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doi:10.4028/www.scientific.net/AMR.576.357

Unconventional Method for Monitoring of Waste Cooking Oil Transesterification

Nabeel A. Adeyemi, AKM Mohiuddin[1,a], Mohamed Elwathig Saeed Mirghani, Ahmad Tariq Jameel

[1]International Islamic University Malaysia, Kuala Lumpur, Malaysia

[a]mohiuddin@.iium.edu.my

Keywords: Transesterification, photodiode, absorbance, Waste Cooking oil, FAME

Abstract. A technique to monitor transesterification of waste cooking oil (WCO) is presented. The technique was developed based on analogue signal from WCO, fatty acid methyl ester (FAME) and commercial palm oil (CPO). A low-pass filter design for the photodiode was used to obtain the characteristic analog signal generated by these oil samples and the signal was correlated to absorbance spectra of the oils using data from Fourier transform infrared (FTIR) equipment. A match was made between the analogue signals of the oil samples and calibrated against the FTIR spectra at 95% confidence level. Depletion of WCO during transesterification in a batch reactor correlated with the time observed for peak yield during biodiesel production. The results of the technique are discussed as a possible way to monitor transesterification process in a batch reactor.

Introduction

Biodiesel is an ester of fatty acid primarily produced by transesterification of vegetable oils and is regarded as a major fuel alternative [1]. The oil contains unsaponifiable matter (chlorophyll, phytosterols, and carotenoids) which is responsible for variation in color characteristic of each oil particularly in the visible spectrum [2]. Pure biodiesel vegetable oils are almost colorless in the visible range [3]. The oil exhibit varying absorption and transmittance level in the near infrared spectrum, making it possible to distinguish various oils and its derivative such as the biodiesel from the base raw material. Difference in levels of spectra using near-infrared (NIR) spectrometry between 1665 nm or 2083-2174 nm [4] have been used to distinguish blends of biodiesel based on the absorbance characteristics of the oil [5]. A commercial sensor has been reported using a differentiating frequency output of 51.84 and 52.62 Hz to differentiate between signal output of the biodiesel and blend [6]. Fourier transform mid-infrared (FT-IR) spectroscopy has also been successfully used for quantification of biodiesel [7]. Similarly, the Brazilian Association of Technical Standards (ABNT) uses infrared absorption of around 1746 cm^{-1} assigned to the molecular vibration of C=O ester bonds in biodiesel molecules to regulate diesel oil using FT-IR spectroscopy. This vibration was chosen for monitoring biodiesel because petroleum-derived diesel does not contain C=bonds in its structure.

The theoretical basis of this technique lies in using the Lambert–beer law, where the concentration evolution is statistically treated with time when pure spectra of substances are known. The pure spectrum of a substance can then be correlated to the recorded absorbance and concentration of the corresponding substance. This is obtained through a calibration matrix where the related absorbance at each wave number is regressed, resolving simultaneously these equations of the component concentration. With this approach, direct spectroscopic analysis is suited within the context of biodiesel production (in or on-line), without sample preparation and reagent consumption. Standard biodiesel monitoring technique requires sample extraction, storage, reaction quenching and immediate analysis [8]. However, the increase in biodiesel production at a smaller scale compared to the expensive intrusive methods used in the laboratory would require methods that are inexpensive.

Hence, the main objective of this work is to monitor biodiesel production during transesterification of WCO. The analogue signal generated from the photodiode sensor with low pass filter amplifier was used and simultaneously calibrated by the FTIR spectra. The reported result was based on a transesterification in stirred vessel using WCO.

Method

Sample Preparation Procedure. Samples of FAME, WCO and CPO, approximately 5 g each, were transferred to respective screw cap test tubes containing 9 mL of anhydrous 1-propanol (Sigma-Aldrich, St. Louis, MO, USA). The mixture was vortexed for 5 min prior to centrifugation at 8006g (IEC Centra-4B Centrifuge) for 1 min at room temperature to separate the solids. The supernatant was then analyzed by FTIR spectrophotometer (Nexus 670, Thermo Nicolet) combined with an attenuated total reflectance (ATR) accessory at different concentration. The absorption spectra of the FAME without any dilution or solvent were measured using a general purpose UV/VIS spectrophotometer (model DU 520, Beckman Coulter, Fullerton, Cal.) for visible absorption spectra from 380 to 530 nm. During the experiment, the spectrophotometer was purged with dry air in order to eliminate water vapor and the spectra were recorded at intervals of 1 nm.

FTIR Analysis. The scanning configuration for the FTIR was set at 64 scans for each sample, after scanning the background, which will automatically be subtracted from the samples spectra. At a range of 4000 cm^{-1} to 400 cm^{-1} the resolution was set at 2 cm^{-1}. WCO, FAME and commercial palm oil with known fatty acid concentration were scanned and the results analyzed using a version of FTIRessential® with a spectra library of organic compounds.

Photodiode Fabrication/Calibration. A photodiode sensor with a low-pass filter was designed as an analogue data sink and connected to a PC card (arduino Duemilanove) powered by a 5V DC power source. The PC card/ photodiode circuitry (Fig. 1) was connected to a personal computer and the signal from WCO was used as the base line signal. Subsequently, reading for FAME and CPO taken and normalized against that of the WCO. This step was repeated, this calibration was replicated to reduce distortion and eliminate errors.

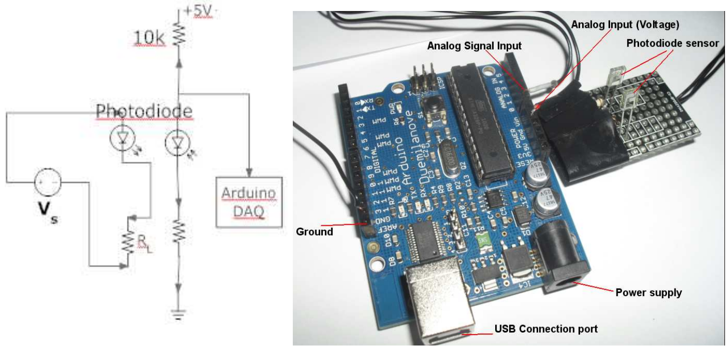

Fig. 1: Circuit diagram and Schematic of the acquisition board

The analogue signal generated was passed on as a calibration after differentiation of the spectra. Afterwards, the analog signal generated with time during WCO cooking oil transesterification was processed by a robust (quadratic) smoothing regression method using weighted linear least squares and a quadratic polynomial model for smoothing data [9] in MATLAB.

Result and Discussion

Esters give three strong infrared bands at 1700, 1200 and 1100 cm^{-1} due to C=O, symmetrical C-C/C-O bonds and symmetrical stretch of O-C/ C-O bonds and the distinctive infrared absorption around 1746 cm^{-1} in biodiesel spectra was used to characterize it. The regions of measurable differences going by the spectra are at (a) 1000 (b) 1500-1350 and (c) 1800 (d-e) 3000-2800 cm^{-1} shown in Fig. 2. The major peaks that represent triglyceride functional groups could be observed around (e) 2923 cm^{-1} (C–H stretching (asymmetry)), (d) 2853 cm^{-1} (C–H stretching (symmetry)), (c) 1741 cm^{-1} (C=O stretching), (b) 1436 cm^{-1} (C–H bending (scissoring)), (a) 1196 cm^{-1} (C–O stretching and C–H bending) [10]. Figure 2 shows the differentiated spectra of WCO, commercial oil and FAME

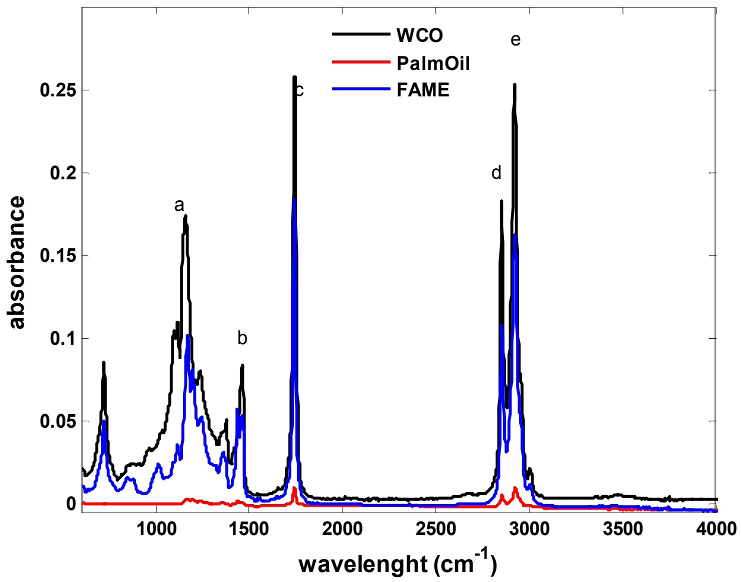

Fig. 2: FTIR absorption spectra of the FAME, WC0 and commercial palm oil

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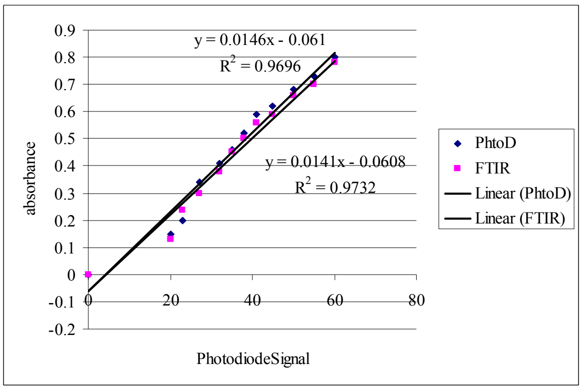

Fig. 3: FTIR absorption spectra of the FAME, WC0 and commercial palm oil

Fig. 3 shows the signal for the WCO from the photodiode plotted against the FTIR absorbance. A similar relationship was obtained for FAME and CPO (not shown). Although this did not represent any quantitative measurement, the difference in photodiode reading. The signal filtering using (i) moving average, (ii) Savitzky-Golay and (iii) lowess (linear fit) methods are shown in Fig. 4. Comparing goodness of fit for each method (Table 1), the loess method gave the best fit and was subsequently used to smooth the analogue signal of the photodiode sensor. Fig. 4 shows different differentiated photodiode signal for WCO, CPO and FAME using the loess method.

Table 1: Goodness of fit of filtering method

		SSE	R^2	Adjusted R^2	RMSE
i	Moving Average	0.008396	0.9675	0.9181	0.01961
ii	Savitzky-Golay	0.01218	0.9731	0.9322	0.02363
iii	lowess (linear fit)	0.001032	0.9963	0.9906	0.00687

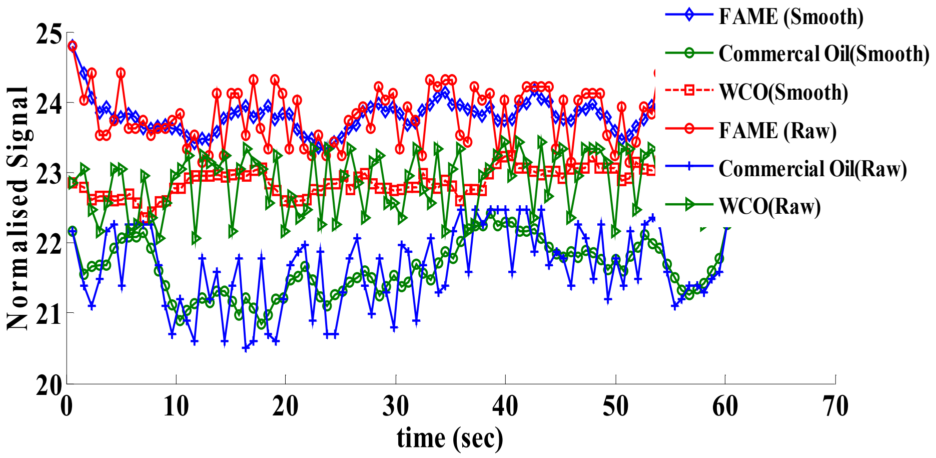

Fig. 4: Comparison of photodiode signal for commercial palm oil, waste cooking oil and FAME sample from WCO

The photodiode sensor monitoring of WCO transesterification in a 2-L reactor at impeller rotational speed of 600 rpm using a Rushton impeller is presented in Fig. 5. Depletion of WCO monitored during a 60 min. At about 30 min, no significant decline was observed in the output signal even as stirring continues. The peak yield time coincides with the lowest photodiode signal value at 30 min.

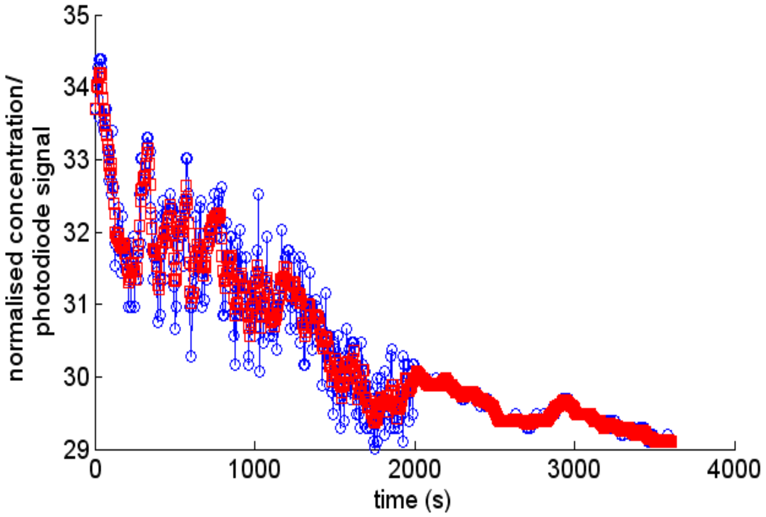

Fig. 5: Photodiode signal monitoring transesterification of WCO.

Conclusion

In this work, WCO transesterification has been monitored based on analogue signal from a photodiode which was calibrated by FTIR spectroscopy. The photodiode design could discriminate spectra of FAME, WCO and CPO. Reaction time of WCO transesterification was fairly presented by this method. Although the scale of production was limited to a 2-L reactor, this design could be developed for preliminary WCO transesterification monitoring at a larger scale.

Acknowledgment

The authors acknowledge the financial support provided by Kementerian Tenaga, Teknologi Hijau dan Air Malaysia under FRGS.

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