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Determination of Acid Number of Biodiesel and Biodiesel Blends

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Abstract Due to an increase in the commercial use of biodiesel and biodiesel blends, both ASTM D 6751 and EN 14214 include the acid number (AN) as an important quality parameter. It was found that determination of AN of biodiesel and biodiesel blends using the ASTM D 974 results in large values of repeatability (up to 73.41%) and larger percentage error (up to 42.88%). Therefore, ASTM D 974 has been modified using a lower concentration of base (0.02 M KOH instead of 0.1 M KOH) as well as reducing the amount of toxic titration solvent from 100 mL to only 10 mL. This makes the modified ASTM D 974 as a green analytical method which uses a reduced amount of toxic solvent. This modified method significantly reduced the maximum percentage error from 42.88 to 5.92%. The application of this modified ASTM D 974 for the determination of AN of biodiesel and biodiesel blends was studied. The accuracy of this modified ASTM D 974 for biodiesel (B100) was measured to be within 3.51% over the AN range of 0.313–0.525 mg KOH/g and maximum repeatability was decreased from 8.37 to 2.75% within this AN range which is far below the ASTM D 974 stated repeatability specifications. For B20, B10, B5, B2, and B1, the most accurate values were measured at AN values of 0.177, 0.067, 0.072, 0.126, and 0.096 mg KOH/g, respectively. Excellent linearity values of R^2 for calculated and experimentally determined AN were obtained. The difference between the experimental and the calculated AN for all biodiesel and biodiesel blend samples was within ± 0.018 mg KOH/g. This extensive study has demonstrated that this modified ASTM D 974 is a reliable method for the determination of AN and could be used for establishing the specifications of AN for biodiesel and biodiesel blends ranging from B1 to B20 in quality standards.

Keywords Acid number · Biodiesel · ASTM D 974 · Biodiesel blends · Biodiesel standards

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Introduction

Biodiesel is defined by the American Society for Testing and Materials (ASTM) as the mono alkyl ester of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat [1]. Due to an increasing interest and the use of biodiesel around the world, the assurance of biodiesel quality has become of paramount interest to the successful commercialization and market acceptance of biodiesel. Therefore, various biodiesel standards have been established around the world, including the United States (ASTM D 6751) and Europe (EN 14214) [2].

ASTM standard D 6751 and European Committee for Standardization (CEN) standard EN 14214 set similar specifications for biodiesel as motor fuel [3, 4]. In both standards, one important quality parameter for biodiesel is the acid number (AN). AN is measured as the mg of KOH required to neutralize the acids in 1 g of the sample [5]. AN is a measure of the degree of oxidation and hydrolysis in the biodiesel [8]. AN measurement detects both weak organic acids and strong inorganic acids. Both ASTM D 6751 and EN 14214 has restricted the maximum value of AN to be 0.50 mg KOH/g for biodiesel (B100). This is due to the fact that free fatty acids (FFA), which can be produced during the production process [7], can result in severe operational problems and is considered as a safety risk during its storage due to the possibility of corrosion by the FFA [8]. Fuel age also affects the acidity of the biodiesel because as the biodiesel ages it becomes more acidic which can be attributed to the hydrolytic cleavage of the ester bond and/or to the oxidation degradation of chain at double bonds [7]. A high AN could leads the fuel prone to polymerization as well as acts as a catalyst for hydrolysis [7]. AN of biodiesel depends on the type of feedstock and how well the biodiesel was processed during and after the production. Production of biodiesel from high FFA content feedstock is gaining momentum around the world due to its economical, commercial, and environmental benefits [1]. This requires an accurate determination of AN to monitor the progress of the biodiesel production process.

AN determination, like kinematic viscosity, is a facile method for monitoring fuel quality [2]. Analytical methods for AN determination can be divided into two titration categories: potentiometric or colorimetric. There are two major ASTM test methods, ASTM D 664 and ASTM D 974, which can be used for AN determination. Determination of AN is described in ASTM D 6751 using the method ASTM D 664, a potentiometric method. However, ASTM D 664 possesses mediocre reproducibility, a problem mentioned in the method itself [6]. The problem is likely due to the variability of electrodes which introduce an additional level of uncertainty [7]. Recently, it has been confirmed that better values of accuracy and repeatability can be obtained only if the ASTM D 664 method is modified by using a tedious electrodes cleaning process for the electrodes, which required almost double the analysis time [8]. This becomes critical for today's commercial production process where fast analytical methods are essential for controlling the quality of biodiesel.

This problem can be address by using ASTM D 974 which is another nonaqueous colorimetric-titration based method which uses KOH in isopropanol with *p*-naphtholbenzein as an indicator and is suitable even for colored samples [2, 7]. ASTM D 974 is a method for measuring the AN of petroleum oils [5]. The European biodiesel fuel standard, EN 14214, used EN 14104 as the reference standard method for the determination of AN which is also a colorimetric acid–base titration method; however, it uses a dilute ethanolic KOH solution with phenolphthalein as an indicator [2]. Furthermore, ASTM D 974 is a versatile method which is easy to perform and duplicate in laboratories as it involves only glassware, solution, and an indicator [7]. Recently, ASTM D 974 has been successfully used for the determination of AN to monitor the biodiesel production from high FFA feedstocks [1]. Analytical results were more consistent using ASTM D 974 than with ASTM D 664 [7].

In the literature, ASTM D 974 has been used to determine the AN of biodiesel [7]. However, in that study, standards were made by adding palmitic acid to soybean oil instead of biodiesel. Furthermore, over 50% of the standards were in the AN range which exceeds the specification for AN in the ASTM standards (0.50 mg KOH/g) [7]. ASTM D 974 has not yet been evaluated for the determination of AN of biodiesel blends. This study quantifies the accuracy and repeatability of ASTM D 974 for refurbished waste oils and fats based biodiesel (B100) and its blends (B20, B10, B5, B2, and B1).

Biodiesel can be used alone (B100) or blended with petroleum diesel in any proportion. It is usually blended with ultra low sulfur diesel (ULSD) at various levels for lubricity improvement and emissions control [9]. Furthermore, when biodiesel is used at low levels (<5%) such as B1 and B2, the user may not experience any significant decrease in power, torque, and fuel economy as compared to when using high level blends such as B20 [9]. Recently, a quality survey of biodiesel blends sold commercially emphasize the need for ASTM standards for the biodiesel blends and monitoring of the quality of the biodiesel blends sold at retailers [10]. This required an easy to use, fast, and economical method to analyze the AN in the field or a retailer location. As a result, field test kits have been developed for cost-effective on-site analysis, which were also based on acid–base colorimetric titration, not on potentiometric method.

Recently, in the USA and Canada, the commercial use of biodiesel has been started as a motor fuel using its blends such as B1, B2, B5, B10, and B20. At present, in the USA, ASTM has set the specifications for biodiesel blends with more than 5% B100 (B6–B20) in standard ASTM D 7467-09 which allows for a maximum AN of 0.3 mg KOH/g. However, no specifications for AN have been set yet for lower biodiesel blends such as B1, B2, and B5. On the other hand, in Canada, the Canadian General Standards Board (CGSB) has developed the specifications for biodiesel blends (from B1 to B5) in CAN/CGSB-3.520. This standard set the maximum AN limit to 0.10 mg KOH/g and uses ASTM D 974 as the reference standard method. However, specifications for blends with high levels of biodiesel (B6–B20) have not been developed. Recently, ASTM D 664 has been evaluated to determine its accuracy and repeatability for biodiesel blends but that of ASTM D 974 was not tested for comparison [8]. Also, the study was limited to only B20 [8]. No study has been reported in the literature for the application of ASTM D 974 for the determination of the AN of lower level biodiesel blends such as B10, B5, B2, and B1. To the best of our knowledge, this study is the first report on the evaluation of ASTM D 974 for the determination of the AN of biodiesel blends (B1, B2, B5, B10, and B20) where accuracy and repeatability were determined.

Experimental

Materials

The refurbished waste oils and fats based biodiesel (B100) was obtained from Rothsay (Quebec, Canada). Ultra low sulfur diesel (USLD) was obtained from Boucher & Jones Fuels (Petro Canada, Waterloo, Ontario). Biodiesel blends, B20, B10, B5, B2, and B1 were prepared by mixing B100 and ULSD at a volume ratio of 1:4, 1:9, 1:19, 1:49, and 1:99, respectively. The following chemicals were supplied by Sigma–Aldrich Chemical Company (Milwaukee, WI): palmitic acid (99%), 2-propanol (anhydrous, 99.5%), toluene (anhydrous, 99.8%), *p*-naphtholbenzein (indicator grade). The titrant solution, 0.1 M KOH (volumetric standard, in isopropanol), was supplied by Fisher Scientific (Ottawa, ON, Canada) which was used to prepare 0.02 M KOH in isopropanol.

Methods

The titration solvent and indicator solution were prepared as detailed in ASTM D 974. Blends of B100 and ULSD were prepared to obtain weight percentages ranging from 0 to 90% as shown in Tables 1, 2, and 3. Also, biodiesel and biodiesel blends with a range of known AN levels ranging from 0.05 to 0.55 mg KOH/g were prepared by adding palmitic acid to the solutions of B1, B2, B5, B10, B20, and B100. As shown in Tables 4, 5, 6, 7, 8, and 9, Bxx-1 represents unspiked samples and Bxx-2 represents samples spiked with palmitic acid. For example B20-1 is not spiked and B20-2 is spiked. Mixtures are derived by blending different wt. % of pure Bxx-1 and pure Bxx-2. The analyst did not know the exact calculated value of AN. The range of AN values of biodiesel and biodiesel blends was restricted to the AN as per the AN specifications in standards for biodiesel and biodiesel blends. For B100 and B20 each sample was titrated in triplicate (in order to compare with the literature reported results of ASTM D 664). For B1 to B10, each sample was titrated six times.

For determining the AN of biodiesel and biodiesel blends, 2 g (measured to four decimal places) of a sample was collected in an Erlenmeyer flask (125 mL). Ten milliliters (otherwise as stated) of titration solvent using a 10 mL pipette and eight drops of the *p*-naphtholbenzein indicator solution were added to each sample. The sample was then titrated against a 0.02 M KOH (otherwise as stated) solution using a 10 mL burette. The titration was deemed complete when a color change from orange to green was observed in the titration mixture that persists for at least 15 s.

The experimental acid number was determined using Eq. 1 as per ASTM D 974 [5]:

$$\text{Acid value, mg of KOH/g} = \left[\frac{(A-B)\times M\times 56.1}{W}\right] \quad (1)$$

Table 1 Calculated and Experimental AN of the B100 and ULSD mixtures as per ASTM D 974 (using 0.1M KOH and 100mL Titration Solvent) (unit: mg KOH/g)

Wt% B100	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
100.00	0.313, 0.315, 0.302	0.310	–	0.0073	0.00	–	–
89.95	0.263, 0.255, 0.301	0.273	0.280	0.0246	24.95	−2.41	−0.007
79.02	0.284, 0.264, 0.248	0.266	0.247	0.0183	19.05	7.50	0.019
70.04	0.201, 0.236, 0.220	0.219	0.220	0.0172	21.72	−0.50	−0.001
60.41	0.177, 0.173, 0.175	0.175	0.192	0.0018	2.85	−8.71	−0.017
49.97	0.148, 0.173, 0.244	0.188	0.162	0.0499	73.41	16.12	0.026
40.08	0.146, 0.144, 0.144	0.144	0.131	0.0012	2.30	10.28	0.013
30.21	0.141, 0.144, 0.148	0.144	0.101	0.0037	7.18	42.88	0.043
20.03	0.089, 0.066, 0.092	0.083	0.071	0.0141	47.25	16.24	0.012
10.07	0.037, 0.038, 0.038	0.038	0.041	0.0003	1.95	−8.24	−0.003
0.00	0.011, 0.011, 0.011	0.011	–	0.0002	0.00	–	–

Application of ASTM D 974 (using 0.1M KOH and 100mL Titration Solvent) to B100 and ULSD mixtures resulted in large repeatability and errors as indicated in tabulated data

[a] Experimentally determined as per ASTM D 974 (using 0.1M KOH and 100mL Titration Solvent)

[b] Calculated AN = [{AN of (B100) x wt% component of (B100) in the mixture} + {AN of (ULSD) x wt% component of (ULSD) in the mixture}/100]

[c] Standard Deviation (SD)

Table 2 Calculated and Experimental AN of the B100 and ULSD mixtures as per modified ASTM D 974 (using 0.02M KOH and 100mL Titration Solvent) (unit: mg KOH/g)

Wt% B100	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
100.00	0.304, 0.309, 0.326	0.313	–	0.0118	0.00	–	–
89.95	0.286, 0.290, 0.286	0.287	0.284	0.0021	1.98	1.18	0.003
79.02	0.278, 0.263, 0.253	0.265	0.253	0.0128	13.39	4.57	0.012
70.04	0.225, 0.217, 0.227	0.223	0.227	0.0048	6.02	−1.78	−0.004
60.41	0.206, 0.204, 0.206	0.205	0.199	0.0009	1.26	3.08	0.006
49.97	0.182, 0.161, 0.180	0.175	0.169	0.0116	18.45	3.37	0.006
40.08	0.143, 0.148, 0.140	0.144	0.140	0.0041	7.84	2.55	0.004
30.21	0.108, 0.114, 0.101	0.108	0.112	0.0067	17.23	−3.78	−0.004
20.03	0.073, 0.076, 0.073	0.074	0.083	0.0015	5.77	−10.87	−0.009
10.07	0.054, 0.056, 0.048	0.053	0.054	0.0045	23.63	−2.14	−0.001
0.00	0.039, 0.018, 0.018	0.025	–	0.0118	0.01	–	–

Application of modified ASTM D 974 (using 0.02M KOH and 100mL Titration Solvent) to B100 and ULSD mixtures resulted in good accuracy and repeatability as indicated in tabulated data

[a] Experimentally determined as per modified ASTM D 974 (using 0.02M KOH and 100mL Titration Solvent)

[b] Calculated AN = [{AN of (B100) x wt% component of (B100) in the mixture} + {AN of (ULSD) x wt% component of (ULSD) in the mixture}/100]

[c] Standard Deviation (SD)

where

A KOH solution required for titration of the sample, mL,
B KOH solution required for titration of the blank, mL,
M Molarity of the KOH solution, and
W Sample used, *g*

Results and Discussion

According to ASTM, the repeatability of a method is defined as "the difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed only in one case in twenty"[5].

In this study, the same operator, the same laboratory, and the same apparatus were used with a short time between tests. These conditions are in accordance with the requirements of ASTM for repeatability. Therefore, the repeatability values were calculated using the following Eq. 2:

$$\text{repeatability}\ (\%) = \left[\frac{2.77\ \times\ \text{SD}}{\text{Experimental mean} \times n}\right] \times 100\% \tag{2}$$

where

n Number of operators involved in the analysis = 1

In this study, the errors were calculated using the following Eq. 3 [8]:

$$\text{Error}\ (\%) = \left[\frac{\text{Experimental AN mean} - \text{Calculated AN}}{\text{Calculated AN}}\right] \times 100\% \tag{3}$$

In the above equation, the calculated AN was based on the sum of the wt% composition of low AN and high AN samples of biodiesel and biodiesel blends mixtures as shown in Eq. 4. The calculated AN is derived from the experimentally determined values of pure Bxx-1 and pure Bxx-2. For example, the calculated AN for B100 samples, will be as follows:

$$\text{Calculated AN} = \left[\begin{array}{l}\{\text{AN of (B100-1)} \times\ \text{wt\% component of (B100-1) in the mixture}\}+ \\ \{\text{AN of (B100-2)} \times\ \text{wt\% component of (B100-2) in the mixture}\}/100\end{array}\right] \tag{4}$$

Table 3 Calculated and Experimental AN of the B100 and ULSD mixtures as per modified ASTM D 974 (using 0.02M KOH and 10mL Titration Solvent) (unit: mg KOH/g)

Wt% B100	Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
100.00	0.309, 0.299, 0.305	0.304	–	0.0046	0.00	–	–
89.95	0.267, 0.278, 0.280	0.275	0.275	0.0068	6.88	0.08	0.000
79.02	0.233, 0.226, 0.239	0.232	0.243	0.0067	7.96	−4.32	−0.011
70.04	0.188, 0.205, 0.216	0.203	0.216	0.0140	19.06	−5.92	−0.013
60.41	0.187, 0.183, 0.189	0.186	0.188	0.0031	4.68	−0.86	−0.002
49.97	0.155, 0.164, 0.148	0.156	0.157	0.0082	14.61	−0.64	−0.001
40.08	0.123, 0.135, 0.125	0.128	0.128	0.0064	13.97	−0.23	0.000
30.21	0.099, 0.096, 0.102	0.099	0.100	0.0031	8.80	−1.14	−0.001
20.03	0.062, 0.077, 0.078	0.073	0.070	0.0088	33.51	3.59	0.003
10.07	0.047, 0.037, 0.041	0.042	0.041	0.0050	33.10	2.19	0.001
0.00	0.009, 0.014, 0.009	0.011	–	0.0026	0.01	–	–

Application of modified ASTM D 974 (using 0.02M KOH and 10mL Titration Solvent) to B100 and ULSD mixtures resulted in good accuracy and repeatability as indicated in tabulated data

[a] Experimentally determined as per modified ASTM D 974 (using 0.02M KOH and 10mL Titration Solvent)

[b] Calculated AN = [{AN of (B100) x wt% component of (B100) in the mixture} + {AN of (ULSD) x wt% component of (ULSD) in the mixture}/100]

[c] Standard Deviation (SD)

Table 4 Calculated and Experimental AN of the B100 samples as per modified ASTM D 974 (using 0.02M KOH and 10mL Titration Solvent) (unit: mg KOH/g)

Samples	Composition (wt %)		Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
	B100-1	B100-2							
B100-1	100	0	0.268, 0.276, 0.281	0.275	–	0.0067	0.00	–	–
B100-2	0	100	0.624, 0.631, 0.644	0.633	–	0.0102	0.00	–	–
Mixture 1	89.45	10.45	0.310, 0.303, 0.321	0.311	0.313	0.0094	8.37	−0.41	−0.001
Mixture 2	79.47	20.53	0.359, 0.362, 0.347	0.356	0.349	0.0077	6.01	2.05	0.007
Mixture 3	69.70	30.21	0.394, 0.386, 0.402	0.394	0.383	0.0084	5.92	2.76	0.011
Mixture 4	59.44	40.56	0.428, 0.423, 0.434	0.428	0.421	0.0059	3.84	1.87	0.008
Mixture 5	48.90	51.10	0.474, 0.478, 0.463	0.472	0.458	0.0080	4.68	2.97	0.014
Mixture 6	40.18	59.82	0.519, 0.497, 0.504	0.507	0.489	0.0108	5.92	3.51	0.017
Mixture 7	30.19	69.81	0.533, 0.539, 0.529	0.534	0.525	0.0053	2.75	1.62	0.009

Application of modified ASTM D 974 to B100 resulted in good accuracy and repeatability as indicated in tabulated data

[a] Experimentally determined as per modified ASTM D 974

[b] Calculated AN = [{AN of (B100-1) x wt% component of (B100-1) in the mixture} + {AN of (B100-2) x wt% component of (B100-2) in the mixture}/100]

[c] Standard Deviation (SD)

Therefore, as an example, for Mixture-1 in Table 4, calculated AN will be determined using Eq. 4 as follows:

$$\text{Calculated AN} = \left[\left\{(0.275 \times 89.45) + (0.633 \times 10.45)\right\}/100\right] = 0.313$$

ASTM D 974 was applied to blends of B100 and ULSD, of which the results are shown in Table 1. It was found that application of ASTM D 974 which used 0.1 M KOH and 100 mL of titration solvent, results in high values of repeatability (up to 73.41%) and very large percentage error (up to 42.88%). This error was anticipated due to the high concentration of base as very small volumes of base were consumed which may contribute to significant error. Therefore, to investigate further, a lower concentration of base was used (0.02 M KOH). It was confirmed that the use of 0.02 M KOH reduced the maximum repeatability value to 23.63% and percentage error to 10.87% as compared to the maximum repeatability value of 73.41% and

Table 5 Calculated and Experimental AN of B20 samples as per modified ASTM D 974 (using 0.02M KOH and 10mL Titration Solvent) (unit: mg KOH/g)

Samples	Composition (wt %)		Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
	B20-1	B20-2							
B20-1	100	0	0.060, 0.052, 0.058	0.057	–	0.0039	18.89	–	–
B20-2	0	100	0.411, 0.430, 0.424	0.421	–	0.0101	6.61	–	–
Mixture 1	94.27	5.73	0.077, 0.072, 0.068	0.073	0.078	0.0046	17.64	−6.60	−0.005
Mixture 2	88.18	11.82	0.104, 0.121, 0.110	0.112	0.100	0.0084	20.91	11.76	0.012
Mixture 3	79.53	20.47	0.141, 0.138, 0.139	0.139	0.131	0.0013	2.66	6.02	0.008
Mixture 4	67.78	32.22	0.191, 0.185, 0.156	0.177	0.174	0.0188	29.42	1.78	0.003
Mixture 5	60.69	39.31	0.194,0.213,0.208	0.205	0.200	0.0098	13.21	2.53	0.005
Mixture 6	49.78	50.22	0.260, 0.251, 0.251	0.254	0.240	0.0054	5.85	5.84	0.014
Mixture 7	39.65	60.35	0.290, 0.288, 0.292	0.290	0.277	0.0019	1.84	4.83	0.013
Mixture 8	29.61	70.39	0.327, 0.322, 0.338	0.329	0.313	0.0083	6.97	5.02	0.016

Application of modified ASTM D 974 to B20 resulted in good accuracy and repeatability as indicated in tabulated data

[a] Experimentally determined as per modified ASTM D 974

[b] Calculated AN = [{AN of (B20-1) x wt% component of (B20-1) in the mixture} + {AN of (B20-2) x wt% component of (B20-2) in the mixture}/100]

[c] Standard Deviation (SD)

Table 6 Calculated and Experimental AN of the B10 samples as per modified ASTM D 974 (using 0.02M KOH and 10mL Titration Solvent) (unit: mg KOH/g)

Samples	Composition (wt %)		Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
	B10-1	B10-2							
B10-1	100	0	0.051,0.031, 0.038, 0.027, 0.028,0.036	0.035	–	0.0088	0.01	–	–
B10-2	0	100	0.305, 0.340, 0.320, 0.323, 0.344, 0.321	0.326	–	0.0143	0.00	–	–
Mixture 1	88.94	11.06	0.069, 0.082, 0.068, 0.074, 0.047, 0.064	0.067	0.067	0.0117	48.20	0.09	0.000
Mixture 2	80.19	19.81	0.085, 0.084, 0.095, 0.097, 0.105, 0.095	0.094	0.093	0.0077	22.76	0.95	0.001
Mixture 3	68.91	31.09	0.125, 0.125,0.130, 0.111, 0.122, 0.119	0.122	0.126	0.0066	14.99	−2.87	−0.004
Mixture 4	59.08	40.92	0.144, 0.166, 0.164, 0.159, 0.147, 0.156	0.156	0.154	0.0088	15.63	1.11	0.002
Mixture 5	40.46	59.54	0.204, 0.201, 0.184, 0.200, 0.190, 0.202	0.197	0.208	0.0079	11.11	−5.48	−0.011
Mixture 6	30.23	69.77	0.242, 0.232, 0.235, 0.225, 0.204, 0.205	0.224	0.238	0.0161	19.85	−5.92	−0.014

Application of modified ASTM D 974 to B10 resulted in good accuracy and repeatability as indicated in tabulated data

[a] Experimentally determined as per modified ASTM D 974

[b] Calculated AN = [{AN of (B10-1) x wt% component of (B10-1) in the mixture} + {AN of (B10-2) x wt% component of (B10-2) in the mixture}/100]

[c] Standard Deviation (SD)

percentage error of 42.88% when higher concentration of base (0.1 M KOH) was used as per ASTM D 974 as shown in Table 2.

Furthermore, there is an emphasis on making chemical processes and analytical methods greener by reducing the amounts of toxic chemicals. The ASTM D 974, required 100 mL of titration solvent which is a mixture of toluene, isopropanol and water in the volume ratio of 100:99:1. Therefore, in an attempt to reduce the amount of toxic chemicals used in ASTM D 974, a lower volume of titration solvent (10 mL) was used with modified ASTM D 974 (0.02 M KOH). It was found that the use of 10 mL titration solvent reduced the maximum percentage error value to 5.92% as compared to the maximum percentage error value of 10.87% when higher amounts of titration solvent (100 mL) were used as per modified ASTM D 974 (0.02 M KOH) as shown in Table 3. Also, even with the reduced volume of titration solvent (10 mL), the values of repeatabilities obtained were similar to those when modified ASTM D 974 (0.02 M KOH) was used with high amount of titration solvent (100 mL). Furthermore, the linearity curves relating the AN determined experimentally by ASTM D 974 (0.1 M KOH and 100 mL titration solvent), modified ASTM D 974 (0.02 M KOH and 100 mL titration

Table 7 Calculated and Experimental AN of the B5 samples as per modified ASTM D 974 (using 0.02M KOH and 10mL Titration Solvent) (unit: mg KOH/g)

Samples	Composition (wt %)		Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN difference (Exp. - Cal.)
	B5-1	B5-2							
B5-1	100	0	0.010, 0.009, 0.005, 0.010, 0.011, 0.006	0.008	–	0.0024	0.01	–	–
B5-2	0	100	0.293, 0.280, 0.291, 0.299, 0.293, 0.292	0.291	–	0.0062	0.00	–	–
Mixture 1	90.42	9.58	0.028, 0.037, 0.039, 0.057, 0.044, 0.035	0.040	0.035	0.0099	68.45	14.35	0.005
Mixture 2	84.16	15.84	0.054, 0.056, 0.054, 0.075, 0.068, 0.060	0.061	0.053	0.0086	38.99	15.83	0.008
Mixture 3	79.99	20.01	0.071, 0.072, 0.080, 0.077, 0.064, 0.067	0.072	0.065	0.0060	23.09	9.67	0.006
Mixture 4	74.96	25.04	0.098, 0.100, 0.085, 0.100, 0.088, 0.101	0.095	0.079	0.0069	20.04	20.75	0.016
Mixture 5	69.97	30.03	0.101, 0.096, 0.110, 0.111, 0.132, 0.113	0.111	0.093	0.0123	30.82	18.84	0.018
Mixture 6	59.53	40.47	0.143, 0.133, 0.127, 0.121, 0.152, 0.141	0.136	0.123	0.0114	23.16	10.43	0.013

Application of modified ASTM D 974 to B5 resulted in good accuracy and repeatability as indicated in tabulated data

[a] Experimentally determined as per modified ASTM D 974

[b] Calculated AN = [{AN of (B5-1) x wt% component of (B5-1) in the mixture} + {AN of (B5-2) x wt% component of (B5-2) in the mixture}/100]

[c] Standard Deviation (SD)

Table 8 Calculated and Experimental AN of the B2 samples as per modified ASTM D 974 (using 0.02M KOH and 10mL Titration Solvent) (unit: mg KOH/g)

Samples	Composition (wt %)		Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN Difference (Exp. - Cal.)
	B2-1	B2-2							
B2-1	100	0	0.018, 0.009, 0.018, 0.009, 0.014, 0.004	0.012	–	0.0058	0.01	–	–
B2-2	0	100	0.377, 0.372, 0.361, 0.449, 0.374, 0.367	0.383	–	0.0327	0.00	–	–
Mixture 1	90.42	9.58	0.061, 0.064, 0.063, 0.053, 0.052, 0.065	0.060	0.050	0.0059	27.20	19.67	0.010
Mixture 2	84.16	15.84	0.080, 0.075, 0.080, 0.076, 0.083, 0.095	0.082	0.071	0.0074	25.11	14.82	0.011
Mixture 3	79.99	20.01	0.102, 0.096, 0.101, 0.104, 0.095, 0.113,	0.102	0.091	0.0065	17.70	12.03	0.011
Mixture 4	74.96	25.04	0.108, 0.115, 0.123, 0.119, 0.110, 0.104	0.113	0.097	0.0071	17.27	16.69	0.016
Mixture 5	69.97	30.03	0.112, 0.120, 0.106, 0.104, 0.106, 0.117	0.111	0.107	0.0065	16.29	3.82	0.004
Mixture 6	59.53	40.47	0.110, 0.113, 0.142, 0.128, 0.141, 0.126	0.126	0.127	0.0135	29.49	−0.43	−0.001

Application of modified ASTM D 974 to B2 resulted in good accuracy and repeatability as indicated in tabulated data

[a] Experimentally determined as per modified ASTM D 974

[b] Calculated AN = [{AN of (B2-1) x wt% component of (B2-1) in the mixture} + {AN of (B2-2) x wt% component of (B2-2) in the mixture}/100]

[c] Standard Deviation (SD)

solvent) and modified ASTM D 974 (0.02 M KOH and 10 mL titration solvent) to the calculated AN of the biodiesel and ULSD mixtures were obtained with the correlation coefficient (R^2) values of 0.9474, 0.9960, and 0.9968, respectively, as shown in Fig 1. This demonstrates that this modified ASTM D 974 method has better linearity. Therefore, this modified ASTM D 974 method, using 0.02 M KOH and 10 mL of titration solvent, was used for the determination of AN values for biodiesel and biodiesel blends.

The results for the determination of the AN for the biodiesel (B100) are shown in Table 4. B100-1 in Table 4 is the original sample with low AN, whereas, B100-2 is the high AN sample prepared by adding a calculated amount of palmitic acid to B100-1. Mixtures 1–7 in Table 4 were obtained by mixing B100-1 and B100-2 at different wt% ratios to produce biodiesel with different AN samples in the range of 0.313–0.525 mg KOH/g. Each sample was titrated three times; the mean, standard deviation (SD), repeatability, percentage error (less error, higher accuracy), and the difference between experimental and calculated AN are also shown in Table 4.

ASTM D 974 cites that the repeatability of 0.05 mg KOH/g in the AN range of 0.1–0.5 mg KOH/g for 20.0 g samples of petroleum oil. This corresponds to 50 and 10% at the AN values of 0.1 and 0.5 mg KOH/g, respectively.

Table 9 Calculated and Experimental AN of the B1 samples as per modified ASTM D 974 (using 0.02M KOH and 10mL Titration Solvent) (unit: mg KOH/g)

Samples	Composition (wt %)		Experimental[a] AN	Mean	Calculated[b] AN	SD[c]	Repeatability (%)	Error (%)	AN Difference (Exp. - Cal.)
	B1-1	B1-2							
B1-1	100	0	0.009, 0.019, 0.004, 0.019, 0.019, 0.008	0.013	–	0.0068	0.01	–	–
B1-2	0	100	0.225, 0.238, 0.226, 0.210, 0.209, 0.230	0.223	–	0.0112	0.00	–	–
Mixture 1	81.03	18.97	0.065, 0.056, 0.051, 0.054, 0.051, 0.057	0.056	0.053	0.0053	26.59	5.25	0.003
Mixture 2	74.32	25.68	0.087, 0.085, 0.077, 0.082, 0.074, 0.073	0.080	0.067	0.0058	20.02	19.05	0.013
Mixture 3	67.05	32.95	0.104, 0.090, 0.083, 0.095, 0.096, 0.086	0.092	0.082	0.0075	22.55	12.45	0.010
Mixture 4	64.68	35.32	0.099, 0.113, 0.091, 0.099, 0.096, 0.082	0.097	0.087	0.0101	28.95	10.92	0.010
Mixture 5	60.22	39.78	0.092, 0.101, 0.104, 0.085, 0.107, 0.085,	0.096	0.097	0.0096	27.89	−1.04	−0.001
Mixture 6	48.78	51.22	0.112, 0.116, 0.110, 0.100, 0.131, 0.104	0.112	0.121	0.0108	26.68	−7.05	−0.008

Application of modified ASTM D 974 to B1 resulted in good accuracy and repeatability as indicated in tabulated data

[a] Experimentally determined as per modified ASTM D 974

[b] Calculated AN = [{AN of (B1-1) x wt% component of (B1-1) in the mixture} + {AN of (B1-2) x wt% component of (B1-2) in the mixture}/100]

[c] Standard Deviation (SD)

ASTM recommends a sample size of 20 g when the AN lies between 0.0 and 3.0 mg KOH/g. In this study, the repeatability of the B100 samples was decreased from 8.37 to 2.75% within the AN range of 0.313–0.525 mg KOH/g as shown in Table 4. These repeatability values are within the stated repeatability values as specified in ASTM D 974 even when the sample sizes were one-tenth as large and also far below the recently reported maximum and minimum repeatability values of 27.64 and 5.45%, determined using the ASTM D 664 method without any modification [8]. In addition, percentage error of modified ASTM D 974 for all B100 samples was measured to be within 3.51% over the AN range of 0.313–0.525 mg KOH/g. At an AN value of 0.525 mg KOH/g, the error was only 1.62% as compared to the literature reported value of 3.30% at an AN value of 0.595 mg KOH/g [7]. From Table 1, the maximum absolute experimental error for all seven samples was up to 3.51%. For B100, an AN of 0.313 mg KOH/g was measured with best accuracy (least error). For B100, the accuracy values are good, which shows that even at small AN, this modified ASTM D 974 can be used.

The results for the determination of the AN of biodiesel blends, B20, B10, B5, B2, and B1 are shown in Tables 5, 6, 7, 8, and 9, respectively, using modified ASTM D 974. The range of AN values of biodiesel blends was restricted to the AN as per the AN specifications in standards for biodiesel blends. For example, for B1–B5, the AN specification is 0.10 mg KOH/g and hence the range of AN selected was 0.035–0.127 mg KOH/g. For blends with high levels of biodiesel such as B10 and B20, the range of AN was 0.067–0.313 mg KOH/g as the standard limit is 0.3 mg KOH/g. For B20, the modified ASTM D 974 can measure AN values even at a level as low as 0.073 mg KOH/g with a small error of −6.60% which is much better as compared to not only ASTM D 664, but even the modified ASTM D 664 method, which measure the lowest AN value of 0.123 mg KOH/g with an error of 4.13% [8]. For B20, B10, B5, B2, and B1, the most accurate values were measured at AN values of 0.177, 0.067, 0.072, 0.126, and 0.096 mg KOH/g, respectively. For all biodiesel blend samples, as the AN values increase, better repeatability was obtained.

The linearity curves relating the AN determined experimentally by modified ASTM D 974 to the calculated AN of the biodiesel and biodiesel blends were obtained as shown in Fig 2. The correlation coefficient (R^2) values obtained for B100, B20, B10, B5, B2, and B1 were 0.9974, 0.9969, 0.9968, 0.9882, 0.9599, and 0.8988, respectively, as shown in Fig 2. This demonstrates excellent linearity. The difference between the experimental AN determined as per modified ASTM D 974 and the calculated AN for all biodiesel and biodiesel blend samples was within ± 0.018 mg KOH/g as shown in Tables 4, 5, 6, 7, 8, and 9 demonstrating the reliability of the modified ASTM D 974 method.

A major limitation for the application of ASTM D 974 was that the color changes during the titration and at the end point in dark-colored samples could not be observed. However, in this study, we found that distilled biodiesel (B100) was colorless and the distilled biodiesel blends samples (from B1 to B20) were very light in color (due to the color of ULSD), which resulted in a color change during the titration end point which was easily observed. Therefore, this study demonstrated that modified ASTM D 974 can be successfully used for the analysis of the AN of distilled biodiesel and biodiesel blends.

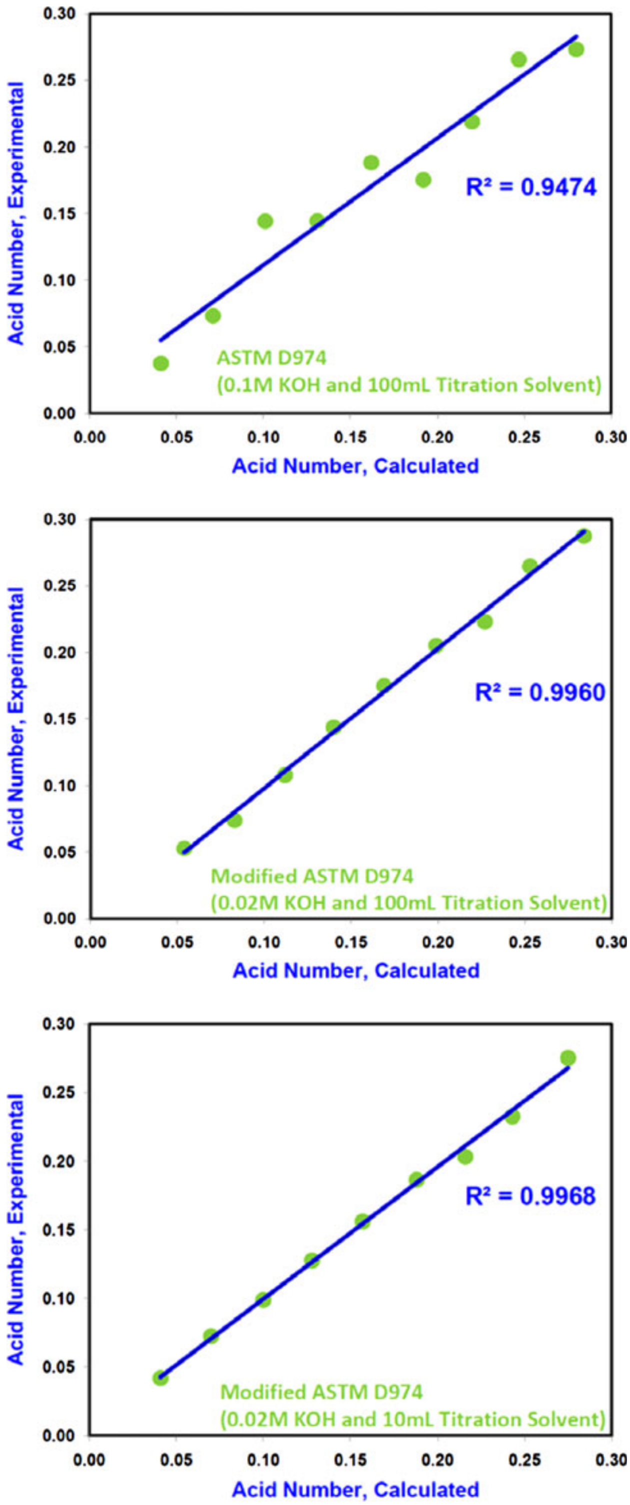

Fig. 1 Experimental AN versus calculated AN of the B100 and ULSD mixtures as per: (1). ASTM D 974 (using 0.1 M KOH and 100 mL titration solvent), (2). Modified ASTM D 974 (using 0.02 M KOH and 100 mL titration solvent), (3). Modified ASTM D 974 (using 0.02 M KOH and 10 mL titration solvent) (unit: mg KOH/g)

In this study, a low concentration of base (KOH), 0.02 M instead of 0.1 M, was used. It is recommended to use an even lower concentration of base, e.g., 0.01 M KOH for low AN biodiesel blends such as B1 and B2. This will increase the volume of KOH required to reach the equivalence point which ultimately enhance the ability to read accurately the volume of titrant consumed. In this study, a 10 mL burette with 0.05 mL subdivision was used as per ASTM D 974 recommendation. However, it is recommended to use a burette of 5 mL with divisions of 0.02 mL (also recommended by ASTM D 974). This will reduce the possibility of misreading the partial divisions.

Conclusion

The ASTM reference standard method D 664, a potentiometric method, has major problems such as mediocre reproducibility, tedious process for cleaning electrodes, and longer analysis time. On the other hand, ASTM D 974 is another non-aqueous colorimetric titration based method which offers various advantages such as being easy to perform, reproducible, cost-effective, and time-efficient. However, it was found that determination of the AN of biodiesel and biodiesel blends using the current ASTM D 974 results in large values of repeatability (up to 73.41%) and larger percentage error (up to 42.88%). Therefore, ASTM D 974 has been modified using a lower concentration of base (0.02 M KOH instead of 0.1 M KOH) as well as reducing the amount of toxic titration solvent from 100 mL to only 10 mL. This makes the modified ASTM D 974 into a green analytical method which uses a reduced amount of toxic solvent. This modified method significantly reduces the maximum percentage error from 42.88 to 5.92%. The application of this modified ASTM D 974 for the determination of AN of biodiesel and biodiesel blends was studied. Application of the modified ASTM D 974 to biodiesel and biodiesel blend was tested with good accuracy and repeatability. Good accuracy and repeatability were also obtained within ASTM D 6751-09a specifications for the AN, which is 0.50 mg KOH/g. For B20, B10, B5, B2, and B1, the most accurate values were measured at AN values of 0.177, 0.067, 0.072, 0.126, and 0.096 mg KOH/g, respectively. Excellent linearity values of R^2 were obtained for biodiesel and biodiesel blends. The difference between the experimental AN determined as per modified ASTM D 974 and the calculated AN for all biodiesel and biodiesel blend samples was within ± 0.018 mg KOH/g. All distilled biodiesel and biodiesel blend samples were found to be very light in color,

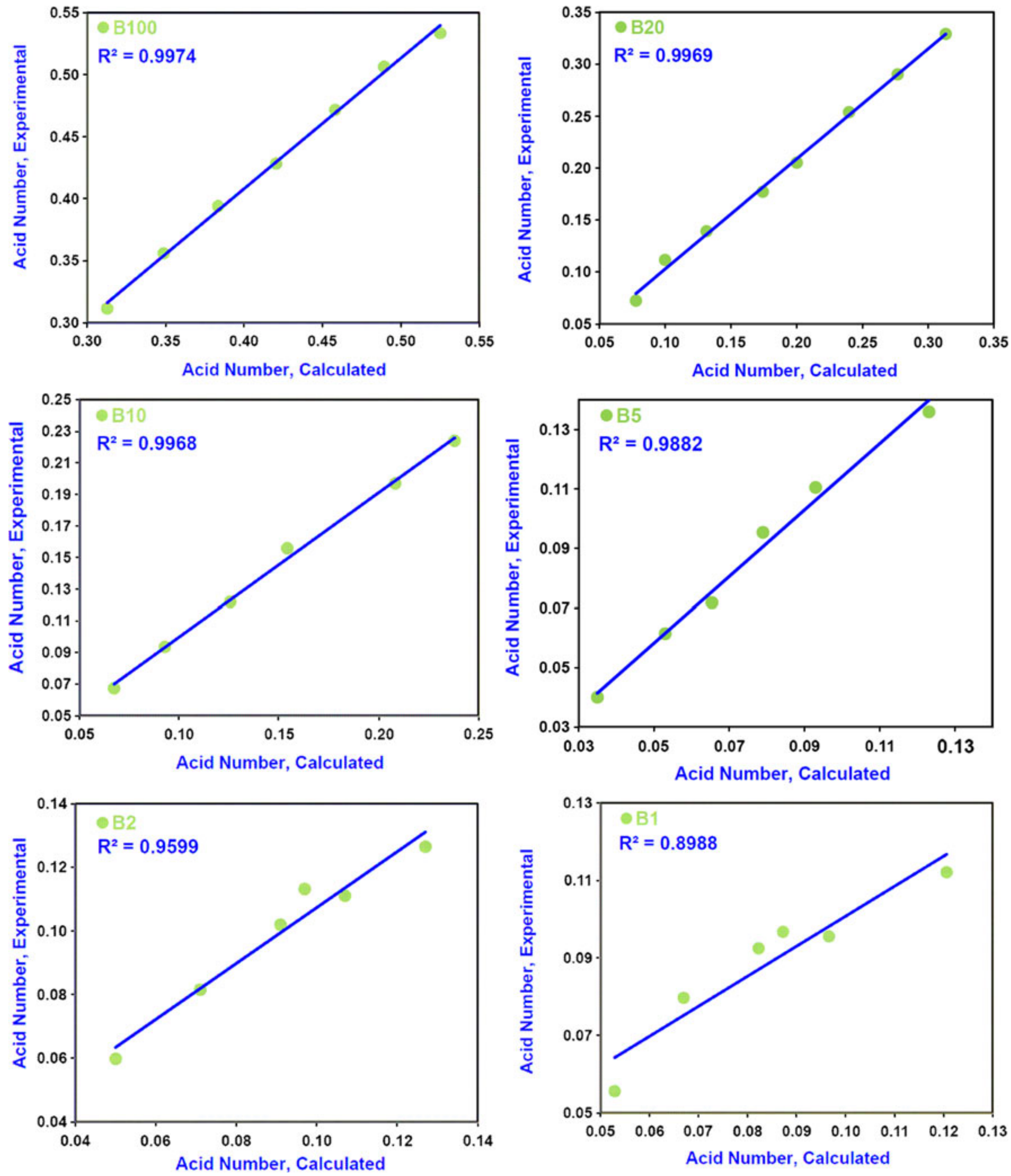

Fig. 2 Experimental AN (as per modified ASTM D974) versus calculated AN for biodiesel (B100) and biodiesel blends (B20, B10, B5, B2, and B1) (unit: mg KOH/g)

which eliminates the major obstacle for the application of ASTM D 974. Also, this study confirms the detection limit of this modified ASTM D 974 up to 0.05 mg KOH/g which shows the specification of 0.1 mg KOH/g for AN can be set for B1–B5. Furthermore, due to the advantages of this modified ASTM D 974, such as easy to perform and cost-effective, it can be used in field biodiesel analytical kits to determine AN on site or at a retailer location.

Therefore, this modified ASTM D 974 could be recommended as a reference method for AN determination of biodiesel and biodiesel blends. This extensive study has demonstrated that this modified ASTM D 974 method is a reliable method for the determination of AN and could be used for establishing the specifications of AN for biodiesel and biodiesel blends ranging from B1 to B20 in quality standards.

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