A new method for determining the acid number of biodiesel based on coulometric titration

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A B S T R A C T

A new method is proposed for determining the acid number (AN) of biodiesel using coulometric titration with potentiometric detection, basically employing a potentiostat/galvanostat and an electrochemical cell containing a platinum electrode, a silver electrode, and a combination pH electrode. The method involves a sequential application of a constant current between the platinum (cathode) and silver (anode) electrodes, followed by measuring the potential of the combination pH electrode, using an isopropanol/water mixture as solvent and LiCl as the supporting electrolyte. A preliminary evaluation of the new method, using acetic acid for doping a biodiesel sample, showed an average recovery of 100.1%. Compared to a volumetric titration-based method for determining the AN of several biodiesel samples (ranging from about 0.18 to 0.95 mg g^{-1}), the new method produced statistically similar results with better repeatability. Compared to other works reported in the literature, the new method presented an average repeatability up to 3.2 times better and employed a sample size up to 20 times smaller.

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1. Introduction

The worldwide need for energy has increased exponentially in the last few years, leading to an increase in the search for renewable energy sources, which can decrease the worldwide dependency on fossil fuels. Thus, the use of ethanol and biodiesel as alternative energy sources has increased, also having been influenced by a variety of political, economic, and social factors [1–4].

Biodiesel is basically composed of fatty acid alkyl esters, which are obtained by the transesterification of vegetable oils or animal fats, using a short-chain alcohol such as methanol or ethanol. As the physical properties of biodiesel are similar to those of diesel (derived from petroleum), the use of biodiesel as a fuel (pure or mixed with diesel) does not require any modification of the diesel engine or of the infrastructure used to store and distribute the diesel. Moreover, biodiesel can be produced from fried oils or residual animal fats and its combustion produces lower amounts of sulfur, particulate material, and greenhouse gases in comparison with diesel combustion [5–8].

The acid number (AN) is one of the analytical parameters usually employed to evaluate the quality of biodiesel. It represents the corrosive potential of biodiesel, which can reduce the lifetimes of fuel tanks and vehicle engines. This parameter, commonly expressed as the weight of potassium hydroxide (in mg) per weight of sample (in g), is related to the fuel's overall content of titratable acids, which is derived from the oxidation of the fuel or from the oil or fat used for its production [9,10].

Some regional and international standards have been established that outline the official methods for determining the AN of biodiesel based on volumetric titration [11–13]. Regional and international regulations have also established limit values for AN results so that biodiesel can be commercialized as a fuel [14–16]. Therefore, some papers have been published recently that deal with determining the AN of biodiesel by employing these official methodologies [9,10,17,18]. In addition, one paper has described a new titration method for AN determination of biodiesel based on sequential injection analysis [19].

The coulometric titration technique is a good alternative to the volumetric method, as coulometric titration is more precise and does not require standard solutions. In the constant-current coulometric titration technique, a given current is applied between a pair of appropriate electrodes for generating the titrand, the amount of which can be calculated by measuring the current and the length of time that the current is applied [20,21]. Therefore, some papers have reported the use of coulometric titration to determine the acidity of different types of samples, such as oils [22], wine [23], rainwater [24], and ethanol [25]. In addition, a review was published recently about the coulometric generation of acids and bases for acid–base titrations in non-aqueous solvents [26]. However, to our knowledge, no paper has specifically aimed at determining the AN of biodiesel using coulometric titration.

Therefore, this paper proposes a new method of determining the AN of biodiesel, using constant-current coulometric titration with potentiometric detection. The new method was evaluated in

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the analysis of several biodiesel samples in comparison with a volumetric titration-based method.

2. Material and methods

2.1. Equipment

The coulometric titration system used in this study consisted of an Ecochemie Autolab PGSTAT30 potentiostat/galvanostat connected to an electrochemical cell containing three electrodes: a platinum electrode (cathode, rectangular shape, about $0.4\,cm^2$ area) and a silver electrode (anode, cylindrical shape, about $11\,cm^2$ area) for the application of a constant current, and a Metrohm 6.0229.100 combination glass pH electrode (containing an internal silver/silver chloride reference electrode in $2\,mol\,L^{-1}$ LiCl ethanol filling solution) for potentiometric detection. The electrochemical cell consisted of two compartments: a lower 20 mL glass compartment and an upper 10 mL plastic compartment, which was connected to the lower compartment by a glass tube containing agar–agar gel (3% w/w in $1\,mol\,L^{-1}$ LiCl). The lower compartment, placed over a magnetic stirrer, contained the platinum and pH electrodes. The upper compartment contained a $1\,mol\,L^{-1}$ LiCl aqueous solution and the silver electrode. A schematic representation of the coulometric titration system is shown in Fig. 1. For comparison purposes, a Metrohm 785 DMP Titrino automatic volumetric titrator was also employed, using a similar combination glass pH electrode for potentiometric detection.

2.2. Samples

Eight biodiesel samples from different sources were analyzed: palm methyl biodiesel (palm sample), palm/fat methyl biodiesel (palm/fat sample), soybean methyl biodiesel (soybean sample), high-oleic soybean methyl biodiesel (ho-soybean sample), soybean ethyl biodiesel (soybean-et sample), soybean/fat methyl

biodiesel (soybean/fat sample), canola methyl biodiesel (canola sample) and castor methyl biodiesel (castor sample).

2.3. Experimental procedure

For each sample titration using the coulometric system, an aliquot of approximately 1.0 g of sample was added to the lower compartment of the electrochemical cell, together with 10 mL of isopropanol, 3 mL of deionized water, and 0.2 g of LiCl (Merck, purity higher than 99% w/w) as the supporting electrolyte. The resulting solution was stirred for 2 min for dissolution of LiCl and stabilization of the pH electrode. Next, the solution was titrated (while being continuously stirred) by sequentially applying a current of 5 mA between the platinum and silver electrodes for 10 s, followed by measuring the potential of the combination pH electrode. During the application of the current, hydroxyl ions were generated at the platinum electrode, while silver chloride was formed over the silver electrode, according to Eqs. (1) and (2), respectively.

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{1}$$

$$Ag + Cl^- \rightarrow AgCl + e^- \tag{2}$$

The samples were also analyzed by volumetric titration, using the same sample size and solvent composition (without LiCl), a $0.01\,mol\,L^{-1}$ KOH standard solution (in isopropanol) as titrand, and the automatic titrator cited previously (based on the ASTM D664 standard [12]). All the samples were analyzed in four replicates and blank titrations were also performed. For the preliminary evaluation of the coulometric method, the effects of water and LiCl on the AN results were studied, and recovery tests were performed using acetic acid (Merck, purity higher than 99.8% w/w) as dopant.

2.4. Calculation of the acid number

For each analysis, the end points of the blank and sample titration curves (potential versus charge for the coulometric titrations and potential versus volume for the volumetric titrations) were determined by second derivatives and used to calculate the AN in mg of KOH per g of sample, according to Eqs. (3) (for the coulometric titrations) and (4) (for the volumetric titrations):

$$AN = \frac{(Q_s - Q_b)MM_{KOH} \times 1000}{F \times m_s} \tag{3}$$

$$AN = \frac{(V_s - V_b)M_{KOH} \times MM_{KOH}}{m_s} \tag{4}$$

where Q_s is the charge of the end point of the sample titration curve (in C), Q_b is the charge of the end point of the blank titration curve (in C), MM_{KOH} is the molar mass of KOH (in $g\,mol^{-1}$), F is the Faraday constant (in $C\,mol^{-1}$), m_s is the mass of biodiesel (in g), V_s is the volume of the end point of the sample titration curve (in mL), V_b is the volume of the end point of the blank titration curve (in mL), and M_{KOH} is the concentration of the KOH standard solution (in $mol\,L^{-1}$).

3. Results and discussion

3.1. Preliminary evaluation of the coulometric method

The effects of the amount of water and the amount of LiCl on the coulometric AN result were studied for one of the biodiesel samples. It is important to point out that water and LiCl play important roles in the coulometric titration of biodiesel because
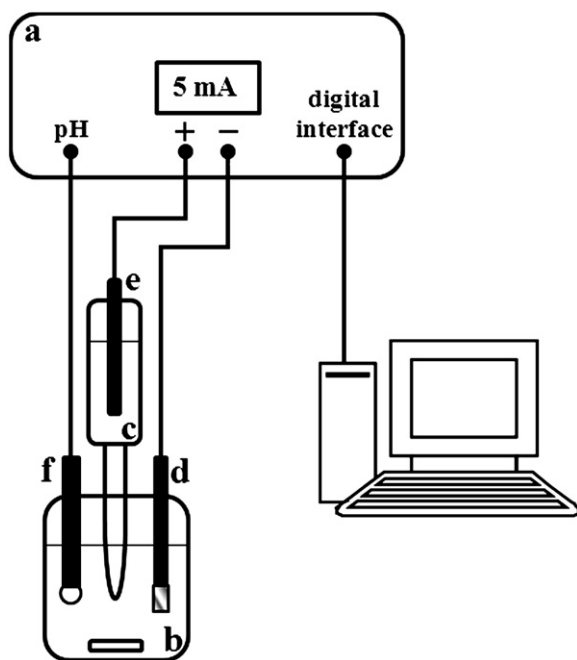

Fig. 1. Schematic representation of the coulometric titration system: (a) potentiostat/galvanostat, (b) lower compartment of the electrochemical cell, (c) upper compartment of the electrochemical cell, (d) platinum electrode, (e) silver electrode, (f) combination pH electrode.

the water is reduced at the platinum electrode and the LiCl provides the necessary ions for the current flow through the solution containing the biodiesel sample. The amount of water added for each titration was evaluated in the range from 1 to 4 mL, while keeping constant the amount of LiCl (0.2 g). Similarly, the LiCl amount added for each titration was evaluated in the range from 0.05 to 0.40 g, while keeping constant the amount of water (3 mL).

Fig. 2a shows the variation of the AN result in relation to the variation of the amount of water from 2 to 4 mL. For 1 mL of water, the coulometric system was not able to apply 5 mA during the titration, probably due to the relatively low availability of water molecules to be reduced at the surface of the platinum electrode. Although the AN result slightly decreased as the water amount increased, as shown in the Fig. 2a, the AN decreased just 0.007 mg g^{-1} for an increase of 2 mL in the water amount added. In the same way, Fig. 2b shows the variation of the AN results in relation to the variation of the amount of LiCl from 0.1 to 0.4 g. For 0.05 g of LiCl, the coulometric system was not able to apply 5 mA during the titration, probably due to the relatively high electrolytic resistance of the solution. Although the AN result slightly increased as the LiCl amount increased, as shown in the Fig. 2b, the AN increased just 0.004 mg g^{-1} for an increase of 0.3 g in the LiCl amount added. As the effect of the water addition on the AN result was lower than 0.7% per milliliter of water and the effect of the LiCl addition on the AN result was lower than 0.3% per decigram of LiCl, both effects were considered negligible in the ranges studied. These results were already expected because,
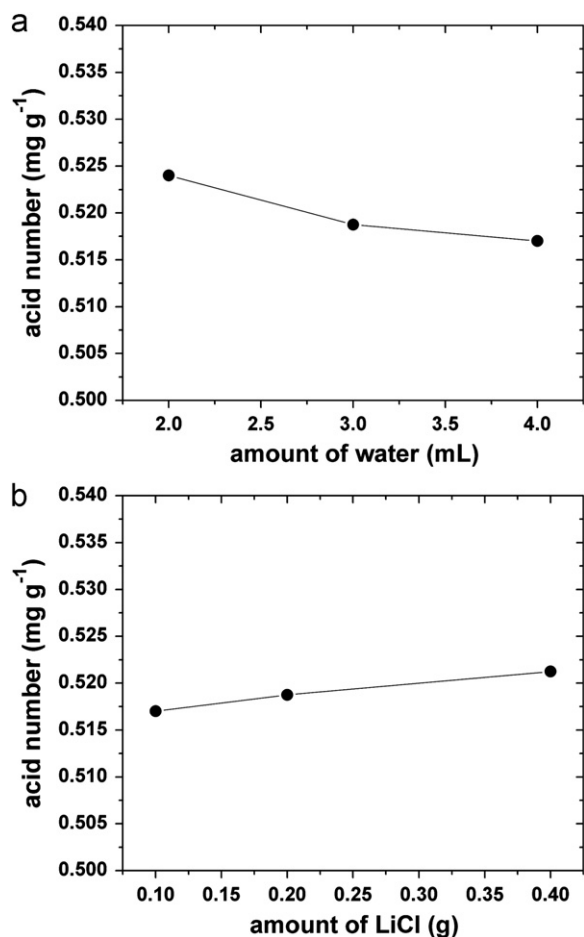
as the blank titrations are taken into account for the AN determination, any effects resulting from the solvent composition or from the type and concentration of the supporting electrolyte are canceled out. Therefore, 3 mL of water and 0.2 g of LiCl were selected to be added for each coulometric titration.

For the recovery study, aliquots of a biodiesel sample were gravimetrically doped with different amounts of acetic acid, giving known theoretical AN increases, and then analyzed in comparison with the non-doped sample. Fig. 3 presents coulometric titration curves obtained for the blank, the non-doped sample, and the doped aliquots, showing clearly the displacement of the inflection region of the titration curves to higher charges as the AN value increases. The results of the recovery study are shown in Table 1. As can be seen, the experimental AN increases resulting from the titration curves were very similar to the theoretical values, with recovery values very close to 100%, demonstrating the high accuracy and current efficiency of the coulometric method.

3.2. Comparison with volumetric titration

Examples of coulometric titration curves obtained for some of the biodiesel samples analyzed are shown in Fig. 4. As can be observed, the titration curves showed good resolution and amplitude around the inflection region, allowing visual differentiation of the samples according to their acidity and precise determination of the AN. The average AN results obtained using the coulometric and the volumetric methods, including the relative standard deviations (RSD) of replicates, are shown in Table 2. Table 2 also shows the results of t-tests, which were performed to statistically compare the results of the two methods. As can be seen, the results obtained using the two methods were very similar to each other, with differences between the average
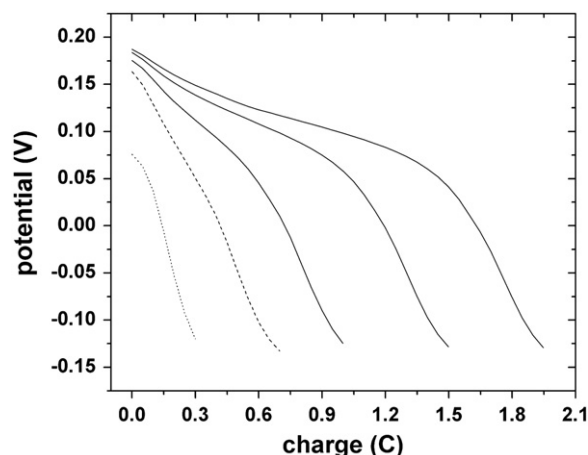

Fig. 2. Variation of the AN result in relation to the variation of the amount of water (a) and the amount of LiCl (b) added for the coulometric titration of one of the biodiesel samples.

Fig. 3. Coulometric titration curves obtained for the blank (dotted line) and for one of the biodiesel samples without doping (dashed line) and after doping with different amounts of acetic acid (straight lines, theoretical AN increases of 0.182, 0.466 and 0.728 mg g^{-1} from left to right).

Table 1
Results of the recovery study using acetic acid for doping one of the biodiesel samples.

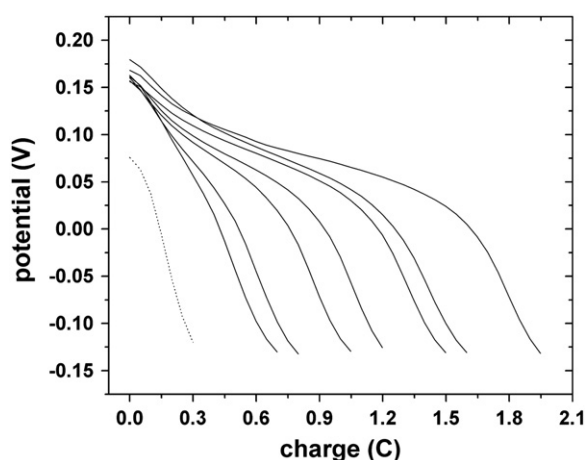| Addition of acetic acid (mg g^{-1})	Theoretical AN increase (mg g^{-1})	Experimental AN increase (mg g^{-1})	Recovery (%)
0.195	0.182	0.182	100.0
0.499	0.466	0.464	99.5
0.779	0.728	0.734	100.8

Fig. 4. Coulometric titration curves obtained for the blank (dotted line) and for several biodiesel samples having different AN values (straight lines).

Table 2
Comparison between the AN results obtained using the coulometric and the volumetric methods.

Sample	Volumetric		Coulometric		t_{calc}/t_{tab}[a]
	AN (mg g^{-1})	RSD (%)	AN (mg g^{-1})	RSD (%)	
Palm	0.651	0.99	0.650	0.45	0.23/2.45
Palm/fat	0.414	3.60	0.400	1.86	1.87/3.18
Soybean	0.514	2.41	0.518	0.68	0.72/3.18
Ho-soybean	0.184	1.79	0.182	1.41	0.73/2.45
Soybean-et	0.713	2.53	0.714	0.91	0.05/2.45
Soybean/fat	0.940	1.71	0.943	0.27	0.42/3.18
Canola	0.258	2.83	0.249	1.68	2.17/2.45
Castor	0.652	3.20	0.661	0.34	0.83/3.18

[a] t-calculated (t_{calc}) and t-tabled (t_{tab}) values derived from t-tests using 95% confidence level.

results lower than 0.015 mg g^{-1}. Actually, as the t-calculated (t_{calc}) value was lower than the t-tabled (t_{tab}) value for all the samples, the results of the two methods were considered statistically similar to each other. In addition, the evaluation of all AN results at once using two-way analysis of variance with repetition (two-way ANOVA) revealed significant differences between the results of different samples (already expected), but no significant difference between the results of the two methods (F-calculated = $0.17 < F$-tabled = 4.04, 95% confidence level). Moreover, the coulometric method presented higher precision, with an average RSD value of 0.80%, which was about 3.0 times lower than that obtained using the volumetric method. Compared to recent papers dealing with the AN determination of biodiesel using volumetric titration [9,10,17,18], the coulometric method presented in this paper showed an average repeatability about 1.8 to 3.2 times better and employed a sample size 2 to 20 times smaller.

4. Conclusions

A new method was developed and evaluated to determine the AN of biodiesel, based on constant-current coulometric titration with potentiometric detection and employing a simple instrumental setup, basically composed of a potentiostat/galvanostat and an electrochemical cell containing platinum, silver, and combination pH electrodes.

As important parameters of the new titration method, the amounts of water and LiCl added for the coulometric titration were studied and was shown not to significantly affect the AN result of biodiesel, since any possible effects are probably canceled out by the blank titration. However, for relatively low water or LiCl amounts, the low availability of water molecules to be reduced at the platinum electrode and the low conductivity of the final solution can prevent the use of currents in the order of milliamperes and the application of the new coulometric titration-based method. In addition, recovery tests using acetic acid as dopant demonstrated the high accuracy and current efficiency of the new coulometric method.

The new method was evaluated for the analysis of several biodiesel samples and compared to a volumetric titration-based method, producing statistically similar AN results with better repeatability. Compared to recent works reported in the literature, all based on volumetric titration, the new coulometric method presented better repeatability and employed a smaller sample size. Due to its better precision and smaller sample size, the new method can contribute to the quality control of biodiesel, with better discrimination between conforming and non-conforming samples around the AN limit values (established by regional and international regulations), while reducing the generation of waste from the analyses. In addition, as the new method constitutes a primary method of analysis (it does not require standard solutions), it can be used alone, by a single laboratory, for the certification of the AN parameter in reference materials of biodiesel, as required by an international standard [27]. Future work might include developing a compact flow-batch coulometric titration system for the automatic determination of the AN of biodiesel.

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