applications. ASTM D664 is commonly used for the TAN determination of B20 though there is no specific standard for biodiesel blends. The current standard for pure biodiesel is set at 0.50 mg KOH/g. A limit of 0.3 mg KOH/g is proposed for B20 by the biodiesel industry. However, engine manufacturers and fuel delivery companies believe that this limit may not be sufficient to protect biodiesel storage and application systems. Since the lower the TAN, the higher quality of the oil, it would be desirable if the acid number could be accurately measured down to 0.15 mg KOH/g in B20 with this method. However, ASTM D664 gives no information on accuracy for petrodiesel, which was believed to be caused by the uncertainty of the acid species that can be identified as contributing to the acid number of petrodiesel [8]. The lower determination limit of ASTM D664 was presumably 0.3 mg KOH/g in biodiesel. In order to investigate the limit, the accuracy of ASTM D664 at various acid levels was evaluated by varying the amount of free fatty acids in biodiesel and B20.

Materials

Soybean oil based biodiesel (B100) was obtained from Wacker Oil Co. (Wacker Oil Co., MI). Certification #2 ultra low sulfur diesel (ULSD) was obtained from Haltermann Products (Channelview, Texas). B20 was prepared by mixing B100 and ULSD at a volume ratio of 1:4. Palmitic acid (99%) was obtained from Nu-Chek Prep (Elysian, MN). The chemicals used to prepare the TAN titration solvent, 2-propanol (ACS), and toluene (ACS) were purchased from Mallinckrodt Baker (Phillipsburg, NJ). The titrant solution used, 0.1 N KOH in isopropanol, was supplied by LabChem (Pittsburgh, PA).

Methods

The titration solvent was prepared as detailed in ASTM 664 [4]. Blends of B100 and ULSD were prepared to obtain weight percentages ranging from 0 to 90% biodiesel. Palmitic acid was added to solutions of B20 and B100 in order to obtain a range of known acid levels ranging from 0.30 to 0.53. TAN was determined for each mixture using the Titrando 809 instrument from Brinkmann (Westbury, NY). Experimental procedures were according to ASTM D664. Each sample was titrated in triplicate. After each titration, the electrode was rinsed with toluene first and then carefully dried with a toluene wetted tissue. The electrode was then immersed in distilled water for at least 10 min. Before each titration, the electrode was taken out of water and gently dried with a tissue.

Results and Discussion

According to the repeatability definition in ASTM D664, only one out of 20 cases for the difference between two successive results by the method should exceed the following values with the same apparatus under constant operating conditions and on identical test samples [4]:

$$\text{Fresh oils} = 0.044(X + 1) \tag{1}$$

$$\text{Used oils buffer end point} = 0.117X \tag{2}$$

where X = the average of the two test results.

Here, the repeatability values were calculated with the following formula [9]:

$$\text{Repeatibility} = \frac{2.77 \times \text{SD}}{\text{Experimental mean}} \times 100\% \tag{3}$$

where SD is the standard deviation.

The errors in this paper were calculated with the following formula:

$$\text{Error} = \frac{\text{Experimental mean} - \text{Calculated TAN}}{\text{Calculated TAN}} \times 100\% \tag{4}$$

where the calculated TAN was based on the sum of the original TAN and the amount of the free fatty acid added to the oil.

The first experiment was done by mixing B100 and ultra low sulfur diesel (ULSD) to adjust the TAN values of the biodiesel blends. The results are shown in Table 1. According to the literature [7], the acceptable repeatability was set as 12% of the mean value. But in this experiment, almost half of the repeatability results are out of this range. The accuracies are very poor. The largest error is up to 23%. After further investigation, it was found that this poor reproducibility was caused by the dehydration of the electrode. ASTM D664 suggests that after each test, the electrode should be cleaned with organic solvent first, soaked in water at least 5 min, and then rinsed with organic solvent immediately before use. Usually intensive cleaning of the electrode with organic solvent is needed for the high viscous oil samples. However, large amount of the organic solvent makes the electrode dehydrated and decreases the sensitivity of the electrode, which causes poor accuracy of the TAN determinations. Based on our findings, 5 min is too short for the recovery of the electrode during the biodiesel sample tests with ASTM D664. Cleaning with organic solvent before use also increases the likelihood of dehydrating the electrode. So, in order to minimize measurement errors attributed to the electrode dehydration during the application, the electrode should be soaked in water for at least 10 min and then dried gently with a tissue before use. The electrode after measuring biodiesel samples needs to be cleaned more thoroughly (i.e. repeated rinse with organic solvent, followed by a long soaking time in water) than after measuring ULSD samples.

With these modifications, we carried out the TAN determination for the B20 and B100 samples. The results are shown in Tables 2 and 3. B20-1 and B100-1 in Tables 2 and 3 are the original samples with low TANs. B20-2 and B100-2 are the high TAN samples prepared by adding calculated amount of palmitic acid to the original ones. Mixtures 1–8 and mixtures 1–5 in Tables 2 and 3 were obtained by mixing B20-1 and B20-2 or B100-1 and B100-2 respectively at different ratios to produce different TAN samples. From Table 2, it can be seen that the lowest repeatability is 0.70% compared with 5.45% in Table 1 whereas the highest is 5.21% compared with 24.89% in Table 1. The overall repeatability in Table 3 is a little higher than those in Table 2. Possible cause of the variability may be hydrolysis of methyl esters in B100 in the aqueous TAN solvents. From Table 2, one can see that the experimental errors of all eight B20 mixture samples range from 0.00 to 4.13%. The absolute experimental errors of all five B100 mixture samples in Table 3 range from 0.00 to 1.14%. The results illustrated in Tables 2 and 3 show good accuracies for ASTM D664 when applied to both B20 and B100 samples. For B20, ASTM D664 can measure TAN values even at a level as low as 0.123 with small error (4.13%). For B100, TAN around 0.3 was measured with the best accuracy. This observation is important because it demonstrates that TAN standards can be set for biodiesel mixtures that reflect the B100 TAN standard.

Application of ASTM D664 to B20 to measure the TAN value even down to 0.123 mg KOH/g was tested with good accuracy, which demonstrates that a lower TAN specification for B20 is possible. Since the electrode is a critical factor affecting the accuracy and reproducibility of ASTM D664, it is recommended to put different guidelines on the electrode use, storage and maintenance procedures with different fuel samples.

Table 1 Experimental means and calculated TANs of B100 and ULSD mixtures with ASTM D664 (unit: mg KOH/g)

V% B100	Exp. results	Mean	Cal.	SD	Repeatability (%)	Err. (%)
100.00	0.262, 0.242, 0.236	0.247	–	0.013	15.28	–
88.48	0.197, 0.212, 0.208	0.206	0.222	0.008	10.46	−7.21
78.12	0.182, 0.183, 0.190	0.185	0.199	0.004	6.53	−7.01
67.87	0.167, 0.150, 0.167	0.161	0.177	0.010	16.85	−8.67
58.73	0.130, 0.151, 0.134	0.138	0.155	0.011	22.33	−10.90
48.69	0.118, 0.111, 0.113	0.114	0.132	0.004	8.76	−13.76
38.75	0.095, 0.089, 0.108	0.097	0.109	0.010	27.64	−10.66
29.89	0.079, 0.078, 0.076	0.078	0.087	0.002	5.45	−11.12
19.17	0.057, 0.057, 0.062	0.059	0.064	0.003	13.63	−8.25
10.50	0.050, 0.047, 0.062	0.051	0.042	0.005	24.89	22.51
0.00	0.016, 0.018, 0.018	0.017	–	0.001	18.45	–

Large repeatability and errors indicate the improper operation of the electrode

Table 2 Experimental means and calculated TANs of the B20 samples with ASTM D664 (unit: mg KOH/g)

Samples	Composition (Wt.%)		Exp. results	Mean	Cal. TAN	SD	Repeatability (%)	Err. (%)
	B20-1	B20-2						
B20-1	100	0	0.083, 0.083, 0.084	0.083	–	0.0006	1.92	–
B20-2	0	100	0.383, 0.383, 0.385	0.383	–	0.0015	1.10	–
Mixture 1	90.06	9.94	0.120, 0.124, 0.124	0.123	0.118	0.0023	5.21	4.13
Mixture 2	79.98	20.02	0.154, 0.153, 0.158	0.155	0.153	0.0026	4.73	1.25
Mixture 3	70.30	29.70	0.187, 0.185, 0.186	0.186	0.187	0.001	1.49	−0.52
Mixture 4	59.58	40.42	0.220, 0.224, 0.224	0.223	0.224	0.0023	2.87	−0.80
Mixture 5	50.00	50.00	0.230, 0.229, 0.229	0.229	0.232	0.0006	0.70	−1.36
Mixture 6	39.78	60.22	0.263, 0.262, 0.263	0.263	0.263	0.0006	0.61	0.00
Mixture 7	30.00	70.00	0.305, 0.300, 0.298	0.301	0.292	0.0036	3.32	2.98
Mixture 8	16.85	83.15	0.336, 0.331, 0.330	0.332	0.332	0.0032	2.68	0.00

Small error and repeatability data in the table indicate good accuracy and repeatability when applying ASTM D664 to B20. Good accuracy was obtained even at the TAN of 0.123

Table 3 Experimental means and calculated TANs of the B100 samples with ASTM D664 (unit: mg KOH/g)

Samples	Composition (Wt.%)		Exp. results	Mean	Cal.	SD	Repeatability (%)	Err. (%)
	B100-1	B100-2						
B100-1	100	0	0.205, 0.201, 0.203	0.203	–	0.002	2.73	–
B100-2	0	100	0.526, 0.533, 0.524	0.528	–	0.0047	2.48	–
Mixture 1	20.12	79.88	0.462, 0.451, 0.459	0.457	0.463	0.0057	3.44	−1.14
Mixture 2	42.29	57.71	0.382, 0.390, 0.408	0.393	0.391	0.0133	9.38	0.71
Mixture 3	50.18	49.82	0.377, 0.375, 0.365	0.372	0.365	0.0064	4.78	2.03
Mixture 4	70.68	29.32	0.299, 0.296, 0.298	0.298	0.298	0.0015	1.42	0.00
Mixture 5	85.93	14.07	0.252, 0.253, 0.249	0.251	0.249	0.0021	2.29	1.05

Small error and repeatability data in the table indicates good accuracy and repeatability when applying ASTM D664 to B100

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