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Monitoring the conversion of soybean oil to methyl or ethyl esters using the refractive index with correlation gas chromatography

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ABSTRACT

A simple method (refractive index) was applied to monitor the progress and the end point of the transesterification reaction of soybean oil to biodiesel (methyl or ethyl esters). Additionally, the same method may be used to determine the methyl or ethyl ester content during the transesterification reaction progress. To do so, blends of biodiesel and soybean oil were prepared at different wt.% to obtain a simple linear correlation with the refractive index and a correlation coefficient (R^2) of 0.9997 and 0.9996 for the FAMEs and FAEEs, respectively. The transesterification process of soybean oil with methanol and ethanol was performed to determine how the refractive index properties change due to the ratio of conversion. It was concluded that in the reaction kinetics of the methanolysis reaction, the efficiency was over 90% in 8 h. Compared with existing chromatographic techniques, the refractive index method for monitoring the transesterification of vegetable oils presented good results. Additionally, the method was rapid, inexpensive and especially suitable for process control applications.

1. Introduction

With the increasing energy crisis due to fossil fuel depletion and environmental degradation, considerable effort has been devoted to the development of alternative fuels [1]. One of the most promising alternative diesel fuels is biodiesel, which is derived from the transesterification reaction of vegetable oils or animal fats with alcohol of lower molecular weights, such as methanol or ethanol, using homogeneous or heterogeneous catalysts (acid, base, or enzyme) [2–4]. The primary advantages of using biodiesel are that it is biodegradable and nontoxic, can be used without modifying existing engines, and produces less harmful gas emissions such as SO_x, CO, unburned hydrocarbons, and particulate material [5,6].

However, incomplete transesterification and/or insufficient purification that results in even a small amount of the original unconverted oil compounds getting into the final methyl or ethyl ester product can cause severe operational problems, such as engine deposits, which can increase the production of hazardous emissions [1–3,7]. Hence, monitoring the conversion of vegetable oils to methyl or ethyl esters is necessary to assess the quality of biofuels.

Different methods have been used for determining or verifying the concentration of biodiesel obtained by the transesterification of vegetable oils. These include techniques such as ^{1}H NMR spectroscopy [8–10], infrared (IR) spectroscopy [10,11], high-performance liquid chromatography (HPLC) [10,12] and gas chromatography [13,14]. However, gas chromatography (GC) [14,15] is the analytical method that is typically used for evaluating FAME conversion and quality according to European standard specifications based on the EN in 14103.

Gas chromatography (GC) is a very sensitive analytical method that measures by-products such as monoglyceride (MG), diglyceride (DG) and unreacted triglyceride (TG), in addition to fatty acid methyl ester (FAME). Nevertheless, this method has some drawbacks, such as requiring very accurate sample preparation. For example, prior to analysis by trimethylsilylation of the free hydroxyl groups in MGs and DGs, the sample must be derivatised. Furthermore, the analysis is time-consuming, and the method requires expensive instruments with highly trained personnel. Because of these requirements, “on-line” application in a transesterification factory would be very difficult [13–15]. Thus, low cost and rapid analytical methods are desirable.

An alternative non-destructive, rapid analytical technique that does not require sample pre-treatment involves measuring refractive indices; this method has received little attention for use in monitoring the quality of biodiesel [16,17]. Because the possible components of the reaction mixture, i.e., MG, DG, TG, and methyl or ethyl esters, have different refractive indices, which change from base oil to biodiesel properties, they can be correlated to the mixture composition to give an indication of the conversion rate of the transesterification reaction.

In the present study, we investigated the use of refractive index measurements for monitoring a transesterification reaction process. This method is simple, rapid, and inexpensive. Thus, it is especially

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suitable for process control applications. As a means of correlating and cross-checking the results with another analytical method, gas chromatography (GC) was selected. Thus, we performed a series of transesterification reactions using refined soybean oil with methanol and ethanol, and the methyl or ethyl ester content of the samples were determined by the refractive index and gas chromatography.

2. Experimental

2.1. Materials

Refined bleached deodorised soybean oil was purchased from local stores, and its physicochemical properties are illustrated in Table 1. The reagents used during synthesis and purification procedures were methanol (99.9%), anhydrous ethanol (99.8%), sodium hydroxide (97%) pellets, and hydrochloric acid (37%). Methyl and ethyl laurate (methyl or ethyl dodecanoate, 98.0% and 95.5%, respectively) were used as an internal standard for GC analysis.

2.2. Synthesis of the methylic and ethylic biodiesel and soybean oil blends for the standard correlation

To obtain a correlative equation among the refractive indices and the ester content, mixtures of soybean oil with methylic or ethylic biodiesel at different proportions were prepared, and the refractive index was measured in each sample. The biodiesel used in these mixtures was synthesised by repeating an alkaline transesterification reaction twice, using 0.6% (w/w) or 0.8% (w/w) sodium hydroxide as a catalyst for methanol (FAME — fatty acid methyl ester) or ethanol (FAEE — fatty acid ethyl ester), respectively. The alcohols were used in excess at 100% vol. The reaction temperatures were 25 °C and 60 °C for the methylic and ethylic routes, respectively, with a reaction time of 1 h. The transesterification reaction was performed in a 250-mL three-neck flat-bottom flask, equipped with a reflux condenser, a thermometer and magnetic stirring. The reactor was initially charged using 50 g of soybean oil and heated to the reaction temperature. Subsequently, the above mentioned amount of catalyst was dissolved in alcohol and added to the reactor, marking the beginning of the reaction. After the end of the reaction period (1 h), the glycerol phase was discarded, and the same amount of alcohol and catalyst used in the previous step was added, and the procedure was repeated. Finally, the resulting biodiesel sample was washed with distilled water at least three times to remove the remaining catalyst and glycerol; the water volume corresponded to 10 wt.% of the biodiesel. However, for the first washing, an HCl (0.1 N) solution was used to neutralise the alkali catalyst. The product was heated to 105 °C under vacuum for the subsequent analyses. The main properties of the biodiesel were evaluated and are shown in Table 1.

In the next step, soybean oil and biodiesel mixtures were prepared in different weight proportions, as follows: B0: 100% soybean oil, B15: 15% biodiesel + 75% oil, B30: 30% biodiesel + 60% oil, B45: 45% biodiesel + 55% oil, B60: 60% biodiesel + 40% oil, B70: 70% biodiesel + 30% oil, B85: 85% biodiesel + 15% oil and B100: 100% biodiesel. The refractive index of these mixtures was measured, and the correlative equation for the refractive index with the ester content was fitted and evaluated. The blends were prepared by weight because the weight fraction does not change with temperature.

Table 1
Soybean oil and biodiesel properties.

Property	Units	Soybean oil	FAME	FAEE	European spec.
Acid value	mg KOH/g	0.099	0.48	0.29	0.5 max.
Kinematic viscosity at 40 °C	mm^2/s	30.1	4.2	4.5	3.5–5.5
Density at 20 °C	g/cm^3	0.9237	0.881	0.876	0.86–0.9
Refractive index at 40 °C		1.4680	1.4498	1.4480	–
Fatty acid esters content	% mass	–	96.54	98.2	96.5

2.3. Product analysis (GC analysis for fatty acid esters)

Biodiesel analyses (fatty acid methyl esters, FAME and fatty acid ethyl esters, FAEE) were performed using a gas chromatograph equipped with a flame-ionisation detector and a capillary non-polar column measuring 30 m in length, 0.25 mm in internal diameter, and 0.25 μm in film thicknesses. The column temperature program was as follows: initial temperature of 135 °C, hold for 3 min, and ramp at 15 °C/min up to 230 °C, hold at 20 min. Nitrogen was used as the carrier gas at 1.0 mL/min. The temperatures of the injector and detector were 250 °C.

The preparation of the sample for analysis and quantification was performed following standard method EN 14103 [18] using methyl or ethyl laurate as an internal standard. The injection was performed in split mode with a split ratio of 80:1 and sample size of 1.0 μL. The biodiesel yield (per cent FAMEs or per cent FAEEs) was calculated using Eq. (1):

$$FAMEs\ or\ FAEEs = (A_{ester} C_{EI} V_{EI} f_{ester\ laurate} / A_{EI} m) x\ P_{EI} \quad (1)$$

where, A_{ester} is the peak area of FAMEs or FAEEs, C_{EI} and V_{EI} are the concentration and volume of the methyl or ethyl laurate solution, respectively, $f_{methyl\ or\ ethyl\ laurate}$ is the response factor, A_{EI} and P_{EI} are the peak area and purity (wt.%), respectively, of the internal standard and m is the mass of the sample.

2.4. Physicochemical properties' measurement of soybean oil and biodiesel

The refractive index was measured to an accuracy of 10^{-4} with an ABBE refractometer at 40 °C, which was thermostatically controlled by bath to maintain the temperature, in keeping with ISO 6320. The measurements were conducted three times for each sample, and the results were averaged. Physicochemical analyses of the soybean oil and biodiesel were performed according to ASTM methods D4052 and D445 for density and kinematic viscosity, respectively, and AOCS Cd 3d-63 for the acid value [19–21]. The values obtained for these properties were compared to the European specifications (EN-14214), for which the accepted values fall between 0.860 and 0.900 g/cm^3 for density, 3.5 and 5.5 mm^2/s for viscosity, and ≤ 0.5 mgKOH/g for the maximum acid value.

2.5. Synthesis of the methylic and ethylic biodiesel for the evaluation of the method

To obtain real data from the soybean oil transesterification reaction progression, a new process of transesterification to methyl esters and ethyl ester was performed; however, a heterogeneous catalyst (dolomite) was employed [22]. It is known that a homogeneous process is faster than a heterogeneous process [23]; thus, this method makes it possible to obtain mixtures with compositions that are very different from that of the standard in Section 2.2.

Methyl esters were produced at different reaction times (1, 2, 4, 8, 16 and 24 h), at 50 °C and with a catalyst amount of 0.6 wt.% and a methanol/oil molar ratio of 6. Ethyl ester synthesis was performed at different temperatures (50, 55, 60, 70 and 80 °C), maintaining the reaction time at 24 h, with a catalyst amount of 0.8 wt.% and an ethanol/oil molar ratio of 6. These new samples were monitored by gas chromatography according to Eq. (1) and compared to the calculated