Biological and Agricultural Engineering

University of Idaho

Quarterly progress report –IV (Final)

Investigation of Biodiesel Quality Sensing Technologies

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Executive summary:

This report describes the results obtained from the project funded by Energy Division of Idaho Department of Water Resources (IDWR). The aim of this project was to explore the alternative ways of biodiesel quality sensors to develop a field sensor for key quality measurements. The goals of this project were aggressive and substantial progress was made in the development of quality sensors.

Accomplishments:

➢ Identified the wavelengths in ultraviolet (UV) range which can be used to detect the biodiesel blend level in a mixture of biodiesel and diesel. The technique uses a power transformation of measured values and was shown to be independent of biodiesel feedstock and diesel composition variations.

➢ A patent was applied and commercial partners were sought to fund the project for further developing the methodology into a working instrument.

➢ Visible spectrum was shown to be usable in detecting the type of biodiesel feedstock and blend level from a mixture of biodiesel and diesel using neural networks techniques.

➢ Use of potassium paramagnet, near infrared absorbance and water absorbance rate was investigated to measure glycerol content. Some results were promising and recommended for further development.

➢ Three technical publications were made, four technical presentations were given and a graduate student was trained.

Conclusions:

➢ Even though, visible range was unsuitable for detecting the relative composition of pure esters, it was possible to detect the blend level and type of biodiesel feedstock because of the natural pigmentation.

➢ An inexpensive biodiesel blend level detector can be constructed using ultraviolet light. A power transformation was needed to nullify the variation coming form varying amount of aromatics in diesel fuel.

➢ Potassium permanganate is not selective enough to react only with glycerol, and hence could not be used in concentrated form. Very faint reaction was detected at lower concentration. It is difficult to show that the temperature raise is coming from glycerol alone. However the technique has potential to be used to measure the oxidative stability.

➢ Water absorbance rate was highly proportional to the glycerol content and initial results shows that the technique can be perfected to accurately measure glycerol content in biodiesel.

➢ Near infrared absorbance was correlated with glycerol with the same batch of biodiesel but when different batch of biodiesel was used absorbance was different. Some kind of transformation technique on the absorbance pattern of glycerol has potential be used to get rid of the variability coming from biodiesel type.

Project Overview:

The University of Idaho has been involved with activities to further the production, utilization, and commercialization of biodiesel for over 30 years. Now that the biodiesel has economic conditions in favor to compete with diesel fuel, there has been an upsurge in biodiesel plant development. Diversified production of biodiesel from various feedstocks poses a challenge in quality assurance. To assist with the development of biodiesel production facilities, particularly in Idaho, the Energy Division of IDWR funded the research for the development of rapid-response quality sensing equipment which small producers, distributors and even consumers could afford. The expected deliverables of the project were:

1. Specifications for a biodiesel quality sensor based on visible light absorption technology.

2. A final report documenting all of the accomplishments of the project.

3. Publication of technical papers and presentations for outreach.

4. Trained grad students who will be prepared to enter bioenergy field.

Summary of the reports:

First quarter

Visible spectrum was investigated as a means to identify different components in biodiesel. In order to identify the contribution of each biodiesel component to overall absorption spectrum, spectra of eleven pure chemical standard components dissolved in 2-propanol – hexane (5:4, v/v). All of the components tested had clear absorption spectra below 350 nm. None of those components contributes to characteristic maximum of the biodiesel absorption spectra in a visible range.

Pure aliphatic acids, esters, and glycerides are colorless substances and did not exhibit absorption in the visible range. Natural fats and oils from plants and animals contain pigments exhibiting visible absorption. Therefore, a characteristic absorption of biodiesel in the visible range can be caused by pigments or other impurities. Different seeds used for biodiesel production have different pigments. For example, canola seed is known for high content of chlorophyll pigments. Part of those pigment constituents remains in biodiesel as impurity, which can be used as a factor for distinguishing between biodiesel from different oils (Fig. 2). The absorptions of vegetable oils in the visible regions are usually due to liposoluble pigments such as carotenoids and chlorophylls. The differences in visible range of spectra between biodiesel blends with the regular diesel were observed; therefore, it was concluded that visible range can not be used to detect glycerol but might be able to use for biodiesel blend detection.

Second quarter

Since pure mono alkyl esters and impurities such as glycerol were transparent in visible spectrum it was concluded that visible spectrum has a limited use in detecting the fatty acid composition or glycerin level. *Even though, visible range is unsuitable for detecting the relative composition of pure esters, it was possible to detect the blend level and type of biodiesel feedstock because of the natural pigmentation.*

The artificial neural networks were used to determine the amount of biodiesel in the samples based on the visible spectra. The network was able to predict biodiesel blend level with the correlation coefficient (R^2 =0.953). However, this method relies on the presence of coloring pigmentation the result may be somewhat unreliable if the biodiesel is bleached or pigmentation is removed by some other means.

In order to get more reliable information about the biodiesel blend and to make it independent of biodiesel feedstock and diesel used, the study was extended to use of ultraviolet light. Ultraviolet (UV) absorption spectroscopy proved to be a reliable and affordable technology for blend level detection based on the patters of the aromatic compounds absorbance. Blends of biodiesel form 6 different feedstocks and US #2 diesels from 5 different sources were tested for robustness of the method. Since the absorbance was too high to reliably measure for undiluted samples, the samples were diluted in n-heptane. It was found that the feedstock and alcohol use (methyl or ethyl alcohol) did not make a significant difference in absorbance of diluted biodiesel in 245 to 305 nm (UV range); whereas, absorbance from 254 to 281 nm were well correlated with the blend levels with $R^2 = 0.99$). Absorbencies at 265, 273 and 280 nm were used to calculate absorbance index which was found to be independent of diesel fuels used. Using three wavelengths allowed to capture the shape information of the absorbance curve and allowed to get rid of variation coming from aromatics content. The root mean square error in predicting blend level from this method was estimated to be 2.88%. The method worked well with biodiesel from different feedstock tested in this research and was independent of diesel fuel use.

Third quarter

In addition of blend level detection, we focused on detecting free and total glycerin level using a chemical component which reacts with glycerin. Potassium permanganate is a strong oxidizing agent with purple colored crystals. Potassium permanganate can oxidize –OH radical group from alcohol and in the process changes its color.

Use of potassium permanganate can be used as a coloring agent to determine the amount of free glycerin the fuel. This method has a potential to be a quick, reliable and low cost test for biodiesel quality testing as once the effective lighting source and wavelength are identified the process can be replicated using a digital camera and an image processing algorithm.

According to the reaction of glycerol and potassium permanganate the temperature should increase 16 °C. Temperature increase was not observed when glycerol diluted in water samples was investigated. This suggests that potassium permanganate is also oxidizing other components than glycerol in increasing the temperature?

With diluted potassium permanganate solution, even though increase in temperature was not prominent, but change of the color was noticeable. Change in color of the aqueous potassium permanganate in buffer K_2HPO_4 was observed when added to biodiesel. Reaction took place slowly and the change in color was visible after 30min. After 24 hours, brown precipitate was observed. Discoloration of the purple permanganate solution, accompanied by the formation of a brown precipitate of manganese dioxide suggests level of unsaturated fatty acids. The method has potential to be used to measure the oxidative stability which even though is not in current ASTM specification but is a very important parameter.

Fourth quarter (This quarter)

Glycerol being a polar solvent attracts water. Mono and di glyceride acts as a co-solvent for water and biodiesel. Biodiesel can also hold some water in itself but the presence of glycerol rapidly increases both rate and equilibrium of water held in biodiesel. In absences of methanol, the absorbed water causes turbidity in the fuel.

Turbidity of the samples was measured as absorption (optical density) at 600 nm (A_{600}) and correlated with amount of free glycerol in the sample. The results showed that it would be possible to estimate the amount of glycerol in the sample. Since time and force of mixing influenced the turbidity, the correlation was affected by the degree of mixing. We believe that once the procedure is standardized, this method can be used to detect the glycerol content of biodiesel.

Publications

The following publications and presentation were made as an outcome of this project:

Journal submission

A. Zawadzki, D. S. Shrestha, B. He. 2006. Biodiesel blend level detection using ultraviolet absorption spectra.. Submitted for Journal of Applied Engineering in Agriculture

Conference publications

Zawadzki, A., D. Shrestha, and B. He. 2005. Use of a spectrophotometer for biodiesel quality sensing. ASAE Paper No. 053133 St. Joseph, Mich.: ASAE.

Zawadzki, A. and D. Shrestha. 2006. Ultraviolet absorption spectra for biodiesel quality sensing. ASAE Paper No. 063043 St. Joseph, Mich.: ASAE.

Technical presentations

"Biodiesel quality" presentations at From Field to Fuel biodiesel workshop, Coeur d'Alene, ID, June 15, 2006.

Presentations at biodiesel workshop in Whitefish, MT sponsored by the State of Montana, "Biodiesel quality" June 13, 2006.

"An Introduction to Biodiesel," presentation to a Logger Education to Advance Professionalism (LEAP) meeting, CoeurdAlane, , ID, March 6, 2006.

"Biodiesel quality," presentation at Biodiesel Utilization Workshop, Boise, ID, Sept. 15-16, 2005.

Training

A graduate student "Artur Zawadzki" worked partially funded by this project and have learned much valuable insights into problems related to biodiesel quality sensing.

Recommendations

Based on the experience gained from this project, we recommend that the following tasks be addressed in a follow-up project:

1. Focus on low cost glycerol measurement using water absorbance rate of biodiesel.

2. Standardize the procedure for quantitative measurement.

3. Develop a sensor for everyday use.

Project Expenditure

Salaries	5404
Fringe benefits	256
Operating	2630
Overhead cost	1710
Total	10,000

Detailed fourth quarter report

Introduction

One of the last steps during batch production of biodiesel is heating the fuel after water washing. The aim of this step is to evaporate remaining alcohol and water and to clarify the fuel. From visual observations, the speed of clarification varies form one batch to another. Several factors may influence the clarification time including the content of glycerol and glycerides, stirring speed or temperature. Conversely, when biodiesel is mixed with water, the fuel becomes turbid and also the degree of turbidity and the time at which it increases and stays, varies for different biodiesel samples.

Fuel turbidity increase upon its mixing with water could be, at least partially, explained by the presence of glycerol and glycerides impurities in biodiesel. According to ASTM standard biodiesel should contain maximum of 0.02 wt. % of free glycerol and 0.24% of total glycerol. Glycerol is somewhat soluble in biodiesel and more soluble in water as glycerol attracts polar water molecules during mixing. Mono and di glycerides could position themselves on water-biodiesel interface when biodiesel is in contact with water, which makes biodiesel turn turbid.

The amount of glycerol and glycerides could influence the speed at which biodiesel absorbs water. He et al. (2006) in has shown that there were no significant differences in moisture absorption among the biodiesel of different origins at the given temperatures and that moisture absorption into biodiesel is a rapid process. However, these studies did not address the issue of water absorption by biodiesel with different glycerol content and water absorption was measured in days rather than minutes. Our study investigated the speed of water absorption by biodiesel in a period of minutes by measuring optical density of biodiesel at 600 nm and correlated with glycerol content.

Methodology

Three different batches of biodiesel were investigated: SME Air Energy, SME AEP and MME. Biodiesel samples were spiked with glycerol in order to investigate glycerol content in a range of 0.005 % to 0.03 %. The visible absorption spectra of biodiesel part of the samples were measured using Beckman 95 Coulter DU520 single beam general-purpose spectrophotometer (Fullerton, California). The absorption spectra in the range of 600-1100 nm at 1 nm interval of different biodiesel batches were scanned using standard 1-cm quartz cuvettes.

All measurements were performed at room temperature. One sample of biodiesel without any spiking was used as a control; another sample was mixed with ethanol only without any glycerol, to observe if alcohol used in spiking influenced the measured absorption values.

Free glycerol in biodiesel was determined according to test method D 6584 using gas chromatograph Agilent GC Chem Station 6890N with flame ionization detector (GC-FID). GC-FID was equipped with J&W Scientific 123-5711 DB-5HT column, 15m, 319µm, 0.10µm nominal, 400ºC. Chromatographic separations were achieved using an oven initial temperature of 50ºC and linear temperature gradient of 15ºC min^{-1} to 180ºC, 7ºC min^{-1} to 230ºC, and 30ºC min^{-1} to 380ºC. The samples for GC-FID analysis were derivatized with N-methyl-N-trimethylsilyltrifluoroacetamide (MSTFA) and mixed with 2 internal standards (1,2,4-butanetriol and 1,2,3-tridecanolylglycerol (tricaprin)) according to test method D 6584.

Results and discussion

Fig 1 shows preliminary results of absorption of biodiesel fraction during mixing with water. The graph suggests dependence of gradient and maximum value of absorption on glycerol content of the sample. Absorption increases in first part of mixing process to a maximum value followed by its decrease. The decrease of the biodiesel absorption could be explained by the decreasing amount of glycerol in the sample. Glycerol is more soluble in water (property utilized during biodiesel production at the washing stage) and is slowly partitioned to the water fraction of the mixed samples.

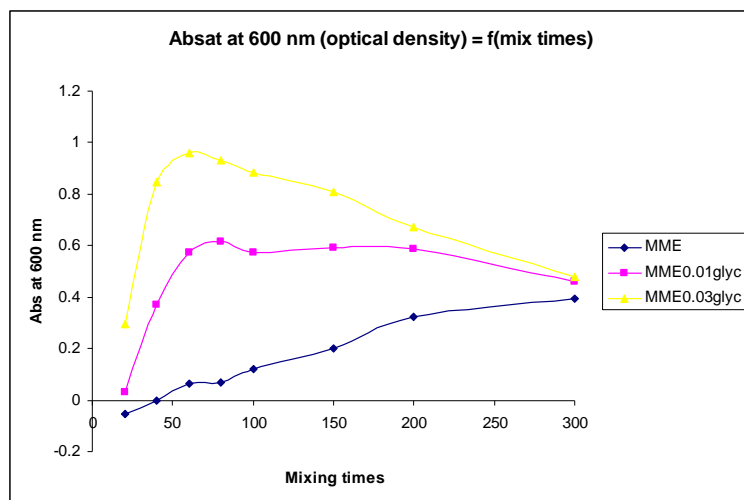**Absat at 600 nm (optical density) = f(mix times)**

Fig.1 Absorption of biodiesel as a function the time of biodiesel and water mixing.

Absorption of biodiesel mixed with water as a function of glycerol content measured by GC standard method is presented at Fig.2. Absorption decreases when the amount of glycerol in the sample is reduced by washing with water during mixing of the sample for 60, 100 and 200 times. Ethanol used for spiking the samples with glycerol had no influence on biodiesel absorption as no change in absorbance was observed for ethanol containing control samples as compared to the ethanol-free controls.

It was also observed that even without mixing the samples, an interface of water and glycerol-containing biodiesel was becoming hazy and the intensity of this haziness, based on visual examination, appeared to depend on glycerol content. In addition to measuring sample

absorption in visible range, near infrared absorption was investigated. Water absorption peak is observed in NIR region at around 977 nm. Biodiesel peaks were observed around 928 and 1038 nm. Differences between two biodiesel peaks as a function of number of times the biodiesel-water samples were mixed were in agreement with the increase in biodiesel absorption at 600nm. Both turbidities measured at 600 nm and infrared may be combined to get a better result. However, before doing that understanding the effect of other impurities such as soap content is necessary.
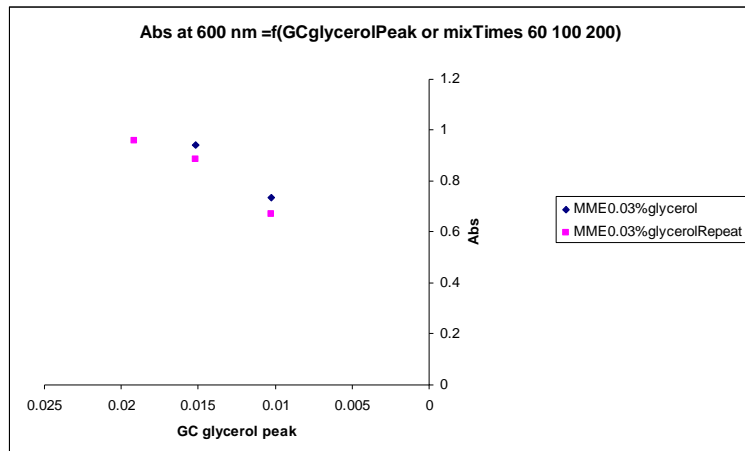

Fig. 2 Absorption of biodiesel as a function of the amount of glycerol content measured by GC.

Conclusion

Preliminary results show a good correlation of biodiesel absorption increase at 600 nm upon mixing with water with the amount of free glycerol in biodiesel samples. Time and force of mixing need to be kept constant to obtain results comparable between samples. Use of NIR also shows some promising result. More research is needed to evaluate the influence of other impurities and standardizing the test procedure.

Reference

He Brian, J. C. Thompson, D. W. Routt, J. H. Van Gerpen Moisture Distribution In Biodiesel And Its Fossil Diesel Blends, ASABE, Portland, Oregon, 9 - 12 July 2006

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