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Short communication

A rapid method for the quantitative analysis of total acid number in biodiesel based on headspace GC technique

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ABSTRACT

The purpose of this work is to introduce a rapid and practical method for quantitatively analyzing total acid number in biodiesel by a reaction headspace gas chromatography. In this method, the carbon dioxide formed by the reaction of acidic species (i.e., fatty acids) in biodiesel and sodium bicarbonate can be measured by GC. The results showed that the complete reaction can be achieved in 25 min at 75 °C. The relative standard deviation of this method in total acid number determination was within 2.93%, the relative differences has been determined by comparing the total acid number obtained from this new analytical technique with the data from the reference technique (i.e., potentiometric titration), which are less than 8.05%. The reaction HS-GC technique is automated, efficient and can be a reliable tool for quantifying the total acid number in biodiesel and related research.

1. Introduction

Biodiesel is a potential alternative to conventional petroleum diesel and mainly contains fatty acid alkyl esters, which is obtained from the transesterification of renewable lipid feedstock (e.g., animal fats and vegetable oils) [1–3]. The total acid number (TAN) in biodiesel is one of the major parameters in evaluating the quality (i.e., corrosive potential) of biodiesel, which is defined as the weight of potassium hydroxide (in mg) needed to neutralize the acidic species (e.g., fatty acids) contained in per weight (in g) of biodiesel [4–7]. Therefore, there is a high demand for a reliable and precise analysis technique for quantifying TAN in biodiesel related products.

The TAN in biodiesel is traditionally quantified by a back-titration technique in an organic solution (isopropanol) system [8], in which an excess amount of potassium hydroxide solution is needed for neutralizing the acidic species in biodiesel. After the reaction of the acids (e.g., fatty acids) in biodiesel with potassium hydroxide, the unreacted potassium hydroxide is titrated with standard solution and thus the TAN in biodiesel can be calculated. The major disadvantage of back-titration technique is the inefficient and time-consuming procedures.

There are also some other techniques in the quantification of TAN, which mainly include potentiometric titration technique (ASTM D664) [9] and colorimetric technique (ASTM D974) [10]. In potentiometric titration technique, it has the drawbacks of large sample size demanding and inefficiency in handling analysis. The colorimetric technique was found to be more accurate than potentiometric technique for biodiesel analysis because this technique avoids errors introduced by the electrode. However, the colorimetric technique is subject to interferences by colored (dark brown (nearly black) color) substances in biodiesel, which would interfere with the endpoint determination during the analysis.

Headspace gas chromatography (HS-GC) is an effective technique for detecting volatile substances in complex samples [11–13]. HS-GC has the many disadvantages (i.e., less sample pre-treatment and independent of sample matrix) associated with the direct injection of sample solution into the GC system. HS-GC is also capable of detecting some non-volatile substances that can be quantitatively converted to volatile substances by some related reactions [14–16]. In a previous work [17], we reported a phase reaction conversion HS-GC method to quantify isocyanate groups in the organic intermediates. It was based on HS-GC detecting the CO_2 formed from the reaction of the isocyanate groups with H_2O in the organic solution. According to the literatures [18,19], the acidic species can react with sodium bicarbonate to generate CO_2, i.e.,

$$RCOOH + HCO_3^- \rightarrow RCOO^- + H_2\,O + CO_2(g) \tag{1}$$

We believe that by detecting the CO_2 generated from the reaction of fatty acids in biodiesel with sodium bicarbonate, the TAN in biodiesel

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could be calculated.

The purpose of this article was to investigate a reaction HS-GC method to quantitative detect the TAN in biodiesel. The major foci were to optimize the conditions (e.g., sample size, $NaHCO_3$ dosage, and equilibration temperature) in the headspace auto-sampler. The validation of the HS-GC analytical technique in the TAN quantification was also assessed.

2. Experimental

2.1. Materials

Isopropanol, hydrochloric acid, sodium chloride and sodium bicarbonate were analytical grade and purchased from a chemical supplier (Shanghai Macklin Co., Ltd. (Shanghai, China)). Palmitic acid was added to appropriate amount of isopropanol in order to obtain a series of palmitic acid standard solutions (ranging from 0 to 1.215 mg KOH/g). The biodiesel samples were collected from several biodiesel related manufactures and companies.

2.2. Equipment

All testing in the research were carried out by using an automated headspace sampler (Thermo HS TriPlus 300, US) connected to a GC system (Agilent GC 7890A, US) equipped with a thermal conductivity detector (TCD) and a GS-Q capillary column (30 m × 0.32 mm i.d. with 0.1 µm film thickness (J & W Scientific, US)), operating at a temperature of 105 °C with nitrogen carrier gas (flow rate = 2.7 mL/min). The headspace operating conditions optimized were as follows: 25 min of strong shaking for sample equilibration temperature at 75 °C; a pressurization pressure of 0.10 MPa, a carrier gas pressure of 0.15 MPa, a vial pressurization time of 15 s, a sample loop fill time of 10 s, a transfer time of 20 s, and a sample loop volume of 3 mL.

2.3. Detecting condition

A 300 mg of biodiesel sample was placed in a sample vial containing 5.0 mL of isopropanol. Afterward, 0.5 mL of sodium chloride solution (2.0 mol/L) and 0.5 mL of sodium bicarbonate solution (0.04 mol/L) were successively transferred to the vial. The sample vial was immediately sealed by rubber septa and analyzed by HS-GC system, using the above-mentioned operating conditions.

2.4. Determining TAN by the reference method

An appropriate weight of biodiesel sample is first added in isopropanol solution containing overdose sodium hydroxide. Afterward, a standard hydrochloric acid solution was selected to back-titrated the rest of sodium hydroxide (detected by potentiometric method). Finally, the TAN in the biodiesel samples can be calculated, i.e.,

$$N = \frac{56.1 \times (c_2 V_2 - c_1 V_1)}{m} \tag{2}$$

where m, c_1, c_2, V_1, V_2, 56.1 represent the the weight (g) of biodiesel sample, the concentration (mol/L) of HCl isopropanol solution and KOH aqueous solution, the volume (mL) of HCl isopropanol solution and KOH aqueous solution, the molecular mass (g/mol) of KOH, respectively.

3. Results and discussion

3.1. Methodology of this method

In the present method, the TAN quantification can be realized by detecting the CO_2 generated from Eq. (1) and the equilibrated vapor CO_2 content formed form Eq. (1) can be obtained according to Henry's law, i.e. [11],

$$H = \frac{C_g}{C_l} \tag{3}$$

where C_g and C_l represent the concentrations of CO_2, H is Henry's law constant, respectively. The content of CO_2 in the vial can be expressed as [11]

$$n = C_l V_l + C_g V_g \tag{4}$$

where n is the number of moles of CO_2 in the vial. V_l and V_g are the the volume of the vapor and liquid phase in the vial, respectively. On the basis of Eqs. (3) and (4), we can obtain

$$n = \left(\frac{V_l}{H} + V_g\right) C_g \tag{5}$$

The TAN in biodiesel sample can be obtained from Eqs. (2) and (5), i.e.,

$$N = \frac{56.1 \times n}{m} = \frac{56.1 \times (V_l + V_g H)}{Hm} C_g \tag{6}$$

where N, m are the TAN (mg KOH/g) of biodiesel sample, the sample weight (g) respectively. Since the vapor concentration of volatile substances in the headspace is linearly proportional to the measured GC peak area; i.e., C_g = fA [11], Eq. (6) can be finally written as

$$N = KA \tag{7}$$

where $K = \frac{56.1 \times (V_l + V_g H) f}{Hm}$

Therefore, the GC peak area of CO_2 can be measured by HS-GC and thus the TAN in biodiesel can be calculated on the basis of Eq. (7).

3.2. Equilibration (reaction) temperature and time

In this method, the TAN in biodiesel can be obtained by quantitatively analyzing the CO_2 formed from Eq. (1), thus the complete reaction (Eq. (1)) should be achieved before conducting HS-GC measurements. In Fig. 1, it presents the normalized GC signal (peak area) for the CO_2 vapor after a 30 min reaction of acidic species in biodiesel between sodium bicarbonate at different temperatures (i.e., 45, 55, 65, 75 and 85 °C), which indicates that the complete reaction can be achieved at the temperatures above 75 °C. Hence, 75 °C was selected as the reaction temperature to guarantee the completeness of the reaction.

The present technique is based on headspace measurement when the sample in the vial reaches equilibrium at 75 °C. Fig. 2 presents the effect of the equilibration (reaction) time on the CO_2 formation from Eq. (1), which indicates that the reaction (Eq. (1)) in the system can be finished in in 25 min at 75 °C. In the following study, 25 min was used

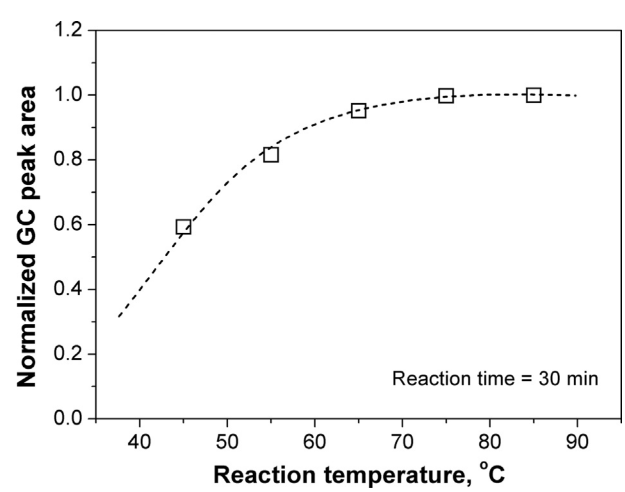

Fig. 1. Effect of reaction (equilibration) temperature.