# Validation of A Miniaturized Near Infrared Spectrometer for Contaminant Assessment in Biodiesel

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***Abstract*** – The challenge to transition into a world of net-zero emissions has promoted the utilization of renewable fuels such as biodiesel. In terms of performance, it's very similar to fossil diesel, while emitting much less $CO_2$. However, biodiesel is very prone for contaminants, were the methods currently employed to detect them are time-consuming and wasteful. This work focused on the utilization of a prototype of a portable miniaturized near infrared (miniNIR) compact spectrometer in the range of 7692 – 4762 $cm^{-1}$ to determine the content of different contaminants in biodiesel, and its performance was compared that of a Fourier transform near-infrared (FTIR) benchtop spectrometer. The models based on principal component analysis-linear discriminant analysis (PCA-LDA) of FT-NIR spectra were generally good, predicting biodiesel contaminants with high accuracies (between 75 to 95%). The miniNIR prototype's PCA-LDA models also enabled the prediction of target contaminants with good accuracies (between 66 and 86%), with the advantageous of portability and low cost in relation to the benchtop equipment. These characteristics can strongly promote the further use of biodiesel.

***Keywords*** – biodiesel; portable NIR spectrometer; contaminants; adulteration; FTIR spectroscopy

## I. INTRODUCTION

The efforts being made to transition into a climate-neutral world have prompted the growing utilization of biofuels, like biodiesel, a biofuel made up of fatty acid alkyl esters, similar in performance to fossil diesel, but whose emissions are significantly lower than that of its fossil counterpart, thanks to the presence of oxygen in ester molecules. Biodiesel is often incorporated into fossil diesel to enhance its properties and reduce emissions [1-3].

Biodiesel is obtained from transesterification reactions between oils and alcohols, and crude biodiesel has to be washed and dried before being used to remove any contaminants, such as free fatty acids, soaps, and residual alcohol, as the presence of these compounds in the fuel hinder its performance [2]. When transesterification is incomplete, biodiesel is often adulterated with cheap vegetable oils, which aren't as volatile as biodiesel, thus causing problems in the combustion of the fuel and possibly damaging engines. Furthermore, diesel/biodiesel blends are prone to have a high raw fatty oil content, either because of incomplete transesterification or of adulteration with cheap vegetable oils to meet production quotas [4].

The need to ensure biodiesel is devoid of contaminants and its rampant adulteration, coupled with the rise in demand for biodiesel, have created a requisite for analytical techniques that can quickly, but effectively, detect contaminants in the fuel. Biodiesel is usually analyzed with liquid and gas chromatography, which are known to be accurate and effective, but have the down-side of being time-consuming, wasteful, and often operate off-line. However, infrared spectroscopy has been successfully used before to make biodiesel contaminant analysis, with a focus on the near infrared (NIR) part of the IR spectra, as this analysis is quick, accurate, and can be operated *in-situ* [5]. The latter of these aspects of the analysis can be further enhanced with the use of portable, miniaturized IR spectrometers, which have an ergonomic design and are easily and quickly operated and can reduce the time and cost of the analysis, thus successfully monitoring biodiesel content and boosting trust in its utilization. The aim of this work was to analyze the performance of a prototype of portable and miniaturized NIR (miniNIR) spectrometer in the detection and quantification of contaminants in biodiesel and compare it to the performance of a benchtop Fourier transform near infrared (FT-NIR) spectrometer.

## II. MATERIALS AND METHODS

Biodiesel blends with different concentrations of diverse contaminants were prepared, and are listed in Table 1. Two different types of used cooking oil, methanol, and glycerol, and there are two different blends with methanol and glycerol because the standard that controls biodiesel content only allows for 0.20%(w/w) of both these contaminants in biodiesel.

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TABLE I. Prepared blends of contaminated biodiesel and their concentration ranges

| Blends | Description | Contaminant concentration range |
|---|---|---|
| BC | Biodiesel with rapeseed oil | 0 – 50%(w/w) |
| BU | Biodiesel with used cooking oil (Type 1) | 0 – 50%(w/w) |
| BUA | Biodiesel with used cooking oil (Type 2) | 0 – 50%(w/w) |
| BM | Biodiesel with methanol | 0 – 50%(w/w) |
| BMM | Biodiesel with methanol | 0 – 0.625%(w/w) |
| BG | Biodiesel with glycerol | 0 – 50%(w/w) |
| BGA | Biodiesel with glycerol | 0 – 0.625%(w/w) |

The samples of the blends were analyzed with a benchtop FT-NIR spectrometer, using a NIR transflection fiber optic probe and operating in the 6800 – 4000 $cm^{-1}$ region of the spectrum, and with a prototype of a miniNIR spectrometer, which uses a LED matrix of 6 individual LEDs which cover the 1300 - 2100 nm region, and it’s based on an embedded Linux PC.

The obtained spectra were pre-processed with different methodologies, and a principal component analysis couples with linear discriminant analysis (PCA-LDA) was used to assess contaminant detection in the biodiesel.

## III. RESULTS AND DISCUSSION

The PCA-LDA analysis of FT-NIR and miniNIR data showed the best accuracies when the data was pre-processed with area normalization and baseline correction, respectively, as shown in Table 2. Although the miniNIR PCA-LDA models show lower accuracy values (between 67 and 86%) than the FT-NIR ones (between 75 and 95%), the predictive power of the miniNIR prototype can be considered reasonable, especially when taking into account the high diversity of contaminants evaluated.

TABLE II Accuracies of the best PCA-LDA analysis based on FT-NIR data pre-processed and miniNIR data

| Target blend | Accuracy based on FT-NIR analysis/% | Accuracy based on miniNIR analysis/% |
|---|---|---|
| All | 75 | 75 |
| BC + BU + BUA | 95 | 72 |
| BC | 84 | 86 |
| BU + BUA | 79 | 67 |
| BM + BMM | 91 | 57 |
| BG + BGA | 78 | 76 |

Compared to the benchtop FT-NIR spectrometer, the miniNIR prototype enables therefore, the prediction of contaminants in biodiesel, with the advantageous of potential portability and much lower costs.

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