APN1079

Measurement of tallow for renewable diesel pre-treatment

Key Words

- Renewable diesel pretreatment
- Phosphorus
- Nitrogen
- Free fatty acid (FFA)
- Real time monitoring
- Repeatability and reproducibility

Abstract

The IRmadillo process analyzer has been used to measure the concentrations of free fatty acids (FFA), nitrogen and phosphorus in samples of tallow taken from the pre-treatment stages of the renewable diesel production process.

Introduction

Around the world, there is a continual effort to move away from traditional fossil-fuel-based energy sources due to their effects on the environment. Biodiesel and renewable diesel are two common, and sustainable, alternatives. These chemicals are produced from triglycerides found in fats, oils and greases. One commonly-used feedstock is tallow, which is the rendered fat from cattle, sheep and similar animals.

The first stage in the process of producing renewable diesels is a series of pre-treatments to remove contaminants from the feedstocks. Contaminants such as metals, phosphorus and free fatty acids (FFA) can lead to fouling of equipment and even deactivation of catalyst beds in the later stages of the process.

Traditionally, the concentrations of these contaminants are measured by either titration or inductively coupled plasma mass spectroscopy (ICP-MS). These are often slow and require manual intervention, so it can be impractical to collect measurements with a high frequency. Continuous monitoring during the pre-treatment stages can improve understanding of the process and allow the process to be controlled to within tight specifications, minimising the risk of process problems downstream.

Here we present the use of a static-optics FTIR instrument, the IRmadillo, to calibrate for FFA, phosphorus and nitrogen in tallow. Although this work was carried out using lab sampling, the IRmadillo's robust static-optics design means that it is ideally suited for installation inline to provide continuous monitoring of the pre- or post-treatment feedstocks.

Experimental

Samples of tallow were analyzed on Keit's IRmadillo spectrometer. Spectra were acquired in triplicate, at a resolution of 16 cm^{-1} and with an acquisition time of 120 seconds. The samples were also analyzed by Keit's customer using their reference methods: ICP for phosphorus and nitrogen, titration for FFA. Models were developed using EVRI's SOLO chemometric modelling software.

Results and discussion

Figure 1 shows the correlation between the IRmadillo's measurements and the reference data for the three species. The grey dots show the data used to calibrate the model, and the red diamonds show the blind predictions of the validation set (one sample was not measured in triplicate, and this data point has been put into the validation set). The red line is the best fit to the data, and the green line is 1:1. Models have been evaluated using root mean squared errors of cross-validation (RMSECV, calculated using subsets of the calibration data) and root mean squared errors of prediction (RMSEP, calculated using the validation set). The RMSECVs are 2.78 ppm, 15.47 ppm and 0.45 wt.% for phosphorus, nitrogen and FFA respectively.

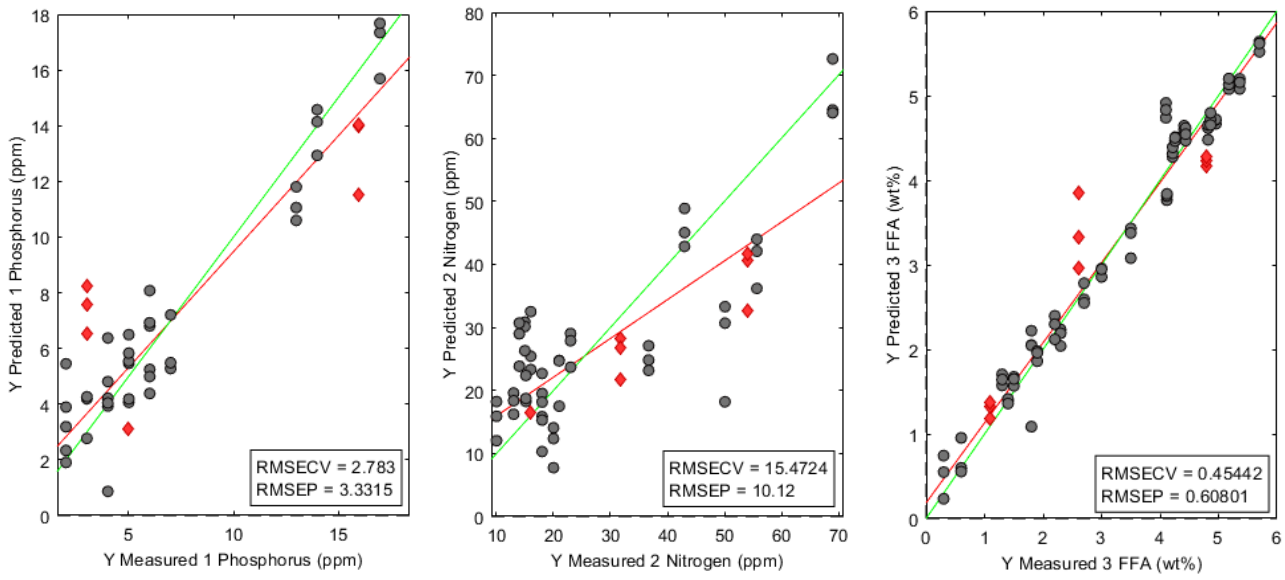

Figure 1: Plots showing the correlation between the IRmadillo's measurements and the reference data for phosphorus (left), nitrogen (centre) and FFA (right).

Image: Example of an inline installation of the IRmadillo in a green diesel plant

Reproducibility and Repeatability (R&R) testing was also carried out for FFA. Reproducibility here is the standard deviation of the residuals between the prediction and reference measurement for the validation samples, and was calculated to be 0.33 wt.% for FFA. Repeatability is the standard deviation of the predictions of a single sample measured continually. The spectra used to calculate repeatability were collected using two-minute averages, and a 30-minute rolling average was subsequently applied. Under these conditions, the repeatability was calculated to be 0.03 wt.%.

Conclusions

This work demonstrates that the IRmadillo can measure the concentrations of phosphorus, nitrogen and FFA in tallow, and demonstrates the reproducibility and repeatability of the measurements of FFA. This proof of concept shows that a robust and reliable static-optics FTIR instrument could be installed inline in a tallow feed line to continuously monitor the concentrations of these contaminants without the need for time-consuming offline sampling.

Chemical	Range	Accuracy
Phosphorus (ppm)	2 - 17	2.78
Nitrogen (ppm)	10 - 69	15.47
FFA (wt.%)	0 - 6	0.45

Table 1: Measurement accuracy of the IRmadillo for the species of interest

Chemical	Repeatability	Reproducibility
FFA (wt.%)	0.03	0.33

Table 2: Repeatability and reproducibility of the IRmadillo's predictions for free fatty acids

Although this work considers only one feedstock, the IRmadillo can monitor these and other species in a range of different feedstocks, from both animal and plant-based sources, including soybean, rapeseed and sunflower oils. We have even been able to provide a model that is completely agnostic to the type of oil present, allowing the customer to switch between feedstocks without needing to change the configuration of their IRmadillo.

Keep in Mind

The IRmadillo is an FTIR instrument, not an NIR instrument. There have been many attempts to use NIR instruments for inline process analysis and process control, but the fundamental physics behind NIR instruments means that it is not able to provide useful information in the renewable diesel and biodiesel industries. The IRmadillo, which operates in the mid-infrared spectral range, has more information available to it and so can be used to detect species that NIR instruments cannot.

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APN1079 (3 June 2024 11:52 am)