



A simple and green analytical method for acid number analysis of biodiesel and biodiesel blends based on potentiometric technique

Aijaz Baig^a, Michael Paszti^b, Flora T.T. Ng^{a,*}

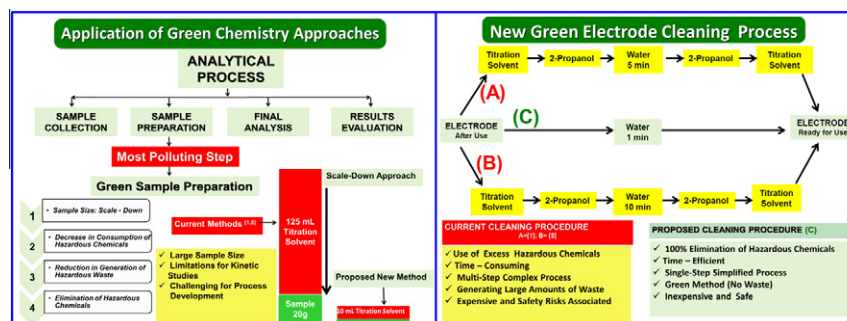
^a Department of Chemical Engineering, University of Waterloo, 200 University Avenue West, Waterloo, ON, Canada N2L 3G1

^b Rothsay, a Division of Maple Leaf Foods Inc., 150 Research Lane, Suite 307, Guelph, ON, Canada N1G 4T2

HIGHLIGHTS

- ▶ A green and simple analytical method using green chemistry approaches is developed.
- ▶ A single-step green aqueous-based electrode cleaning procedure is developed.
- ▶ Accurate and reliable results for acid number of biodiesel and its blends obtained.
- ▶ This method could be used in R&D and QC labs for biodiesel and its blends analysis.
- ▶ Recommended as a reference method for the determination of acid number of biodiesel.

GRAPHICAL ABSTRACT



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ABSTRACT

Acid number is an important quality parameter for biodiesel and biodiesel blends and has been included in various quality standards including ASTM D 6751 and EN 14214. In this paper, a new simple and green potentiometric method based on green chemistry approaches has been developed to determine the acid number of biodiesel and biodiesel blends. This new method uses a reduced amount of titration solvent and recommends the use of a small sample size instead of large sample size as stated in the ASTM reference method D664. A time-efficient electrode cleaning procedure has been developed which completely eliminates the use of toxic solvents for cleaning the electrodes. This proposed green method significantly reduced the maximum % error from 101% to only –18% and repeatability was decreased from 290% to 100% when compared to ASTM D 664 method using the sample size of 2 g. This proposed green analytical method could be used for the determination of acid number of biodiesel and biodiesel blends in R&D as well as in industrial quality control laboratories as a simple, time-efficient, cost effective, and environmentally friendly method for acid number determination.

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1. Introduction

Biodiesel is defined by the American Society for Testing and Materials (ASTM) as the mono alkyl esters of long chain fatty acids derived from a renewable lipid feedstock, such as vegetable oil or animal fat [1]. Recently, due to an increasing interest and the use of biodiesel around the world, the assurance of biodiesel quality

has become a critical factor that could play a vital role in the successful commercialization and market acceptance of biodiesel.

Therefore, various biodiesel standards have been developed around the world, including the United States (ASTM D 6751) and Europe (EN 14214) [2]. Quality standards for biodiesel, as motor fuel, have been established in ASTM standard D 6751 and European Committee for Standardization (CEN) standard EN 14214 [3,4]. In both standards, one important quality parameter for biodiesel is the acid number (AN). According to ASTM D 664, AN is measured as the mg of KOH required to neutralize the acids in 1 g of the sample

* Corresponding author. Tel.: +1 519 888 4567x33979; fax: +1 519 888 4347.
 E-mail addresses: a6baig@uwaterloo.ca (A. Baig), ftng@uwaterloo.ca (F.T.T. Ng).

[5]. AN is a measure of the degree of oxidation and hydrolysis in the biodiesel [6]. Hydrolysis during biodiesel production process can result in the formation of free fatty acid (FFA). This is because FA can be formed by the hydrolysis of ester linkages in both the TG feedstock and the biodiesel during its manufacture [7]. Furthermore, FFA 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 [6]. Therefore, both ASTM D 6751 and EN 14214 has restricted the maximum value of AN to be 0.50 mg KOH/g for biodiesel (B100). AN of biodiesel depends on the type of feedstock and how well the biodiesel was processed during and after the production. Due to the high cost of refined vegetable oils, alternative inexpensive feedstocks with high FFA content are gaining momentum around the world for the production of biodiesel due to its economical, commercial, and environmental benefits [1]. This requires the development of time-efficient, reliable, and low cost analytical methods for an accurate determination of AN to monitor the acid number of biodiesel and biodiesel blends [6,8,10].

Biodiesel can be used alone (B100) or blended with petroleum diesel in any proportion. Generally, it is blended with ultra low sulfur diesel (ULSD) at various levels in order to improve the lubricity and emissions control [9]. In the past few years, the commercial use of biodiesel has been increased as a motor fuel using its blends such as B2, B5, and B20 in the USA and Canada. 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. On the other hand, in Canada, the Canadian General Standards Board (CGSB) has not developed the specifications for biodiesel blends with high levels of biodiesel (such as B20) [10].

Currently, ASTM D 664 is a reference method for measuring the AN of biodiesel and biodiesel blends in ASTM D 6751 which is based on potentiometric titration in a non-aqueous medium and is suitable even for colored samples [5,6]. ASTM D 664 has been applied even to heavy oils and bitumens for acid number analysis [11]. In spite of few studies, the detection limit of ASTM D 664 remains debatable [6]. Furthermore, due to an increase in R&D work for the development of new innovative processes for the production of biodiesel from alternative inexpensive feedstocks which contain a high amount of FFA, kinetics studies are required for process development. In order to study the kinetics in small R&D lab scale batches (batch size generally varies from few grams to hundreds of grams), withdrawing large samples such as 20 g (as required by ASTM D 664 to determine the AN within the ASTM D 6751 specified range of 0.5 mg KOH/g) from the reactor for analysis, makes it nearly impossible to obtain accurate kinetic data. However, this could be achieved by using a small sample size for AN determination. Recently, a modified ASTM D 664 has been used to determine the AN of biodiesel and biodiesel blends [6]. However, in that study, not only large sample sizes, large amounts of toxic titration solvent, and complex electrode cleaning procedure using toxic solvents were used, similar to those as specified in ASTM D 664, but also it recommends a longer time for soaking the electrode with water which almost doubles the analysis time [5,6,10]. Furthermore, these analytical methods generate large amount of hazardous waste which is highly undesirable due to economic and environmental issues. Recently, potentiometric and visual titration-based methods were developed in an attempt to reduce the use of toxic titration solvents, however, such methods still employed large sample sizes and large amount of organic solvent (1:1 mixture of ethanol and water) [12,13]. Even, by using low toxic calibration fluids, these problems still remains a challenge for green analytical chemistry (GAC) [14]. This becomes critical for today's commercial production processes where time-efficient, cost-effective, and environmentally green analytical methods are essential for meeting the quality standards specifications for biodiesel and biodiesel blends.

These problems can be addressed by using green chemistry approaches to minimize the toxic chemical consumption and waste generation which could have advantages of reducing operational costs, including those spent on waste treatment and disposal [15]. "Green Chemistry is the use of chemistry techniques and methodologies that reduce or eliminate the use or generation of feedstocks, products, by-products, solvents, reagents, etc. that are hazardous to human health or the environment" [16]. As a result of emergence of green chemistry in the late 1990s, in the past few years, a paradoxical situation has been developed as most of the analytical methods employed for analysis generate a large amount of hazardous chemical waste, which has significant impact on the environment [17]. This becomes more critical in some cases, where the chemicals used for analysis are even more toxic than the species being analyzed. As a result, GAC emphasized the use of smaller sample size, decrease the consumption of toxic chemicals and reduce the generation of hazardous waste.

To the best of our knowledge, this study is the first report using green chemistry approaches, such as reduction of sample size, reducing the use of toxic chemicals, decreasing the generation of hazardous waste, and eliminating the use of toxic chemicals in the electrode cleaning process, to develop a green potentiometric analytical method for the determination of the AN of biodiesel (B100) and biodiesel blends (B20) where accuracy and repeatability were determined. Also, a single-step green aqueous-based electrode cleaning procedure has been developed.

2. Experimental

2.1. Materials

Biodiesel (B100) produced from waste oils and fats was obtained from Rothsay (Quebec, Canada). Ultra low sulfur diesel (ULSD) was obtained from Boucher & Jones Fuels (Petro Canada, Waterloo, Ontario). Biodiesel blends, B20 was prepared by mixing B100 and ULSD at a volume ratio of 1:4. The following chemicals were supplied by VWR Canada: 2-propanol (anhydrous, 99.9%), toluene (anhydrous, 99.5%), ASTM Type-II water, and 0.1 M KOH (volumetric standard, in isopropanol). Palmitic acid (99%) was supplied by Sigma–Aldrich Chemical Company (Milwaukee, WI). Benzoic acid (certified ACS) was supplied by Fisher Scientific (Ottawa, ON, Canada) whereas Metrohm electrode storage solution was supplied by Metrohm Ltd. (Switzerland).

2.2. Electrodes and instrumentation

A Metrohm 808 Titrand auto titrator equipped with a stirrer from Metrohm (Switzerland) and a data acquisition software using solvotrode non-aqueous glass electrode with LiCl saturated solution in ethanol electrolyte was used to detect the endpoint potentiometrically.

2.3. Methods

The titration solvent was prepared as detailed in ASTM D 664 [5]. Blends of B100 and ULSD were prepared to obtain weight percentages of biodiesel ranging from 20% to 80% as shown in Tables 1 and 2. Also, biodiesel blends with a range of known AN levels ranging from 0.127 to 0.567 mg KOH/g were prepared by adding palmitic acid to the solutions of B20 and B100. As shown in Tables 3 and 4, 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

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