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Fourier Transform Infrared Spectroscopy (FTIR) Method To Monitor Soy Biodiesel and Soybean Oil in Transesterification Reactions, Petrodiesel−Biodiesel Blends, and Blend Adulteration with Soy Oil

Naresh N. Mahamuni and Yusuf G. Adewuyi*

Chemical Engineering Department, North Carolina Agricultural and Technical State University, Greensboro, North Carolina 27411

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An analytical method has been developed using Fourier transform infrared spectroscopy (FTIR) to determine biodiesel content in the reaction mixture to monitor the transesterification reaction. It is also shown that it can be used to determine biodiesel content in biodiesel−petrodiesel blends. The method with small modifications can also be used to determine the oil content in the adulteration of biodiesel−petrodiesel blends. Soybean oil is used as the model oil, and its methyl ester is used as biodiesel. The method uses a software viz. Enformatic FTIR Collection Manager (EFCM) to develop a calibration model and predict the concentration of biodiesel and oil. The software uses the nonlinear classical least square (CLS) method for calibration. It is shown that the method can be used to measure the amount of biodiesel accurately to the extent of 98.11% accuracy for biodiesel−oil mixtures and biodiesel content in the biodiesel−petrodiesel mixture (blend) with an accuracy of 99.99%. The method has also been used to determine the oil content and biodiesel content in the biodiesel−petrodiesel−oil mixture (blend adulteration) with an accuracy of about 95.32%.

1. Introduction

Monoalkyl esters of long-chain fatty acids derived from vegetable oils, animal fats, or their mixtures are a suitable fuel for diesel engines. These fatty acid methyl esters (FAMEs) or fatty acid ethyl esters (FAEEs) are, in general, called biodiesel because they are derived from renewable sources, are biodegradable, and owing to their use as fuel in diesel engines. Biodiesel as a fuel for diesel engines has many advantages, such as better cetane number, higher flash point, better lubricity, lowered exhaust emissions of CO, particulate matter, and unburned hydrocarbons, and complete elimination of sulfur compounds. However, a slight increase in NO_x emissions has been observed with the use of biodiesel as a fuel as compared to that of petrodiesel.[1]

Biodiesel can be used as a complete replacement (B100) for petrodiesel, or it can be used in blends of biodiesel with petrodiesel (B2−B80). B2 is a 2% biodiesel and 98% petrodiesel mixture. It is used in some European countries and Brazil. It can also be used as an additive to petrodiesel in as low as 1% to improve the lubricity of petrodiesel to acceptable levels.[1] In recent years, there has been a dramatic increase in the use of biodiesel as a fuel. The world production of biodiesel has gone up from 0.2 billion U.S. gallons in 2000 to almost 1.1 billion U.S. gallons in 2007.[2] The U.S. biodiesel production has gone up from 2 million gallons in 2000 to 450 million gallons in 2007.[3]

As the production and use of biodiesel increase, the chances of the adulteration of petrodiesel−biodiesel blends with oil also increase. Also, there is an urgent need to easily monitor the conversion of vegetable oil to biodiesel at plant levels. The estimation of biodiesel in the petrodiesel−biodiesel blends is another area of concern. Hence, there is the need to develop a simple, fast, reliable, and accurate analytical method to address all of the above issues.

There are many analytical methods, such as gas chromatography with flame ionization detector (GC−FID),[4,5] gas chromatography with mass spectrometry detector (GC−MS),[6] high-pressure liquid chromatography (HPLC) with UV, atmospheric pressure chemical ionization (APCI detectors) or evaporative light-scattering detector (ELSD detectors),[7] gel-permeation chromatography (GPC),[8] size-exclusion chromatography (SEC),[9] thin-layer chromatography (TLC),[10] near-infrared spectroscopy (NIR),[11] nuclear magnetic resonance (NMR),[12] viscometry,[13] and Fourier transform infrared spectroscopy (FTIR), for biodiesel

* To whom the correspondence should be addressed. Telephone: 1-336-334-7564 ext. 107. Fax: 1-336-334-7417. E-mail: adewuyi@ncat.edu.

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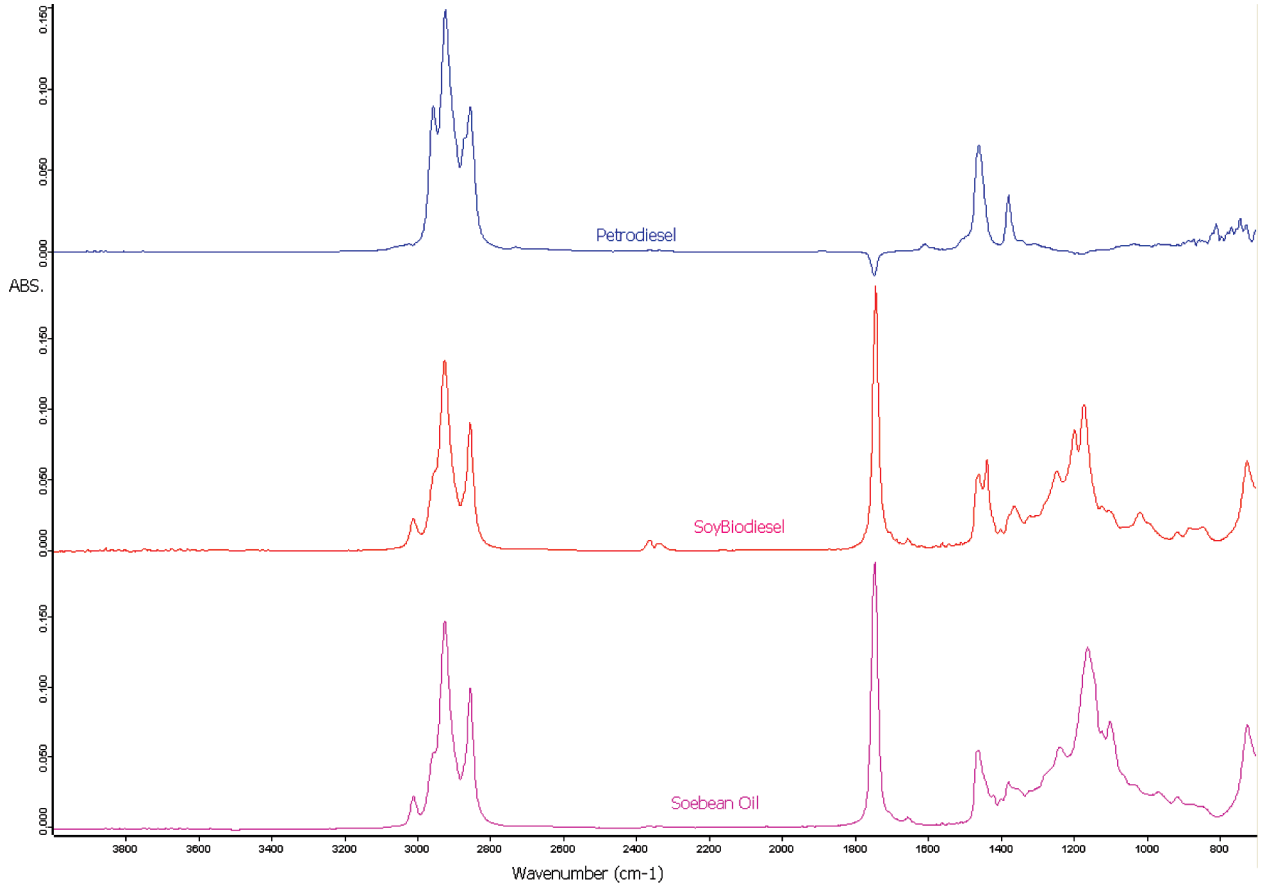

Figure 1. MIR spectra of soybean oil and its methyl ester and petrodiesel.

analysis.[14,15] Chand et al.[16] have recently used thermogravimetric analysis for the quantification of biodiesel. However, many of these methods are developed for either monitoring the transesterification reaction or blend composition or adulteration. There is not a single method that can perform all of the three tasks. Also, all of these methods have drawbacks, which hinder their use for practical situations, such as in the biodiesel manufacturing plant or in a blending unit. For example, GC is a very good method to find the compositions of biodiesel, monoglycerides (MG), diglycerides (DG), and triglycerides (TG). However, it involves a lot of sample processing steps, such as derivatization, using reagents, such as *N*,*O*-bis(trimethyisilyl)trifluoroacetamide (BSTFA) and *N*-methyl-*N*-trimethylsilyltrifluoroacetamide (MSTFA).[4,15] Also, the use of an internal standard is needed to obtain accurate results in the case of GC, GC−MS, and HPLC. The time required for analysis is quite long in most of the cases, and the method is a sample-destructive technique. Similarly for HPLC analysis, costly chemical reagents are required for separation of sample compounds. HPLC also involves the use of very sophisticated and costly detectors, such as APCI, MS, and ELSD. TLC is a cheap analytical technique but is not reliable. Its accuracy is low, and also, it is sensitive to humidity. NMR is a very good technique for biodiesel analysis, but again, it is a very costly instrument to use and maintain on a daily basis in a plant or blending unit. In addition to these limitations, skilled and, hence, costly labor is required to use these techniques. Hence, their wide use in plants and blending units is a point of concern for manufacturers and distributors.[4,14,15]

Table 1. Characteristics Regions of Oil and Biodiesel Spectra Used for Quantification

region (cm^{-1})	assignment	soybean oil	soy biodiesel	reference
1425−1447	CH_3 asymmetric bending	absent	present	26
1188−1200	O−CH_3 stretching	absent	present	26
1370−1400	O−CH_2 groups in glycerol moiety of TG, DG, and MG	present	absent	25
1075−1111	O−CH_2−C asymmetric axial stretching	present	absent	26
1700−1800	C═O stretch	present	present	17,21
2800−3000	symmetric CH_2 stretching and the asymmetric CH_3 and CH_2 stretching	present	present	19

FTIR, FTNIR, and FT-Raman spectroscopy with the use of partial least square (PLS) multivariate calibration modeling have been used recently with great success for biodiesel analysis. FTIR is a fast, cheap, reliable, accurate, and nondestructive method for biodiesel analysis. The science of FTIR is very much mature, and libraries of IR bands are available for component analysis. It should be noted that a fair amount of time is required for sample preparation, but that is comparable to other techniques, such as GC, HPLC, and NMR. However, it does not require the use of internal standards for quantification, as in the case of GC and HPLC, and it is not as costly and time-consuming as NMR spectroscopy. Also, the accuracy of the calibration can be improved by increasing the number of calibration samples and validation samples. Soares et al.[17] have used the PLS calibration method using FTIR to analyze blends of raw soybean oil and biodiesel from different sources, such

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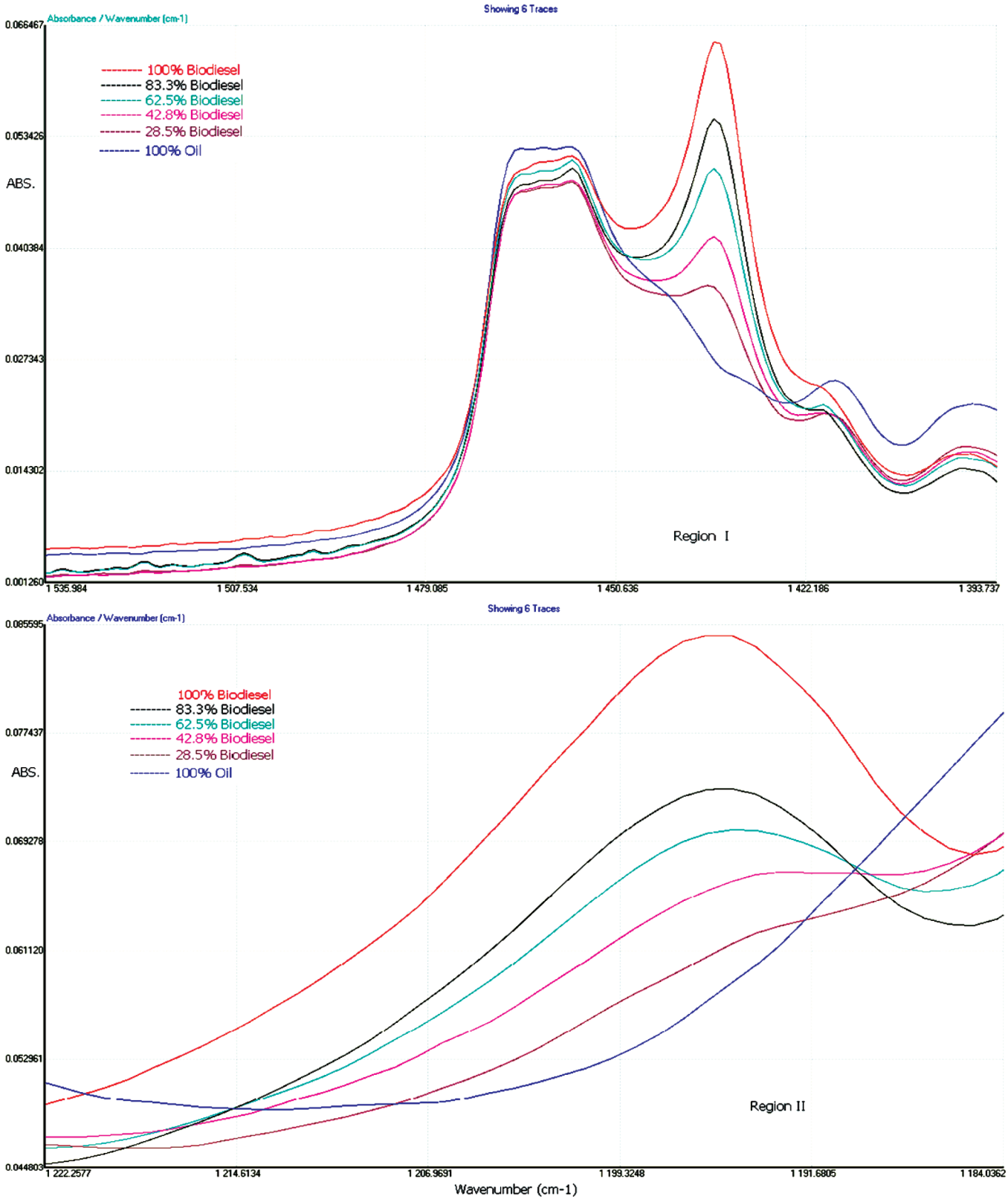

Figure 2. Spectral variation in the peaks with variation of biodiesel.

as cotton, castor, and palm oil. Pimentel et al.[18] developed multivariate calibration models based on mid-range infrared spectroscopy (mid-IR) (wavenumber 4000−200 cm^{-1}) and near-IR spectroscopy (wavenumber 12 800−4000 cm^{-1}) to determine the content of biodiesel in diesel fuel blends considering the presence of raw vegetable oil. Oliveira et al.[19] used PLS and an artificial neural network (ANN) in combination with mid-IR and near-IR spectroscopies to design calibration models for the determination of methyl ester content in biodiesel blends

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with petrodiesel. Trevisan et al.[20] proposed a method involving an online IR determination of biodiesel yield in the transesterification reaction. Zagonel et al.[21] developed an analytical method to monitor ethanolysis of degummed soybean oil using FTIR and principle component analysis (PCA) and PLS methods of multivariate analysis. Baptista et al.[22] used PCA and PLS multivariate analysis with near IR spectroscopy to predict the methyl ester content in biodiesel. They also used the method to analyze the methyl ester content of individual acids, such as linolenic acid, myristic acid, palmitic acid, stearic acid, oleic acid, and linoleic acid. Oliveira et al.[23] used principle component regression (PCR), PLS, and ANN calibration models with FTNIR and FT-Raman spectroscopy to identify adulterations of B2 and B5 blends with vegetable oil. Knothe[24] used near-IR spectroscopy to determine the blend level of biodiesel in conventional diesel fuel. Dube et al.[25] and Siatis et al.[26] also used FTIR spectroscopy to monitor the biodiesel production.

The methods developed thus far use either a PLS, PCA, or PCR technique to develop a calibration model. However, the procedure to develop the calibration model using these techniques is quite tedious, as reported in the literature.[18−26] They require the simultaneous decomposition of both the concentration and absorption matrices to calculate the spectral loadings [also called principal components, Eigen vectors, loadings, or latent variables (LVs)]. These spectral loadings are then ranked to determine the ones that have the greatest contributions to the calibration spectra. Subsequent steps involve the use of a mean-centering technique to remove the average spectra to reduce the total number of latent variables. Finally, parameters such as the root-mean-square error (RMSE), root-mean-square error in calibration (RMSEC), root-mean-square error in cross-validation (RMSECV), and root-mean-square error in prediction (RMSEP) are used to measure the accuracy and performance of the model. Although PCA or PLS regression gives a concise and robust model, the mathematical steps involved are considerably more complex than other multivariate methods.[27] The mathematical details of these techniques are reported elsewhere.[28,29]

In the present work, an effort was made to simplify the process of calibration modeling using commercial software by eliminating the time-consuming process of manually taking a spectra and converting it into concentration through multivariate modeling. The simplicity of using this software lies in the fact that concentration measures are obtained directly from this software. The software develops the model based on the calibration method chosen. Calibration samples over the given range of concentration measures and the nonlinear CLS quantification mode are chosen to describe the data, which are then stored by some method name. The method is then used to predict the concentrations of the unknown samples when the analysis is performed. Of course, a sample validation step is required to check the accuracy of the calibration model developed by the software. The strength of this technique lies in the fact that once the calibration is performed very carefully and validation of the model is executed with a sufficient number of samples, there is no need for additional calibration. The same calibration model can be used as long as the materials remain the same. This allows any scientist or worker, such as an operator in a biodiesel plant or at a blending and distribution unit or a technician in a quality-control and quality-assurance department (QC and QA department) of a biodiesel plant, to use the FTIR to determine the concentration of biodiesel to either monitor its concentration during the transesterification reaction or in blends and in cases of their adulteration with oil.

2. Experimental Section

2.1. Materials. Pure soybean oil was obtained from M.P. Biomedicals, LLC (Solon, OH). The certificate of analysis from the supplier shows that FFA content of the oil was 0.03%, the iodine value was 130, and the peroxide value was 0.2 meq/g. Methanol of ACS grade was obtained from Fisher Scientific (Somerville, NJ). Potassium hydroxide (pellets) of ACS reagent grade was obtained from Aldrich Chemical Co., Inc. (Milwaukee, WI). Biodesel standards, such as linoleic acid methyl ester, palmitic acid methyl ester, *cis*-11-eicosenoic acid methyl ester, arachidic acid methyl ester, methyl oleate, linolenic acid methyl ester, and stearic acid methyl ester, were obtained from Sigma-Aldrich, Inc. (Atlanta, GA). Motor vehicle diesel fuel 2D 15 ppm sulfur (ultra-low-sulfur diesel fuel) was obtained from the Colonial Pipeline Company (Alpharetta, GA). It was graciously supplied to us by Berico Fuels, Inc. (Greensboro, NC).

2.2. Synthesis. Soybean oil was reacted with methanol in a molar ratio of 1:10 (oil/methanol) under reflux conditions and constant high-speed magnetic stirring in a flat bottom spherical flask for 3 h. Potassium hydroxide (1 wt % by weight of oil) was added to methanol and stirred vigorously to dissolve it into methanol in a separate Erlenmeyer flask. This methanol solution was then added to the oil in the flat bottom spherical flask for the transesterification reaction. At the end of the reaction, two layers formed. The upper layer contained methanol and biodiesel, whereas the bottom layer contained glycerol. Distillation was carried out to remove methanol from biodiesel. The two layers of pure biodiesel and glycerol were separated under gravity using a separating funnel overnight. The biodiesel thus obtained was washed with water and allowed for separation under gravity. The biodiesel thus obtained was stored in an amber-colored bottle at 10 °C in a refrigerator for future use. No sediments were observed on biodiesel storage during refrigeration.

2.3. Samples. Three types of samples were prepared viz.: (1) biodiesel−soybean oil mixtures, (2) biodiesel−petrodiesel mixtures (blend), and (3) biodiesel−soybean oil−petrodiesel mixtures (blend adultered with soybean oil). These samples were prepared on the basis of their predefined weight percentages in the mixture. A Mettler PM400 weighing balance was used to prepare these mixtures. These samples ranged from 1 to 100% (w/w) biodiesel in biodiesel−oil mixtures, from 1 to 100% (w/w) biodiesel in biodiesel−petrodiesel blend, and from 1 to 40% (w/w) oil in oil−biodiesel−petrodiesel mixtures. Because the weight percentage was used during the monitoring of the transesterification reaction, it was decided to use the weight percentage throughout the manuscript for the sake of continuity. The density of ULSD petrodiesel at 15.5 °C is 850.76 g/L, and the density of soybean-based biodiesel at 15.5 °C is 874.73 g/L. Because the difference in densities is very low (maximum $\sim$ 2.7%), the difference in the weight percentage and volume percentage in the blend is negligible at any given blend level (<2.7%). One set of samples was used to develop calibration using the EFCM software, and another set of

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samples of different concentrations from the earlier set were used to validate the calibration model.

It should to be noted that the word biodiesel as used in this paper denotes only soybean-based biodiesel, and all references to petrodiesel should be understood as ULSD motor vehicle diesel fuel 2D.

2.4. Attenuated Total Reflectance (ATR)−FTIR Analysis. ATR−FTIR spectra were obtained using a TENSOR 27 FTIR spectrometer from Bruker (Bruker Optics, Inc., Billerica, MA). The FTIR was equipped with an ATR sampling accessory MIRacle ATR from PIKE Technologies (PIKE Technologies, Inc., Madison, WI) and was supplied with a room-temperature deuterated L-alanine triglycine sulfate detector (DLATGS detector). All spectra were collected at 20 ± 1 °C using an average of 16 scans and with a spectral resolution of 2 cm^{-1}. The background spectra were obtained using a clean ATR accessory with a continuous zero air purge from Parker−Balston zero air generator. After each spectrum was recorded, the cell was cleaned by successive treatments with heptane. The average spectrum from triplicate analysis ranging from 4500 to 650 cm^{-1} was treated chemometrically using EFCM software, version 1.6, procured from FTIR.com (Benton, ME). The software uses a browser of spectra to perform nonlinear CLS quantitative analysis. The detail of the theory behind the working of the software is given in the Supporting Information. The software is supplied with the spectra of known samples along with concentrations. It is expected that, the higher the number of samples, the better the calibration model developed. The software is also supplied with the IR regions of the spectra, in which the absorbance changes with concentration. Thus, the software develops a calibration model, which relates absorption in the supplied IR regions with the given concentrations. The calibration model developed is then validated with known validation samples. A good fit between the actual concentration and that predicted by the calibration model implies that the model can be used to predict the concentrations of unknown samples.

The nonlinear CLS quantitative analysis algorithm has earlier been successfully used for gas analysis,[30] but to the best of our knowledge, this work reports the first time that it has been used for liquid sample analysis using FTIR.

3. Results and Discussion

3.1. Method for Biodiesel Analysis To Monitor Transesterification of Soybean Oil. Mid-range infrared, 4000−400 cm^{-1} (MIR) spectra of soybean oil and its methyl ester are shown in Figure 1. It is evident from Figure 1 that there is not much difference in the MIR spectra of soybean oil and its methyl ester. Still there are some regions, such as region I, 1425−1447 cm^{-1}, and region II, 1188−1200 cm^{-1}, where there is a slight difference in the spectra of oil and biodiesel. These peaks are present in the biodiesel spectra but not in the oil spectra. There are other regions, such as region III, 1370−1400 cm^{-1}, and region IV, 1075−1111 cm^{-1}, that are present in oil spectra but absent in its biodiesel spectra. There are also other regions, such as 1700−1800 cm^{-1} corresponding to the C═O bond[17,21] and 2800−3000 cm^{-1} corresponding to the CH stretching mode of olefins.[19] However, these regions are present in both oil and biodiesel and so were not considered for quantification. Table 1 shows these regions and their corresponding chemical bonds. In the regions of spectra selected for quantification of biodiesel in the biodiesel−oil mixture, the peak height/area increases as the biodiesel composition increases. Figure 2 shows these variations of peaks as the biodiesel composition changes.

Multivariate Analysis. The entire FTIR spectra of 12 standard mixtures of biodiesel with oil were processed using the EFCM software by supplying each spectrum to the software along with the concentrations of the biodiesel for that spectrum and the regions selected as characteristics of the biodiesel, viz. region I and region II, in each case. With the supply of the spectrum, concentration, and specific region (the region where the difference of peaks of the given constituent is the largest from the peaks of the other constituents in the mixture), the software then develops a calibration model using the nonlinear CLS method to correlate the concentration with the peak area. A nonlinear CLS method uses multiple spectra per compound for calibration. This method provides more accurate results because the relationship between the concentration and the peak height is not linear and also because the concentration increase results in an increase in the intensity as well as a shift of the peak position (because of molecular interactions, such as hydrogen bonding). The details of the method are given in the Supporting Information. The calibration model thus developed can then be used to predict the concentration of unknown samples from their spectra. The software analyzes the spectra of unknown composition of biodiesel−oil mixtures and provides the biodiesel concentration. Table 2 shows the standard mixtures used for the calibration model using the EFCM software. The software was then used to predict the concentration of biodiesel in the validation samples. The validation samples are samples of known concentrations of the components. The compositions of the validation samples were different from that of the calibration samples. Table 3 shows the composition of the validation samples.

Table 2. Standard Mixtures Used in the Multivariate Analysis for the Biodiesel−Oil Mixture

sample	soybean oil (wt %)	soy biodiesel (wt %)
1	88.90	11.10
2	93.75	6.25
3	98.00	2.00
4	1.96	98.04
5	6.25	93.75
6	16.67	83.33
7	28.57	71.43
8	37.50	62.50
9	44.45	55.55
10	51.14	48.86
11	100.00	0.00
12	0.00	100.00

Table 3. Validation Samples Used for the Biodiesel−Oil Mixture

	actual		predicted	
sample	soybean oil (wt %)	soy biodiesel (wt %)	soybean oil (wt %)	soy biodiesel (wt %)
1	28.57	71.43	32.2	67.80
2	42.86	57.14	42.40	57.60
3	57.14	42.86	59.70	40.30
4	71.43	28.57	75.10	24.90
5	85.71	14.29	89.50	10.50
6	100.00	0.00	100.00	0.00
7	0.00	100.00	0.00	101.00

The actual and predicted composition of the biodiesel in the biodiesel−oil mixture is depicted in Figure 3. It is evident from the Figure 3 that there is a very good match between the predicted value of biodiesel composition and the actual value. It appears that the model is under predicting the biodiesel composition by about an average of 2%, especially in the lower region of biodiesel composition. The RMSEP was found to be 0.1246. This is in the same range as reported by Soares et al.,[17] Trevisan et al.,[20] and Baptista et al.[22] The RMSEP was calculated using eq 1

$$\mathrm{RMSEP} = \sqrt{\frac{\Sigma(C_{\mathrm{actual}} - C_{\mathrm{predicted}})^2}{N}} \qquad (1)$$

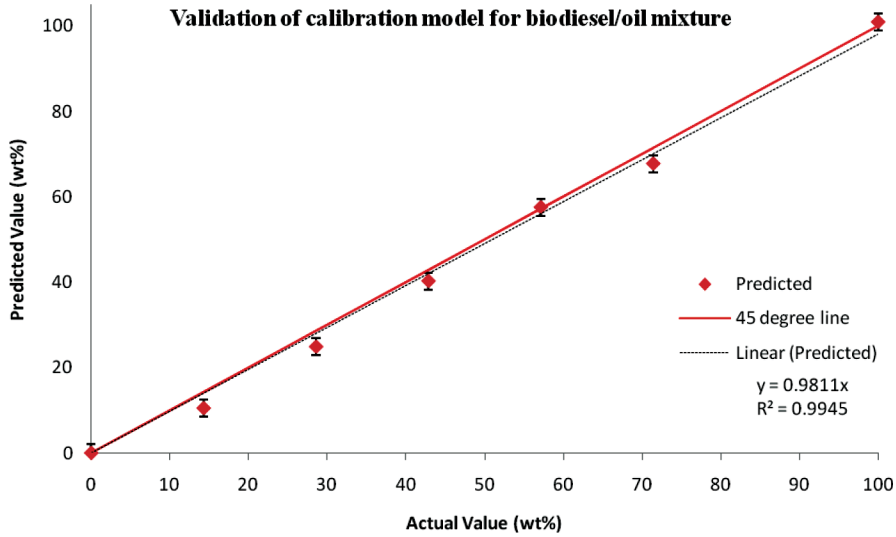

Figure 3. Predictive capability of multivariate calibration for the biodiesel−oil mixture.

where C_{actual} is the actual concentration of species, $C_{predicted}$ is the predicted concentration of species, and N is the total number of samples analyzed.

Thus, it can be noted that this is a very easy, simple, and fairly accurate method to find the biodiesel composition in biodiesel oil mixtures. This method can easily be applied to the monitoring of the transesterification reaction at the plant site. A QC or QA technician after some training should not have any problems in using this method for biodiesel quantification.

3.2. Method for Biodiesel Analysis in the Biodiesel−Petrodiesel Blend. A similar method to the one discussed in section 3.1 was developed to determine biodiesel concentrations in the blends. It is hoped that this will help authorities easily check the amount of blend level to ascertain the biodiesel composition required by law. Figure 1 shows the spectra of biodiesel and petrodiesel. As can be observed from Figure 1, there is a large difference in the peak arrangement of petrodiesel and biodiesel. There are regions, such as 1700−1800 cm^{-1} and the fingerprint region of biodiesel (1000−1300 cm^{-1}), which are not present in the petrodiesel spectrum. The chemical bonds because of which these regions of IR absorption appear are listed in Table 1 There are other regions, such as 2800−3000 cm^{-1}, that are present in biodiesel as well as petrodiesel. These regions are due to the absorption of IR by the CH olefinic bonds.

Multivariate Analysis. Because there were many differences in the biodiesel and petrodiesel spectra, only regions that also can be easily extended to the case where the presence of small amounts of oil cannot interfere with biodiesel analysis were selected. Hence, only the region 1427−1472 cm^{-1} was selected for biodiesel quantification in the blends. This was the region that was only present in the biodiesel spectra and was absent in both the petrodiesel spectra and the oil spectra. This region appears due to the absorption by $-CH_3$ asymmetric bending in methyl ester of soybean oil.[26] A total of 10 standard mixtures of the biodiesel−petrodiesel blend were used for calibration. These standard mixtures along with their compositions are shown in Table 4.

After the calibration model using the EFCM software was developed for blends, it was used to predict the composition of blends in terms of biodiesel weight percentage for validation samples. The biodiesel composition of the validation samples was different from the ones used for calibration. Nine samples of known composition were used for validation. Table 5 shows

Table 4. Standard Mixtures Used in the Multivariate Analysis of the Biodiesel−Petrodiesel Blend

sample	biodiesel in blend (wt %)	petrodiesel in blend (wt %)
B0	0.00	100.00
B2	2.00	98.00
B5	5.00	95.00
B10	10.00	90.00
B20	20.00	80.00
B35	35.00	65.00
B50	50.00	50.00
B65	65.00	35.00
B80	80.00	20.00
B100	100.00	0.00

Table 5. Validation Samples Used for Biodiesel−Petrodiesel Blend

	biodiesel in blend (wt %)		petrodiesel in blend (wt %)	
sample	actual	predicted	actual	predicted
B0	0.00	0.00	100.00	0.00
B3	3.00	4.00	97.00	96.00
B7	7.00	7.35	93.00	92.65
B25	25.00	24.94	75.00	75.06
B55	55.00	56.13	45.00	43.87
B70	70.00	69.96	30.00	30.04
B85	85.00	84.83	15.00	15.17
B95	95.00	94.54	5.00	5.46
B100	100.00	100.00	0.00	0.00

the composition of validation sample blends. It can be seen that the composition of the validation samples is different from that of standard samples used for calibration.

The actual and predicted compositions of the biodiesel in the blend are plotted in Figure 4. It can be observed from Figure 4 that the developed calibration model predicts the actual values very well, with the average error below 0.01%. The RMSEP value for this calibration model is 0.1194. This is in the same range as the values obtained by Pimentel et al.[28] and Oliveira et al.[29]

3.3. Method for Biodiesel Analysis in Biodiesel−Petrodiesel−Oil Blends (Blend Adulteration). As the use of biodiesel as a blending agent with petrodiesel increases, the chances of oil being added to the blend to reduce the overall cost of the fuel increases. This is because the cost of oil is much lower than that of biodiesel or petrodiesel. However, this has the harmful effect of valve plugging, ring sticking, injector fouling, particle agglomeration, engine deposits, or coke forma-

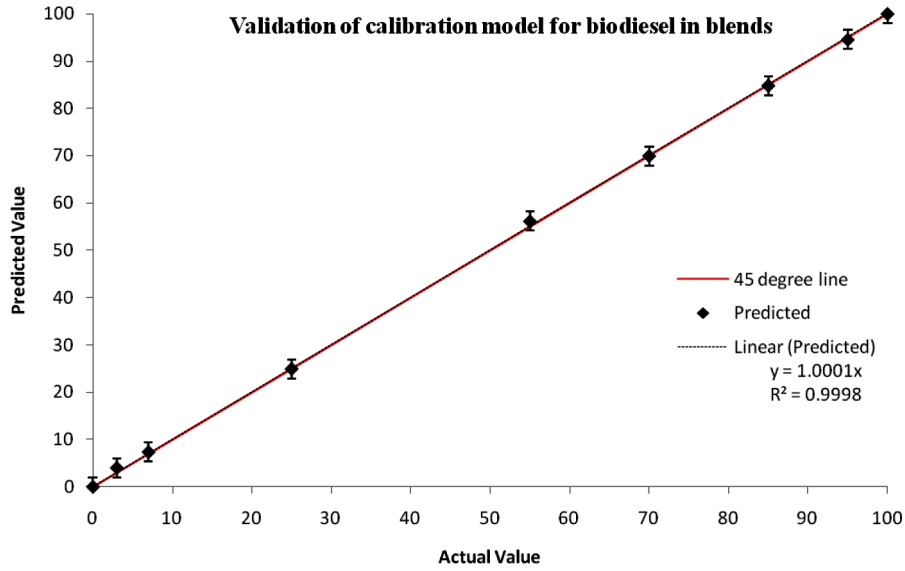

Figure 4. Predictive capability of multivariate calibration for the biodiesel−petrodiesel blend.

tion in the diesel engines, reducing its performance and deteriorating the diesel engine in the long run.[33,34] To stop this unscrupulous activity, authorities will need to find out the amount of adulteration in the blends. Also, there is a real chance of blending of a biodiesel that was taken from a production batch of incomplete conversion of oil into biodiesel. Hence, it is of utmost importance to detect the amount of oil present in the blend. Figure 1 shows the spectra of petrodiesel, biodiesel, and oil. As can be observed from Figure 1, it is very difficult to find a region of the spectra that is uncommon to all of the three spectra. It is to be expected that a region of the spectrum selected as characteristic of oil should not interfere with the spectra of biodiesel or petrodiesel. Also, the region should show changes in its peak height/area or position as the composition of oil varies. There are regions, such as 2800−3000 cm^{-1}, that are present in all of the spectra but are of no use for the quantification of oil in the presence of biodiesel or petrodiesel. There are regions, such as 1700−1800 and 1000−1300 cm^{-1}, that are not present in the spectrum of petrodiesel but are present in the spectrum of biodiesel. These regions cannot be considered as the peaks caused by biodiesel at these wavenumbers because they interfere with the peaks of oil. However, there is a narrow region in the spectra of the adultered blend (1070−1112 cm^{-1}) where there is the least interference from biodiesel or petrodiesel with that of the oil peaks. Hence, this region was considered for the quantification of oil in the presence of both biodiesel and petrodiesel.

Multivariate Analysis. The analysis process consists of determining the contents of oil in the blend and the biodiesel content in the adultered blend. Seven standard mixtures of known compositions in oil, biodiesel, and petrodiesel were prepared and used for the calibration data. The compositions of these standards are presented in Table 6. The region 1070−1112 cm^{-1} considered here for oil quantification in the presence of biodiesel and petrodiesel is normally assigned to −C−O stretching.[31] Figure 5 shows the variation in the spectra in this region as the amount of oil changes in the adultered blend.

Table 6. Standard Mixtures Used in the Multivariate Analysis of the Adultered Blend

sample	oil in adultered blend (wt %)	biodiesel in adultered blend (wt %)	petrodiesel in adultered blend (wt %)
B4	1.00	3.00	96.00
B8	3.00	5.00	92.00
B15	4.00	11.00	85.00
B20	10.00	10.00	80.00
B30	15.00	15.00	70.00
B45	25.00	20.00	55.00
B80	30.00	50.00	20.00

The calibration model developed using the EFCM software after feeding the spectrum, region, and concentration corresponding to each of these samples was then used to predict the composition of the validation samples. In all, 11 samples were used for validation of the calibration model for oil analysis in the adultered blend. The actual compositions of validation samples were all different from those used in standard samples, as presented in Table 7.

Figure 6 shows the predictive capability of the developed calibration model for oil in the adultered blend. As shown in Figure 6, the match between the actual oil content and the predicted oil content is not very good. This is especially true in the higher range of oil adulteration (greater than ∼20%). However, the model is very good for the prediction of oil content below 20% oil. There is some interference observed from biodiesel when the content of biodiesel is very high, especially above 50%. However, this does not limit the utility of the current method because the maximum biodiesel blend used and allowed today in the practical world is B20. An adulteration of more than 20% oil added to the petrodiesel/biodiesel blend would drastically change the physical properties of the blend, such as density, viscosity, and appearance, and be easily detectable. The calibration model gives a very good fit for oil detection in this region for oil concentrations below 20%. Hence, the present model is reasonable for the detection of adulteration of petrodiesel/biodiesel with oil. Thus, the use of FTIR is recommended in conjunction with other methods. The samples that appear to be suspicious can be sent for further detailed analysis using more accurate methods, such as GC−MS. However, for initial fast screening, the present method is adequate. The average error in the prediction of the oil content is about ∼1−2%. The model underpredicts the amount of oil in the lower region (<20% oil)

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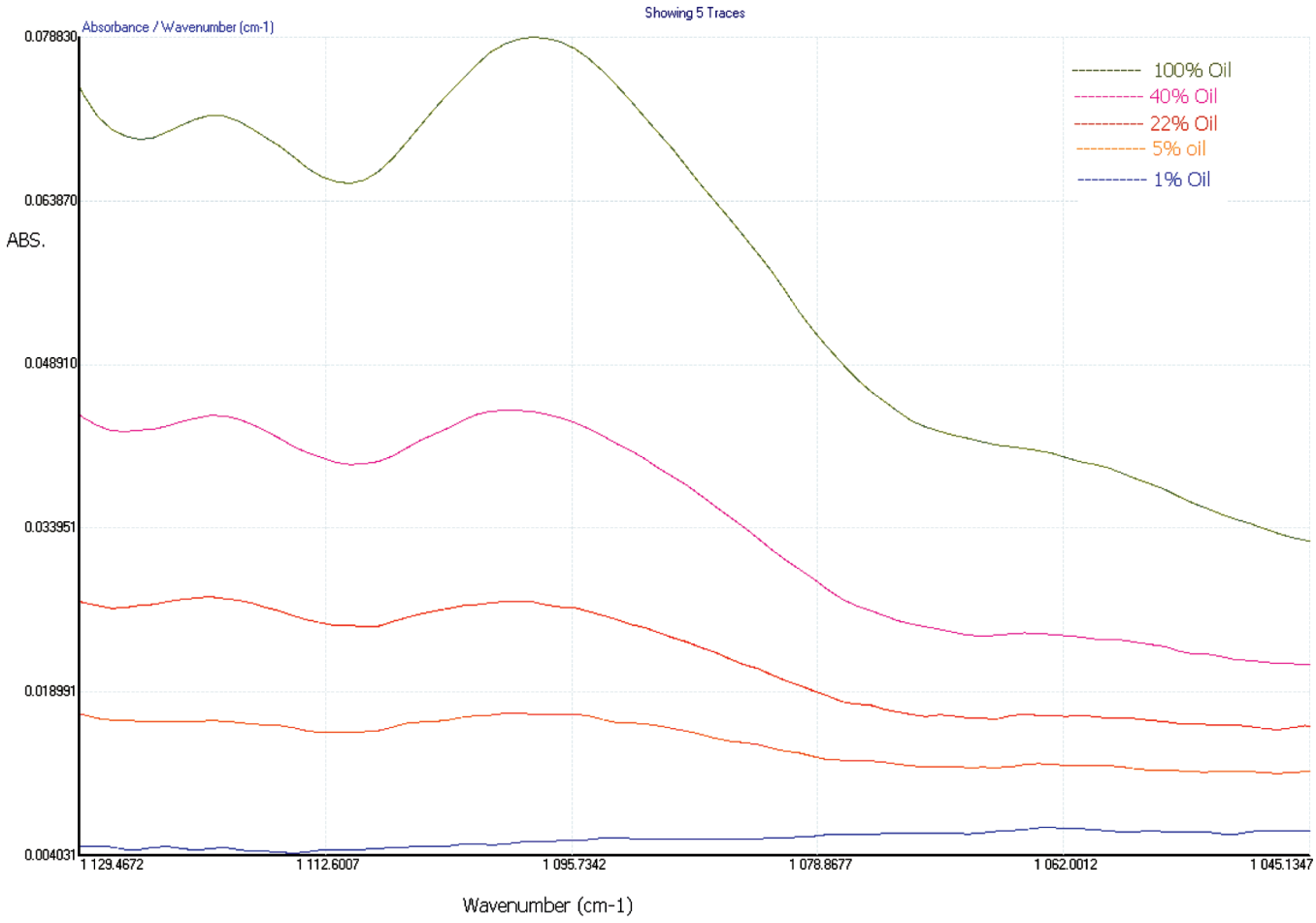

Figure 5. Variation in the peak for oil in the adultered blend.

Table 7. Validation Samples Used for the Biodiesel−Petrodiesel Adultered Blend

sample	biodiesel in adultered blend (wt %)	petrodiesel in adultered blend (wt %)	oil in adultered blend (wt %)		oil in biodiesel (wt %)
			actual	predicted	
B2	1.00	98.00	1.00	0.57	50.00
B5	3.00	95.00	2.00	1.50	40.00
B10	6.00	90.00	4.00	3.40	66.66
B17.65	11.85	82.35	5.80	5.89	35.86
B10	3.00	90.00	7.00	5.10	70.00
B25	13.00	75.00	12.00	11.90	48.00
B35	15.00	65.00	20.00	18.50	57.14
B37.5	25.00	62.5.00	12.50	14.67	33.33
B50	33.33	50.00	16.67	19.58	33.34
B90	50.00	10.00	40.00	37.70	44.44
B93.34	66.68	6.66	26.66	31.20	28.56

by about 2%, whereas it overpredicts the oil concentration by about 2% in the higher region (>20% oil). The RMSEP for this calibration model was 0.2. This might be due to the interference from biodiesel absorption at high concentrations in the region that was selected for oil calibration. The range of RMSEP obtained is similar to what Flavia et al.[23] have observed with FTNIR and FT-Raman using PLS and PCR calibration models.

It is also important to know the amount of biodiesel present in the blend after quantifying the amount of oil present in the adultered blend. The calibration model developed for biodiesel quantification in section 3.2 was used to measure the amount of biodiesel in the validation samples of adultered biodiesel. This was carried out for all of the samples used for calibration as well as validation for oil in the adultered blend. Thus, the biodiesel content of 18 samples was determined. Figure 7 shows the actual versus predicted amount of biodiesel in the adultered blend. It can be seen from Figure 7 that the model developed in section 3.2 is capable of predicting the biodiesel content in the adultered blend. It can also be observed that the model is overpredicting by an average of 7−8% compared to the actual amount of biodiesel. This may be because of the possible interference attributable to absorption from oil in the same region considered for biodiesel quantification. The accuracy of the present model can further be improved by increasing the number of standard samples used for developing the calibration model. The further improvement of the calibration model and its application to biodiesels from different sources is beyond the scope of the current study and is the subject of a future study.

Hence, this study demonstrates the easiness with which this method can be employed for the determination of oil

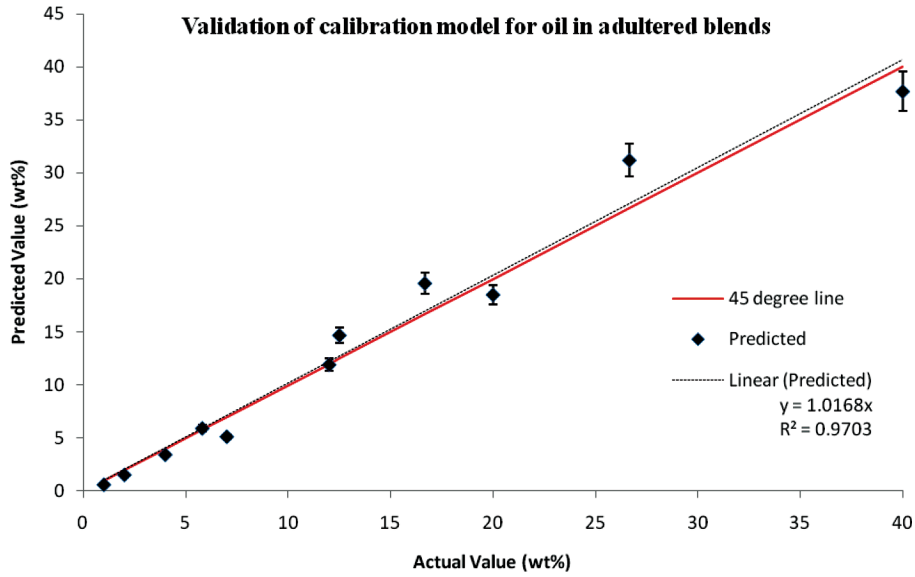

Figure 6. Predictive capability of multivariate calibration for oil in the adultered blend.

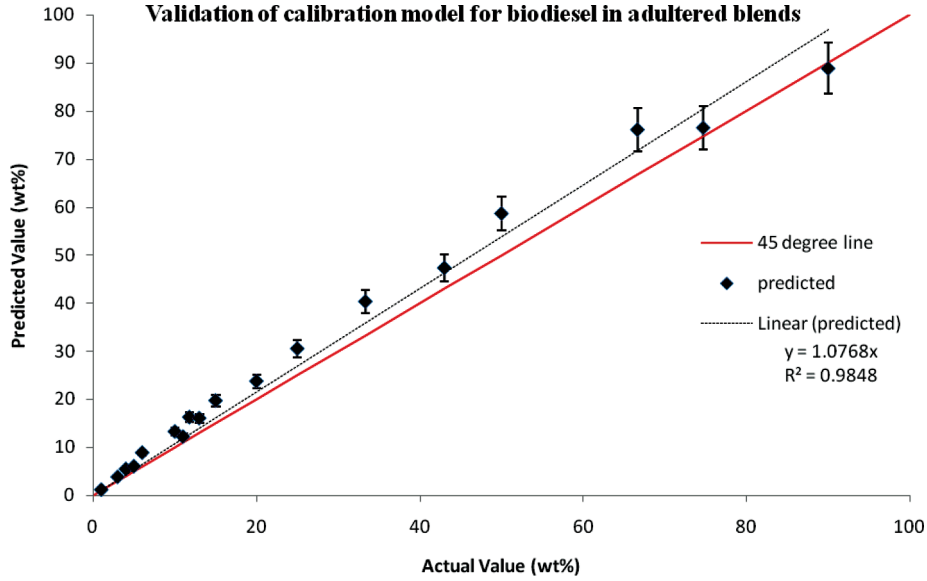

Figure 7. Predictive capability of multivariate calibration for biodiesel in the adultered blend.

and biodiesel in all sort of situations, such as monitoring of the transesterification reaction, blend determination, and adulteration by oil. However, the success of using this technique practically lies in identifying the specific regions to be selected while developing the calibration model. Because these regions have already been identified in this study, they can be used as determined. However, caution must be taken in extrapolating the results of this work and applying them to oils other than soybean oil and their corresponding methyl esters.

It must be noted that there is room for further refinement of this method, and improvements can be performed in the near future by considering different types of oils (i.e., oils from different sources) and different types of biodiesels and petrodiesels and their mixtures. Also, quantification of the interferences caused by the presence of biodiesel during analysis of oil and vice versa can be the subject of further studies on analysis of blend adulteration. This will ultimately help improve the accuracy of prediction of the calibration model for oil and biodiesel analysis in adultered blends over the whole range of 1−99%, which, in turn, will become a universal calibration model for prediction.

4. Conclusions

A simple, easy to operate, fairly accurate, fast, and cheap method has been developed for oil and biodiesel quantification using FTIR and commercial software. A nonlinear CLS-based algorithm is adequately used to develop a calibration model for biodiesel analysis using FTIR. The success of the method heavily depends upon the identification of non-interfering regions corresponding to individual species, such as oil, biodiesel, and petrodiesel. These regions have been identified and used successfully for analysis of oil and biodiesel. The method is also applicable to blends of biodiesel and petrodiesel. However, further adoption of this method to a blend of multiple biofuels and petrofuels requires careful evaluation. The procedure developed in this study has also been successfully used by our group in the analysis of

biodiesel synthesized via ultrasound-enhanced, base-catalyzed transesterification of soybean oil.[35]

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Supporting Information Available: Further details on the software algorithm. This material is available free of charge via the Internet at http://pubs.acs.org.

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