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Evaluation of Potentiometric Methods for Acid Number Determination in Commercial Biodiesel Samples and Proposal of Alternative Method

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Abstract: The acid number (AN) is an important parameter that informs the quantity of free fatty acids (FFA) and acids originating from degradation reactions of biodiesel during production process and its storage. Due to the need to research and evaluate new environmentally friendly methods that reduce the toxic use solvents and minimize amounts of sample without significant loss of precision in the AN measurements by ASTM D664 method, the aims of this work were: i) to establish a procedure of cleaning and hydration of glass electrode to perform AN analyzes according ASTM D664 method in two commercial B100 biodiesel samples produced at Brazilian central-west region; ii) to propose the modification of the ASTM D664 method by reducing the amount solvent mixture and the sample size and to compare AN values obtained for cited samples with those obtained by ASTM D664 and EN 14104 methods. We proposed a simple procedure of cleaning and hydration of electrode. In this procedure, after each titration of the sample, electrode is rinsed with small portion of ethanol (approximately 5 mL) and then the electrode is immersed in distilled water by 15 min. The method proposed in this work is a modification ASTM D664 method, reducing by half the amount of sample and using only 50 ml solvent mixture against 125 for the official method. The acid number values determined indicate that biodiesel samples are in agreement with the maximum value stipulated by ANP resolution. By statistical analysis with confidence level of 95%, the results obtained with the proposed method are significantly equivalent to the official method ASTM D664, presenting satisfactory results, since the modification reduced the amount of solvent mixture by 60% and the sample amount by 50% used in the analysis, contributing to environmentally friendly analyzes and favoring both sustainable development and economic issues linked to biofuel research.

Keywords: commercial biodiesel; acid value; potentiometric titrations; alternative method

1. INTRODUCTION

The biodiesel is considered as a promising substitute for petroleum-derived fuel, mainly due to environmental advantages [1]. Biodiesel is defined by American Society for Testing and Material (ASTM) as monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock such as vegetable oils or animal fats [2]. According to Brazilian regulatory agency, Agência Nacional de Petróleo, Gás Natural e Biocombustíveis (ANP), the main raw materials used to produce this biofuel through transesterification reactions are soybean oil (70.06%) and animal fat (14. 23%). In the Brazilian central-west region in addition to soybean oil (77.47%) and bovine fat (6.65%), residual frying oil represents only 0.25% of total production [3].

Due to an increasing of use biodiesel around the world, the quality has become a critical factor that could play a vital role in the successful market acceptance that biofuel. Therefore, various quality biodiesel standards have been developed around the world such as ASTM standard D6751 and European Committee for Standardization (CEN) standard EN14214. In both standards, one important quality parameter for biodiesel is the acid number (AN) [2]. The acid number is a parameter that informs the quantity of free fatty acids (FFA) and acids originating from degradation reactions of biodiesel during

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production process and its storage. The degradation reactions are hydrolysis and oxidation of the triglycerides and monoesters formed during the production process and its storage [4]

During storage of biodiesel, humidity absorption and oxidative degradation processes contribute to the presence of water, peroxides and carboxylic acids of low molecular mass [5]. Biodiesel ester molecules, in the presence of oxygen, are hydrolyzed to alcohol and carboxylic acids molecules. The conversion of esters into alcohols leads to reduction in the flash point and the conversion of esters to carboxylic acids increases the acid number [6], which is of the most used parameter to monitor biodiesel degradation. Therefore, the acid number is an indication of the oxidation degree of biodiesel and of the extension to which it could be degraded [7]. Free fatty acids are the major causes of high acid number in biodiesel. A biodiesel with low acid number is considered safe for storage and transport, while those with acid value above specifications can cause corrosion during storage and various operational problems such as engine deposits, filter clogging and fuel deterioration [8].

In the ANP Resolution No. 45 of 8.25.2014 the recommended methods for determining acid number of biodiesel are American (ASTM D664), European (EN 14104) and Brazilian (ABNT-NBR 14448) [9]. Methods ASTM D664 and ABNT 14448 are equivalent with respect to the solvents and reagents employed. [4] In the American method ASTM D664, 20 g of sample is weighed and 125 mL of the toluene/isopropyl alcohol/water mixture (1.0: 0.95: 0.5 v / v / v) is added, carrying out the titration with 0.1 mol L^{-1} KOH solution in isopropanol. In the EN 14104 method, 20 g of biodiesel sample is weighed and dissolved with a solvent mixture of ethanol and diethylether (1: 1 v / v), the mixture is titrated with 0.1 mol L^{-1} KOH in ethanol [9].

All solvents used in ASTM D664 and EN 14104 methods present the ability to easily dry the glass membrane of the electrode used for identifying titrations end points leading to slower and less accurate AN determinatios [4, 10]. Futhermore, these methods use solvents such as toluene, diethyl ether and isopropyl alcohol, considered to be toxic to the health of those who handle it [4,7]. However, despite the disadvantages, American method D664 is useful when samples are deeply colored [7], in which case indicator color changes may not be visible. In addition, the titration may be automated, but its repeatability is only acceptable. This is undoubtedly due to the many problems associated with the variability of electrodes [10]. In the progress of biodiesel analysis, important issues are the development of alternative and practical analytical methods that can be used in analyzes during production, handling and storage process [11]. Although methods have been established by official standards, the literature points to the need to develop new analytical methods that are increasingly fast and, as far possible, at lower cost [5].

In relation to acid number determination in biodiesel samples, the proposal of alternative methods and practical alterations for standard methods have been described in the literature [2, 4, 7]. In these works, the alteration of potentiometric methods for AN determination in biodiesel evolves substitution in solvent mixture for sample dissolution [4], reduction in sample size and in volume of solvent mixture for sample dissolution [2] and establishment of practical procedures for cleaning electrode and its re-hydration glass membrane [2, 4, 7].

The procedures proposed for cleaning electrode and its re-hydration glass membrane are very different in these works. Tubino and Aricetti [4] report in their proposed method that electrode (Metrohm Solvotrode with 3.0 mol L^{-1} LiCl solution in ethanol) was washed after each titration, in sequence, with ethanol and distilled water. Then electrode was immersed in distilled water for about 60 s. During the two weeks the electrode was kept for 24 h in solution of 0.1 mol L^{-1} HCl for cleaning and hydration.

Using ASTM D664 method Wang et al. [7] proposed, between each titration, the electrode should be rinsed as follows: titration solvent, then 2-propanol, then 10 min of soaking the electrode in water, then 2-propanol, and finally again with the titration solvent. In another work [2], the authors Baig, Paszti and Ng. proposed that instead of a rinsing with the all solvents listed and of long soaking time in water [7], only 1 min of strong water spray wash, is sufficient to clean the electrode (Metrohm Solvotrode with LiCl saturated solution in ethanol electrolyte).

The reduction in use of toxic titration solvent (10 mL instead of 125 mL required by ASTM D664) and in sample size (2 g instead of 20 g fixed by ASTM D664) were also proposed for AN determination in biodiesel and biodiesel blends samples by Baig, Paszti and Ng [2]. Although this proposed method shows cost effective and environmentally friendly, the precision of AN determinations was not so good. Relative standard deviation (RSD) values obtained by data shown for

B100 biodiesel (namely B100-1) and B20 biodiesel blend (namely B20-1) were 27.06% and 25,17%, respectively. Besides the method proposed was developed and evaluated for a unique kind of B100 biodiesel produced from waste oils and fats.

Due to the need research to evaluate new environmentally friendly methods that reduce the use of toxic solvents and minimize amounts of sample without significant loss precision in the AN measurements by ASTM D664 method, and considering the AN is of the most used parameter to evaluate the degradation of biodiesel, the aims of this work were: i) to establish a procedure of cleaning and hydration of glass electrode (in case, Solvotrode electrode filled with LiCL 2.0 mol L^{-1} in ethanol electrolyte) to perform acid number analyzes according to the ASTM D664 method in two commercial B100 biodiesel samples produced by methyl transesterification route at Brazilian central-west region; ii) to propose the modification of the ASTM D664 method by reducing the amount of solvent mixture by 60% and the sample size by 50% and to compare AN values obtained for cited samples with those obtained by ASTM D664 method and EN 14104

2. MATERIAL AND METHODS

Two samples of biodiesel were used to determine acid number, the first identified by A1 was supplied by the company ADM, located in Rondonópolis, Mato Grosso (MT), produced from soybean oil in natura by a methyl route. The second sample was provided by the company Delta Biocombustíveis, located in Rio Brilhante, MS. The second sample, A2, was produced from a blend composed of 50% animal fat and 50% soybean oil by methyl route.

The acid number analyzes were performed according to official methods (ASTM D664, EN 14104) and proposed method using the Titrino Plus 848 automatic titrator (Metrohm) [12], using the LL Solvotrode electrode filled with LiCL 2.0 mol L^{-1} in ethanol as internal solution (Metrohm, ref. 6.0229.100). For each analysis performed with the titrator, specific solutions were prepared and the standardizations of the titrant solutions of each method were also carried out. For the official acid number method according to EN 14104, solutions were prepared: KOH 0.1 mol L^{-1} in ethanol, 0.5 mol L^{-1} aqueous KOH solution, solvent mixture ethanol: diethyl ether (1: 1, v/v) for dissolution of the sample [13]. For the official method according to ASTM D664 and proposed alternative method, solutions, KOH 0.1 mol L^{-1} in isopropanol, solvent mixture toluene:isopropanol:water (1: 0.95: 0.5 v/v/v) [14]. All the titrant solutions were standardized according to standard procedures established in a Metrohm company manual. The tests were performed in quadruplicate.

Acid Number Analysis by Official and Alternative Methods

The Titrino Plus 848 titrator enables the determination of the acid number by standard methods, following the official American, European and Brazilian standards, all of which are accepted by the ANP. For the official methods, 20 g of biodiesel sample was used, dissolved with solvent mixture, ethanol and diethylether (1: 1 v/v), for EN 14104 and toluene/isopropyl alcohol/water (1.0: 0.95: 0.5 v/v/v) for ASTM D664. The dissolved sample was titrated with 0.1 mol L^{-1} KOH in isopropanol (ASTM D664) or ethanol (EN 14104), standardized against benzoic acid (Sigma Aldrich, 99.9%).

Before AN determination by standard methods ASTM D664, EN 14104 and modified ASTM D664 in this work, a procedure for cleaning and hydrate membrane of glass electrode was studied using ASTM D664 method applied for sample A1. For establishment of the procedure, factors as type of solvent for cleaning (toluene/isopropyl alcohol/water (1.0: 0.95: 0.5 v/v/v) solvent mixture or ethanol) by rinsing the electrode and time of soaking the pH-sensitive glass membrane of electrode in distilled water (5, 7, 10 or 15 min.) were evaluated. In soaking step, the ground joint diaphragm has not been immersed in distilled water. The proposed procedure of cleaning and hydration of glass electrode was used in all furthers AN determination.

The acid number determinations were also made using the methodology proposed in this work in which the official ASTM D664 method was modified. In this method, only 10 g of sample were weighed and the dissolution of this was in 50 mL of solvent mixture replacing 125 mL. A 50.0 mL volume of toluene/isopropyl alcohol/water (1.0:0.95:0.5%, v/v/v) solvent mixture were added to sample and sample solution obtained was titrated with 0.1 mol L^{-1} KOH solution in isopropanol standardized with benzoic acid. As in the official analysis, titration of the blank solution was also done, where 50 mL of the solvent are

also titrated with 0.1 mol L^{-1} KOH. After each analysis, the electrode was thoroughly cleaned with ethanol and immersed in water for 15 minutes to rehydrate its membrane. The acid value was calculated using equation (1), where A is the volume of the titratable solution obtained in milliliters for titration of the sample, B is the volume of titratable solution in milliliters for the titration of the blank, C is the concentration titration solution in mol L^{-1} and *m* is the mass of the sample in grams.

$$Acid\ number = \frac{(A-B)\times C\times 56.1}{m}\ mg(KOH)g^{-1} \qquad (1)$$

Data processing

The results for acid number determinations were analyzed by BioEstat5.3® program. For the tests, ANOVA analysis of variance was performed with a significance level of 95% and Tukey's test *a posteriori* [15].

In order to evaluate de precision of AN determinations by three methods used in this work, the values of repeatability were calculated. 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 equation 2 [16]:

$$\text{Repeatability} = \frac{2.77 \text{ x SD}}{\text{Experimental mean}}\ x\ 100\% \qquad (2)$$

where is the number of operators involved in the analysis = 1 [2, 7, 16].

3. RESULTS AND DISCUSSION

As shown in Table 1 the physicochemical results showed that the commercial biodiesel samples are conform European Commission, ANP and the American Society of Testing and Materials (ASTM D6751) standards for quality requirements, except for sample A1 in case of oxidative stability at 110 ºC and iodine value for EN 14111/2003.

Table 1. Main physicochemical properties of biodiesel commercial samples.

Parameters	Method	Specification*	Results	
			Biodiesel (A1)	Biodiesel (A2)
Density at 20 °C (kg m^{-3})	ABNT NBR 14065/2013	850-900	881.43	874.2
Kinematic Viscosity at 40 °C (mm^2s^{-1})	ASTM D 445/2015	3.0 - 6.0	4.123	4.456
Water content (mg kg^{-1})	ASTM D 6304/2007	maximum of 200	59	160
Ester Content (% m/m)	EN 14103/2011	minimum of 96.5	98	97.9
Free glycerol (% m/m)	ASTM D 6584/2013	maximum of 0.02	0.001	0.007
Total glycerol (% m/m)	ASTM D 6584/2013	maximum of 0.25	0.173	0.169
Monoacylglycerol (% m/m)	ASTM D 6584/2013	maximum of 0.70	0.605	0.483
Diacylglycerol (% m/m)	ASTM D 6584/2013	maximum of 0.20	0.101	0.190
Triacylglycerol (% m/m)	ASTM D 6584/2013	maximum of 0.20	0.006	0.004
Iodine value (g I_2 $100g^{-1}$)	EN 14111/2003	maximum of 120	126.7	103
Oxidation stability at 110 °C (h)	EN 14112/2003	minimum of 8	7.54	9.96

The potenciometric titrations methods for AN determination in biodiesel samples require the use amount of organic solvents for cleaning the electrode with soaking time in water to regenerate the membrane electrodes which were dehydrate by the use of organic solvents to dissolve the sample. In this work, in order to obtain acceptable repeatability at least five titrations in sequence using Solvotrode electrode (filled with LiCl 2.0 mol L^{-1} in ethanol as internal solution, Metrohm), we proposed a simple procedure of cleaning and hydration electrode. In this procedure, after each titration of the sample, the electrode is rinsed with small portion of ethanol (approximately 5 mL using a Pasteur pipet) and then the bulb of electrode (but not the ground joint diaphragm) is immersed in distilled water by 15 min.

The acid number is related to the amount or concentration of free fatty acids. The higher this value the greater the degradation of the biodiesel sample [5]. Table 2 shows the acid number for biodiesel

commercial samples produced from different raw materials. The AN values were obtained by three methods evaluated and using the procedure of cleaning and hydrate of the electrode proposed in this work. The acid number indicate that the biodiesel samples agree with the maximum value stipulated by the resolution ANP 45/2014 that is of 0.5 mg KOH g^{-1}.

Similar values of acid number were found by Candeia et al. [17] for biodiesel produced in the laboratory from soybean oil by methyl route, with acid number of 0.28 mg KOH g^{-1}. Tubino and Aricetti [4] using biodiesel of animal fat (swine lard) found an acid number of 0.29 mg KOH g^{-1}.

Table 2. Statistical analysis for the acid number data determined for samples A1 and A2.

Sample Biodiesel	Acid number (mg KOH.g^{-1})						
	Limit ANP 45/2014	ASTM D664	RSD (%)	ASTM Modified	RSD (%)	EN 14104	RSD (%)
A1	0.5	0.2901± 0.0028[a]	0.97	0.2930±0.0011[a]	0.38	0.2789±0.0001[b]	0.04
A2	0.5	0.3844±0.0029[a]	0.75	0.3806±0.0052[a]	1.37	0.3743±0.0033[b]	0.88

Data represented by Mean ± SD (standard deviation). n= 4. Mean with equal letters in the row did not differ significantly from each other by the Tukey's test ($p < 0.05$).

The determination of the acid number for the three methods, including that proposed in this work, showed good precision as described in Table 2 with relative standard deviation (RSD) values below 1.4%. The key point to achieve this good precision was carefully execution procedure of rehydration membrane of glass electrode between samples titrations. For AN determination in biodiesel and biodiesel blend samples using proposed method by Baig, Paszti and Ng [2], RSD values obtained by data shown for B100 biodiesel (namely B100-1) and B20 biodiesel blend (namely B20-1) were 27.06% and 25.17%, respectively. Tubino and Aricetti [4] report using their proposed method for AN determination and the electrode Solvotrode with 3.0 mol L^{-1} LiCl solution in ethanol that mean value of RSD was 1.5% (1.5% for soy biodiesel) in analysis of six samples of biodiesel.

Figure 1 shows well defined potentiometric (blank and sample) titration curves for determination of the acid number of biodiesel sample A2 produced with soybean oil and animal fat (50: 50%) using the modified ASTM D664 method proposed in this work in the assays. The consumption of hydroxide in titration is mainly due to the free fatty acids formed by the hydrolysis of ester bonds of monoglycerides during the storage and the long-term transport of biodiesel. It is an indicator of aging, oxidation and degradation of biodiesel. High acid number has been associated with corrosion and formation of deposits in engine parts, mainly in the fuel injector, as well as the reduction of the useful life of the same [18].

With the obtained values of acid number, the statistical analyzes were performed (Table 2) in order to prove the efficiency of the proposed alternative method. In this work, we chosen the modification of ASTM D 664 method because this method adopts blank titration, not used in EN 14104 method. The blank titration allows us detect problems about quality of isopropanol solvent like high acidity which for cheaper brands generally lead to greater values of volume of titrant solution in blank titration and to no realistic values of acid number.

According Tukey's test for AN determination in the samples, the modified ASTM D664 official method proposed in this work showed no significant difference with the ASTM D664 method, which proves efficiency of the same in replacing the standard method. However, both ASTM D664 and modified ASTM D664 methods differ significantly from the EN14104 method which may be due to the different normative methods, and the proposed method is a modification of official ASTM D664 method and not to the EN14104 method. ASTM D664 and EN14104 methods use different solvents. In American method, blank analysis is necessary while the European method requires that solvent mixture (ethanol/ diethyl ether, 50/50 %(v/v)) has been neutralized, just before use, with KOH in presence of phenolphthalein solution.

In order to confirm good precision for AN determination obtained by three methods evaluated and using the procedure of cleaning and hydrate of the electrode proposed in this work, values of repeatability shown in Table 3 were calculated by equation 2. The repeatability values obtained for modified ASTM D664 method in this work are below 4.0%. For AN determination in biodiesel and biodiesel blend samples using proposed method by Baig, Paszti and Ng [2], repeatability values obtained for B100 biodiesel

samples and B20 biodiesel blend were up to 34.39% and 61.68%, respectively.

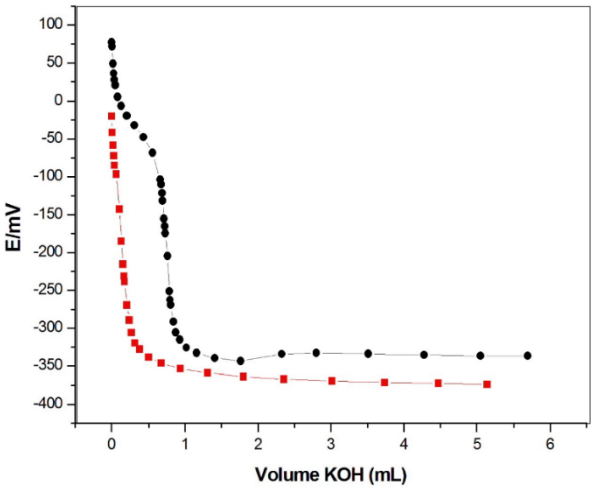

Figure 1. Potentiometric titration curves of blank (red) (solvent mixture: toluene /isopropanol/water) and of sample A2 (black) according to ASTM D664 modified method with 0.1 mol L^{-1} KOH titrant solution.

Table 3. Repeatability values obtained from the acid number determined for samples A1 and A2.

	Repeatability (%)		
Sample	ASTM D664	modified ASTM D664	EN14104
A1	2.67%	1.04%	0.10%
A2	2.09%	3.78%	2.44%

In this work, the proposed method based on modification of ASTM D664 has been developed to determine acid number of biodiesel using small sample size (10.0 g instead of 20.0 g), reduced volume of mixture of toxic solvents (50 mL instead of 125 mL) at blank and sample titrations. Therefore, proposed method of acid number determination reduces by 60% the amount of solvents and by 50% the size of sample as shown in Table 4. These characteristics of the proposed method contribute to more environmentally friendly analyzes and favor both sustainable development and economic issues linked to biofuel research.

Table 4. Advantages of proposed method versus ASTM D664 method, considering analysis with four replicas

Method	Sample (g) by replica	Solvent (mL) by replica	Blank solvent (mL) by replica	Total of sample (g)	Total of solvent (mL)
ASTM D664	20	125	125	80	1000
Modified ASTM D664	10	50	50	40	400

4. CONCLUSION

The proposed method has proved to be efficient because it uses smaller amounts of sample and of solvents used in the analysis. By Tukey's test *a posteriori* at 95% confidence level for assays data it was shown that acid number values obtained by proposed method are statistic equivalent to those ones proved by official method ASTM D664 from which has been modified.

The equivalence between these methods (ASTM D664 and the proposed method ASTM D664 modified) make sure to use the proposed method with reliability in the results, contributing to the decrease in toxic waste generation and amounts of reagents and samples used in the acid number analysis, turning this modified method more environmental friendly and less expensive in routine analysis. Furthers studies using biodiesel samples prepared from different feedstock (vegetal and animal oil and fats or its blends) should be done for comparing AN values obtained by the proposed method and ASTM D664 one to prove equivalence for other kinds of biodiesel samples.

By comparing the official methods ASTM D664 and EN14104, it was found significant difference of found acid number to two commercial samples of biodiesel studied. This may be justified due to the methods using different mixtures of solvents and the American method use the blank titration while the European method requires that pH of solvent mixture (ethanol/ diethyl ether, 50/50 %(v/v)) has been adjusted, just before use, with KOH in presence of phenolphthalein solution.

5. ACKNOWLEDGMENTS

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