Hydroxyl Content and Refractive Index Determinations on Transesterified Soybean Oil

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ABSTRACT: Biodiesel, a promising alternative diesel fuel, is produced by transesterification of vegetable oils or animal fats with methanol. One of the main problems in the industrial application of the transesterification process is how to determine the conversion of oils to methyl esters. In this work, a quick analytical method was developed for monitoring the transesterification reaction of soybean oil with methanol. The conversion of oils to methyl esters could be determined by applying a simple linear correlation with hydroxyl content of the transesterified mixture or refractive index of the product. The results were in agreement with the values measured by ^{1}H NMR spectroscopy. Compared with existing chromatographic and other methods, this method for monitoring the transesterification of vegetable oils with methanol is simple, rapid, and inexpensive and is especially suitable for process control purposes.

Paper no. J11318 in *JAOCS 83*, 869–872 (October 2006).

KEY WORDS: Hydroxyl value, refractive index, transesterification.

The transesterification of vegetable oils or animal fats with methanol in the presence of a catalyst (usually a base such as NaOH or KOH) affords the corresponding methyl esters. These esters have significant potential as an alternative diesel fuel (better known as biodiesel) both in neat form and blended with conventional diesel fuels. Biodiesel is a promising nontoxic, biodegradable, and renewable fuel. Being essentially free of sulfur and aromatics makes it a cleaner-burning fuel than petroleum diesel, with reduced emissions of SO_x, CO, unburnt hydrocarbons, and particulate matter (1).

During the course of transesterification of vegetable oils with methanol, the final product, methyl esters of FA, can be significantly contaminated with glycerin and MG, DG, and TG owing to incomplete transesterification and insufficient purification. In using these methyl esters as automotive diesel fuel substitutes, now the most important field of application, the presence of these components can lead to serious engine problems and hazardous emissions. So it is important to monitor the progress of the transesterification reaction, determine the conversion of vegetable oils to methyl esters, and assess the quality of biodiesel fuels.

The usual analytical methods for evaluation of the conversion to FAME in the transesterification of vegetable oils have been based on GLC (2–6), TLC/FID (7), HPLC/density detection (8,9), or pulsed amperometric detection chromatography systems (10). In addition to NMR (11,12), NIR spectroscopy (13) and an alternative spectrophotometric method (14) have been used for determining the yield of the transesterification reaction of vegetable oils with methanol.

The analytical methods just outlined are commonly very sensitive and measure, besides FAME, by-products such as MG and DG as well as unreacted TG. However, they have some drawbacks, such as the requirement during sample preparation of high accuracy; moreover, chemical derivatizations of the sample and tedious calibrations are often necessary for analyses, and the time required for the analysis is usually long; simultaneously, high-cost instruments must be equipped and technical personnel are required to collect and interpret the data, so that "on-line" applications in a transesterification factory are very difficult.

During the course of our studies on the use of solid bases as catalysts for the transesterification of soybean oil with methanol, we developed a reliable and quick analytical method to monitor the progress and end point of the transesterification reaction and to determine the yield of the transesterification reaction, without any derivatization of the samples. The proposed method is based on hydroxyl content or refractive index measurements, since the possible components of the reaction mixture, i.e., glycerin, MG, DG, TG, and methyl esters have different hydroxyl contents and refractive indices. The hydroxyl content or refractive index differences are sufficient to give an indication of the conversion to methyl esters in the transesterification reaction. As a means for correlating and cross-checking results with another analytical method, the ^{1}H NMR method was selected. Since the quantification method by NMR was discussed in a previous publication (11), no further discussion will be presented here. In the ^{1}H NMR-based monitoring of transesterification of vegetable oils, the conversion to methyl esters was determined by the integration values of the protons of the methyl ester moiety (at approximately 3.7 ppm) and the a-carbonyl methylene groups (at about 2.3 ppm) found in all fatty compounds (11).

EXPERIMENTAL PROCEDURES

Commercial edible-grade soybean oil was obtained from a local market and refined again to reduce FFA and water contents. According to GC analysis (Shimadzu DC-9A), the FA

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*To whom correspondence should be addressed. E-mail: xwenlei@163.com composition was 12.3% palmitic acid, 5.8% stearic acid, 26.5% oleic acid, 49.4% linoleic acid, and 5.9% linolenic acid. The acid value was less than 0.1 mg KOH/g, and the average M.W. was 874 g/mol, calculated from the saponification value (SV = 192.6 mg KOH/g).

A 250-mL two-necked glass reactor equipped with a mechanical stirrer and a water-cooled condenser was charged with 30 g (34.3 mmol) soybean oil, 20 mL methanol (494.3 mmol), and 2% (w/w) catalyst. The mixture was stirred vigorously and refluxed for the required reaction time. Once the transesterification reaction had finished, the mixture was filtered and the residual methanol was distilled off completely with the help of a rotary evaporator at 334 K under vacuum for the subsequent analyses.

Reaction times from 0.5 to 10 h were used to obtain a wide range of conversion to methyl esters, including samples with low methyl esters and high MG and DG contents. Obviously, such samples do not fulfill the standards for fuel-grade oils. However, they were used for checking the proposed method. Typically, a high molar ratio of methanol/oil is used in the transesterification of vegetable oils to biodiesel. After the reaction has finished, large amounts of the methanol are unreacted, and the reaction products have separated into two phases, namely, an ester phase and a glycerin phase. Chiu *et al.* (15) found that methanol is preferentially distributed into glycerin, and only a relatively small amount is dissolved in biodiesel. However, when the conversion to methyl esters was much lower in our experiments, the two liquid layers did not form, possibly owing to the formation of a small amount of glycerin and of the intermediate MG and DG, which act as a surface agent.

The organic hydroxyl group is commonly determined by acetylation (16,17). The sample is heated with an excess of acetic anhydride in pyridine, then water is added, and the resulting acetic acid is titrated with alcoholic potassium hydroxide. A blank containing the same amount of acetic anhydride but without samples is treated with water, and the acetic acid formed is also titrated. The hydroxyl content is calculated from the difference between the blank and sample titrations with potassium hydroxide. However, this analytical method has the disadvantage that methanol interferes in the determination. Therefore, for precise results the excess methanol must be removed completely by rotary evaporation under reduced pressure after the transesterification reaction has finished.

The hydroxyl content of the transesterified mixture was determined according to AOCS. Official Method Cd 13-60 (16,18). First, the transesterified mixture (containing methyl esters, glycerin, MG, DG, and unreacted TG) was acetylated by a mixture of acetic anhydride and pyridine at a temperature of 368–373 K, with vigorous magnetic stirring, in a measured quantity sufficient to provide an excess of reagent. Then the appropriate volume of distilled water was added, and the mixture was heated for 10 min for the complete conversion of excess acetic anhydride into acetic acid. The acetic acid was titrated with a standardized potassium hydroxide solution. Simultaneously, a blank test without the sample was carried out under the same conditions. The hydroxyl content is given by the formula:

$$\text{hydroxyl content} = \frac{56.1\times T\times(V_0 - V)}{m} + \text{A.V.} \qquad [1]$$

where V is the number of mL of the standardized ethanolic potassium hydroxide solution used for the test portion; V_0 is the number of mL of the standardized ethanolic potassium hydroxide solution used for the blank test; T is the exact normality of the ethanolic potassium hydroxide solution used; m is the mass, in g, of the test portion; and A.V. is the acid value of the sample.

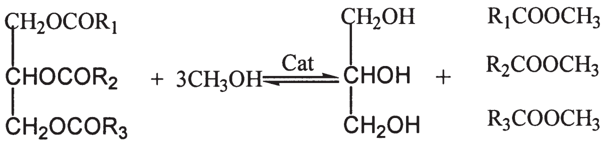
For ^{1}H NMR and refractive index analyses, the transesterified mixture was washed three times with the appropriate volume of a saturated aqueous NaCl solution to ensure complete removal of glycerin. The organic phase was separated by decantation, dried with anhydrous magnesium sulfate, and then submitted to ^{1}H NMR analysis (model DPX-400; Bruker) in $CDCl_3$ using tetramethylsilane as internal standard. The conversion of the soybean oil to a mixture of methyl esters was determined by the ratio of the signals at 3.68 ppm (methoxy groups of the methyl esters) and 2.30 ppm (α-carbon CH_2 groups of all FA derivatives) according to Reference 11.

The refractive index was determined by using a refractometer at 303.15 K.

For analysis, pure methyl ester was obtained by repeating the transesterification twice using sodium methoxide as a catalyst. A mixture of 8.0 g soybean oil, 20 mL methanol, and 0.2 g (2.5%, w/w) sodium methoxide was refluxed for 30 min under vigorous stirring. The lower phase was discarded. Then the same amount of methanol and catalyst as above was added, and this procedure was repeated. The purity of the methyl ester mixture is 100% as checked by ^{1}H NMR spectroscopy and GC. Besides, no visible glyceryl-related signals were found at 4.1–4.4 ppm in the ^{1}H NMR spectroscopy.

RESULTS AND DISCUSSION

The transesterification of vegetable oils is a catalytic reaction whereby a TG reacts with methanol to produce glycerin and a mixture of FA esters. The simple stoichiometry of the applied transesterification reaction is illustrated in Scheme 1. However, the transesterification process is a sequence of three consecutive and reversible reactions transforming the TG into a DG, then into a MG and, finally into glycerin and the FAME. At each reaction step, one molecule of methyl ester is produced for each molecule of methanol consumed. If an excess of methanol is used, glycerin is formed in appreciable amounts and separates from the oil phase, thus improving the yield of



SCHEME 1

TABLE 1
Conversions of Soybean Oil Determined by Different Analytical Methods

Entry	Hydroxyl content	Conversion (OH) (%)[a]	Refractive index (RI)	Conversion (RI) (%)[b]	Conversion (^{1}H NMR) (%)[c]
1	8.0	0	1.4704	0	0
2	43.6	21.5	1.4660	23.2	22.6
3	83.2	45.4	1.4616	46.1	45.5
4	99.7	55.4	1.4599	55.4	52.9
5	113.5	63.7	1.4580	65.6	62.7
6	128.1	72.5	1.4560	76.1	73.4
7	145.7	83.6	1.4544	84.5	82.1
8	173.5	100	1.4515	100	100

[a] Conversion (OH), determined by hydroxyl content.
[b] Conversion (RI), determined by refractive index.
[c] Conversion (^{1}H NMR), determined by ^{1}H NMR spectroscopy.

methyl esters. Obviously, the increase in amount of methyl esters is followed by an increase in hydroxyl content of the liquid portion in the same step, because one free alcohol is liberated from a TG when one molecule of methyl ester is formed in the transesterification reaction. Therefore, when the methanol is removed, the free alcohols on the MG, DG, and glycerin are titrated essentially to determine how much methanol reacted to displace the glycerin and create free alcohols, and consequently the conversion can be evaluated by titrating free alcohols on bound and free glycerin. So, it is reasonable that a linear relation is exhibited between the conversion of vegetable oils and the hydroxyl content of the transesterified mixture, which shows that the hydroxyl content can indicate the conversion to methyl esters.

The hydroxyl content of the refined soybean oil was 8.0 mg KOH/g (0% conversion; there were no visible –OCH_3 signals at about 3.7 ppm in the ^{1}H NMR spectra). After the soybean oil had been reacted completely with methanol, the hydroxyl content of the transesterified mixture was 173.51 (100% conversion). From the data, a linear correlation between the conversion (*Y*) and the hydroxyl content (*X*) can be developed as:

$$Y(\%) = \frac{100}{(173.51 - 8.0)} \times (X - 8.0) \qquad [2]$$

The conversion to methyl esters can be determined by Equation 2 when the hydroxyl content of the transesterified mixture is known. The results are shown in the third column of Table 1.

The conversion was also confirmed by the refractive index of the product at 303.15 K, which depends linearly on the conversion to methyl esters between 1.4704 (0% conversion) and 1.4515 (100% conversion). The results are listed in the fifth column of Table 1.

For cross-checking purposes, the conversions determined by the ^{1}H NMR method were also listed in Table 1. The agreement between the conversions determined by ^{1}H NMR spectra data and those determined by the refractive index or the hydroxyl content was good; the differences were less than 4%. Furthermore, the relationships between the conversions as determined by ^{1}H NMR and the hydroxyl contents of the transesterified mixtures or the refractive indices of the products were investigated. As illustrated in Figures 1 and 2, there was a linear correlation between the conversion of soybean oil and the hydroxyl content or the refractive index. Such a linear correlation verifies further the reliability of the method. Thus, the suggested correlation could allow for the determination of the conversion to methyl esters in the transesterification process by measuring the hydroxyl content or the refractive index. From these results, we think that the progress of the transesterification reaction could be monitored by the hydroxyl content of the transesterified mixture or the refractive index of the product and the conversion can be determined by this simple and quick method.

The proposed analytical method was developed using soybean oil. To extend it to other vegetable oils, specific calibration

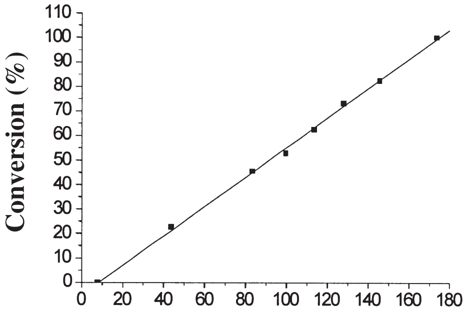


FIG. 1. Relationship between the hydroxyl content of the transesterified mixture and the conversion as determined by ^{1}H NMR spectroscopy.

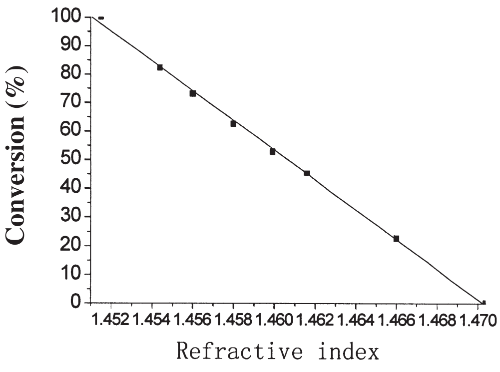


FIG. 2. Relationship between the refractive index of product and the conversion as determined by ^{1}H NMR spectroscopy.

curves for each vegetable oil should be prepared because of their different compositions. Once the correlations are developed for the various oils, the conversion of vegetable oils in the transesterification reaction could be evaluated directly by this method.

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[Received January 23, 2006; accepted July 19, 2006]