

FTIR On-line Monitoring of Biodiesel Transesterification

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Abstract

An *on-line* biodiesel transesterification monitoring method was developed using FTIR (Mid-IR) with a temperature controlled transmission cell. Several FTIR absorption bands (1198 cm^{-1} , 1363 cm^{-1} , 1377 cm^{-1} , 1436 cm^{-1} and 4430 cm^{-1}) were chosen to monitor the changes of the functional group in the canola-methanol transesterification process with base catalyst. The generated dynamic reaction curves through the monitored FTIR bands were used for reaction completeness and biodiesel conversion judgement, which were confirmed with GC. The transesterification process was evaluated on the canola to methanol molar ratio (1:6-1:12 mol/mol) and catalyst concentration (0.33%-1.67% ml/g, 50% NaOH volume to oil weight) with the developed method. Both the Beer's law and PLS calibration models were established to quantify the reaction components. The developed *on-line* FTIR method is easier and faster than other existed methods such as TLC or GC to monitor the transesterification reaction. It also is able to provide detailed dynamic information on the process, which can facilitate the accurate control on the process conditions for an improved product yield and consistency.

Introduction

Biodiesel is considered an environmentally friendly alternative to conventional diesel fuel, being biodegradable, renewable, with low emission characteristics. It is commonly produced from triglycerides (TG) obtained from vegetable or animal sources which are catalytically transesterified to produce fatty acid methyl esters (FAMEs) using excess methanol in the presence of a strong base such as sodium hydroxide or potassium hydroxide. The production of FAMEs by base catalysis is simple, rapid and reliable at relatively low temperatures and pressures, making it a reasonably economic commercial process. Other alcohols, such as ethanol can be substituted for methanol to produce biodiesel, yielding ethyl esters and glycerine instead of methyl ester and glycerine, however, methanol is preferred because it costs less and is easier to separate from glycerol (Bondioli 2004)(Gerpen 2005; Meher, Vidya Sagar et al. 2006).

A wide variety of sources of TG can be used for biodiesel production, including biomass (like algae), vegetable oils, animal fats and recycled grease. The fatty acid

composition of the feedstock strongly influences the properties of the biodiesel produced; including cetane number, cloud and pour points, oxidative stability, and viscosity (Knothe 2005; Divya BAJPAI and V.K. TYAGI 2006). The presence of free fatty acids (FFAs) and moisture in the feedstock are key variables affecting the efficiency of the biodiesel production process resulting in soap formation and incomplete conversion of TGs to FAMES as well as complicating subsequent biodiesel purification. For high FFA feedstock, direct acid catalyzed esterification can be used minimize FFAs and thus improve biodiesel yield. Other variables such as temperature, amount of catalyst, use of co-solvents and reaction time also affect the efficiency of the process (Gerpen 2005). At the conclusion of the transesterification process, biodiesel contains residual methanol, moisture, triglyceride and FFA or partly reacted by-products such as mono- and diglycerides which affect biodiesel quality. Basic quality standards exist for biodiesel to ensure for the satisfactory diesel engine operation under a variety of conditions. The two main bodies include the American Society for Testing and Materials (ASTM) 6751-02 in North America and EN 14214 in Europe, both describing detailed requirements in terms of biodiesel composition, physical properties and the relevant standard test methods associated with ensuring these are met.

The key analytical method for determining final biodiesel quality in both the ASTM and EN standards is Gas Chromatography (GC). This method is widely applied to determine various key contaminants such as mono-, di- and tri-glycerides and glycerol. The drawback of the GC method is that it is time consuming in terms of sample preparation and analysis, requiring the **derivatization of mono-, di-glycerides and glycerol to be analyzed**. Other methods to analyze biodiesel/monitor biodiesel production have also been reported, including HPLC (Holcapek, Jandera et al. 1999; Karel Komers 2001; Türkan and Kalay 2006), Gel permeation Chromatography (GPC) (Dubé, Zheng et al. 2004), size-exclusion chromatography (Arzamendi, Arguiñarena et al. 2006), NMR (Gelbard) and Near-IR FTIR spectroscopy (Zagonel, Peralta-Zamora et al. 2004; Knothe 2006) and viscosity analysis (Ellis, Guan et al. 2008). Among these methods, FTIR spectroscopy has excellent potential in terms of providing qualitative and quantitative data for lubricants and fuels, including biodiesel, without extensive sample preparation. From a qualitative and quantitative standpoint, mid-FTIR spectroscopy has seen extensive development and application in relation to “condition monitoring” of lubricants, a procedure which has evolved into an ASTM practice (ASTM E2412-04). It has also been developed extensively as a quantitative analytical procedure for assessing edible oil quality (van de Voort F 1996; Ma K 1997) parameters as well as determining acidity and moisture in lubricants and fuels (van de Voort et al, 2005, 2006). These mid-IR methods tend to be based on straight-forward Beer’s Law relationships without having to resort to more advanced and less intuitive chemometric procedures such as partial least squares (PLS) regression. Near IR in contrast has an advantage in terms of sample handling, but relies on more advanced chemometrics to devise calibrations, which require representative samples. Both have been used successfully for the determination of the methyl ester contents of diesel/biodiesel blends (Oliveira, Montalvão et al. 2006), with NIR spectroscopy having been proposed as a means to monitor the transesterification reaction using a coupled fibre optic probe (Knothe 1999). Here quantification was based on the differences of NIR spectra of methyl esters and TAG at 6005 and 4440 cm^{-1} ,

where methyl ester has peak but TAG only display shoulders. In the mid-IR spectral region, the conversion of TGs to FAMES involves the loss of the glycerol moiety, resulting in a decrease in peak height at 1378 cm^{-1} . The peak at 1378 cm^{-1} , which is attributed to the terminal CH_3 groups in TG, DG, MG, FFA, and FAME and to the OCH_2 groups in the glycerol moiety of TG, DG, and MG, has been monitored with FTIR-ATR (attenuate total reflectance) during biodiesel process (Dubé, Zheng et al. 2004). The results of FTIR-ATR have been correlated to Gel Permeation Chromatography data and the two methods were considered equivalent.

The limitation associated with the established chromatographic methods as well as the IR methods is that they all provide compositional information only well after the fact rather than real time data. It would be useful to have a means of monitoring the biodiesel transesterification process in real time as well as provide final compositional data. (Manolito E. Bambase, 2007 #19) FTIR spectroscopy has the potential to provide a direct, rapid and non-destructive means to do this and to facilitate a more detailed study of the transesterification process and hence its optimization. This paper presents the development and performance of a mid-FTIR system capable of real time, on-line analysis of the biodiesel process and its end product quality.

Materials and Procedures

Materials

The biodiesel feedstocks used in this study consisted of canola oil (Brenntag, Rexdale, ON, Canada) and rendered animal fats (Rothsay Inc., Ste. Catherine, QC, Canada.). Reagent grade methanol, ACS grade sodium hydroxide (NaOH) and concentrated sulphuric acid (98%) were obtained from Fisher Scientific, Canada. Mono-, di- and triglyceride standards were obtained from Sigma-Aldrich, Bellefonte, PA, USA and ethyl ester standards were purchased from Nu-Chek Prep (Elysian, MN, USA).

FTIR Instrumentation and Software

The instrument used in this study (Figure 1) was a modified Continuous Fuel Dilution Analyzer (CFDA), a custom engineered FTIR system manufactured by Thermal-Lube Inc. (Montreal, Canada). This system was originally designed for real time analysis of crankcase oil fuel dilution caused by biodiesel formulations in test-bed engines (<http://www.thermal-lube.com/english/analytical/cfda.html>).



Figure 1. the CFDA system used on real-time monitoring of transesterification process.

This system was composed of an ABB-Bomem FTIR spectrometer equipped with a temperature controlled CaF₂ transmission cell mounted on a movable stage as well as UMPIRE IA (Universal Method Platform for Infra Red Evaluation Interval Analysis) software. The latter allows the instrument to be controlled in terms of cell temperature, cell stage movement, carries out spectral data processing and presents graphical outputs of the changes occurring over time. All spectra were collected at a resolution of 4 cm⁻¹ by co-addition of 8 scans ratioed against an open-beam air background. Two cells were used, having path lengths of 40µm or 200µm, respectively, linked via a recirculating loop using a micro-pump to transport the sample continuously from the reaction vessel through the cell and back. Figure 2a and b presents photo and overall flow schematic diagram of the plumbing of the system respectively.

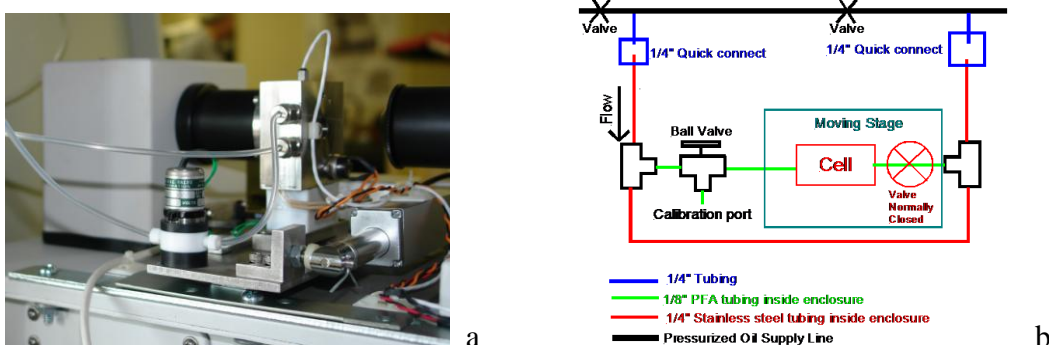


Figure 2. a). the movable stage with temperature controlled transmission cell of the CFDA system; b). an overall flow schematic diagram of the plumbing of the CFDA system.

Biodiesel Production and Monitoring

Canola oil or tallow was mixed with methanol in a mole ratio from 1:6 to 1:12 in an Erlenmeyer reactor mounted with a reflux condenser. The mixture was stirred with a magnetic stir bar, heated and maintained at 65 ±2 °C. A micropump transported the sample through the tubing loop system and by-pass the transmission cell in a constant flowrate of 1-2 ml/min (Figure 2). For canola feedstock, which contained no appreciable FFAs, 0.2-1.0 ml 50% aqueous NaOH was added to the oil/methanol mixture. For tallow feedstock, which was high in FFA, it was first reacted with methanol in the presence of 0.3ml sulphuric acid to transform FFA into FAMES first, and then followed by the base catalysis. Process monitoring was always started prior to any addition of reagents to obtain a baseline with sample spectra collected every minute.

Results and Discussion

Biodiesel production by transesterification of triacylglycerols should proceed quickly if the feedstock has low moisture and FFA content, but can be problematic if these optimal conditions are not met. Canola oil represents a more or less ideal feedstock for biodiesel production, clean neat oil. Tallow on the other hand is a more realistic feedstock, dirty, containing particulates, moisture and FFA. These two systems are likely to behave quite

differently and variability in the feedstock will may change the process substantially. The challenge here is to monitor the process in real time, on-line. FTIR spectroscopy provides a tool by which one can follow spectral changes resulting from the reaction; however this is usually done at-line, e.g. taking the sample from the reactor and making the measurement. In the CFDA system, this process is facilitated by its unique mobile stage which houses the transmission cell. A mobile stage is required so that fresh backgrounds can be taken between samples so that water vapour and instrumental drift will be ratioed out continually, providing quality data. The other aspect is the temperature controlled cell which provides a stable temperature for spectral measurements and which can be set to match that of the process (65 °C). Mid-FTIR spectroscopy provides access to many of the key functional groups which are affected by reaction, the loss and the formation of ester linkages, production and loss of OH, etc. With the product changing these functional groups undergo well marked changes and can be used to monitor the process. The key challenge is to balance and optimize the pathlength to provide access to these signals on scale (short path lengths) as well as have sufficient pathlength to allow the product to readily flow and present the instrument with a representative sample. If this balance can be achieved, then using an FTIR transmission cell to collect the information of the reactants and products from the transesterification process can provide a rapid and convenient means to monitor process on-line and determinate the endpoint of the reaction.

The FTIR spectra of TG and FAME can be distinguished in MID-IR and NIR regions. Figure 3a and 3b illustrate the IR spectra of canola oil and its corresponding methyl esters in these regions respectively. FAME of canola oil has several absorption features which can be used to differentiate it from canola oil. In mid-IR region, FAME has several characteristic peaks at 1198 cm^{-1} , 1363 cm^{-1} and 1436 cm^{-1} . When the amount of FAME increases, these peaks increase correspondently. The peak at 1198 cm^{-1} is assigned to O-CH₃ initial methyl group stretch. The peak at 1436 cm^{-1} is considered to be the -CH₃ asymmetric bending vibrations (Siatis *et al*). At 1100 cm^{-1} (attributed to the C-CH₂-O vibration) and 1377 cm^{-1} , the absorbance of FAME decreases with the increase of FAME amount. In NIR region, FAME and canola oil have a similar infrared spectra except at 4430 cm^{-1} , where FAME has a peak, but canola oil display a shoulder at this place. Therefore, the monitoring of canola oil transesterification process could be established by utilised the changes of these peaks. Another distinguishing signal at 6005 cm^{-1} was also reported (Knothe 1999).

In the study, the sample spectra were directly collected by UMPIRE IA software from the mixture of canola oil and methanol at the beginning of the reaction through a 45 μm transmission cell in every minute with a reaction temperature at 65 °C. After a few collection of spectra, the base catalyst NaOH was added into the mixture to initiate the transesterification reaction. The spectra were collected directly without the separation of reactant and product components and the monitoring stopped till the magnitude of the monitored peaks reach plateau without further change. The transmission cell was heated at 65 °C through out the spectra collection. Figure 3c and 3d show the infrared spectra in both 1100-1500 cm^{-1} region and 4200-4500 cm^{-1} region during a canola transesterification process with NaOH catalyst.

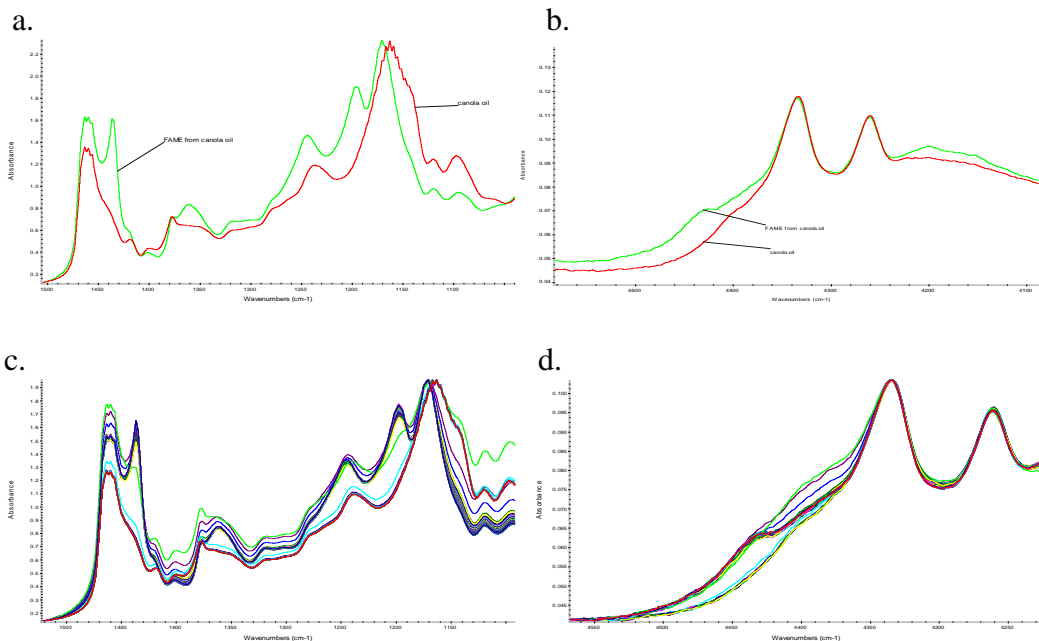


Figure 3. Comparison of spectra of canola oil and the corresponding FAME in a) Mid-IR region; b) NIR region; c) Mid-IR monitoring canola oil converted to FAME; d) NIR monitoring canola oil converted to FAME

The transesterification process of vegetable oil or animal fat to its corresponding FAME can be illustrated in reaction curves by monitoring the changes of certain peaks along the reaction time (corresponding to changes of certain functional groups) by using FTIR during the reaction. Figure 4 demonstrated several reaction curves of a canola oil transesterification process by monitoring the transmission IR spectra at 1363 cm^{-1} , 1377 cm^{-1} , 1436 cm^{-1} and 1198 cm^{-1} along the reaction time. All these plots (peak area) demonstrated to be sigmoid-shaped curves with peaks at 1198 cm^{-1} , 1363 cm^{-1} and 1436 cm^{-1} increased with FAME produced, while the peak at 1377 cm^{-1} decreased with the increasing of FAME amount. These dynamic reaction curves reveal that the methyl transesterification reaction is fast with the addition of base catalyst at the beginning and a steep curve is formed in the reaction curve when most amount of canola oil is converted into FAME. Afterward, the reaction slows down and a flat plateau on the curve is formed, at which an excess amount of methanol gradually drives the reaction to the endpoint when the reaction reaches equilibrium. All these reaction curves can be utilized to monitor the reaction course and judge the endpoint of the transesterification process. The peak at 1198 cm^{-1} demonstrated the strongest signal change with a big increase after the addition of base catalyst. Among these peaks, only the peak at 1198 cm^{-1} which based on the vibration signal of O-CH_3 has a simple quantitative character with a linear calibration by directly applying Beer's Law, at which both methanol and glycerol have very little change in their absorbance and canola oil display a shoulder. A linear calibration of FAME with variable methanol amount was developed and confirmed with standard

samples with peak 1198 cm^{-1} (Figure 5). At other places, methanol and glycerol interfere the quantitative analysis of FAME.

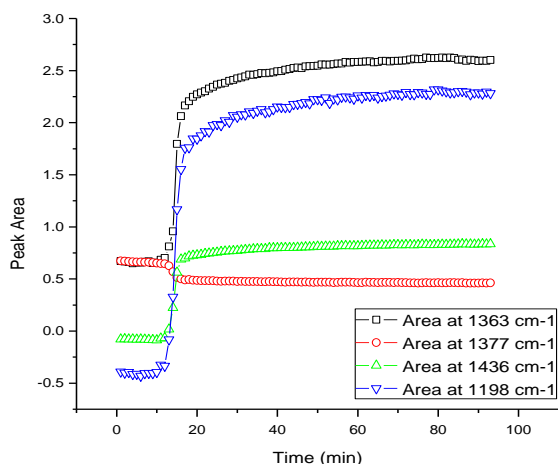


Figure 4. The reaction curves of canola oil transesterification process monitoring four Mid-IR peaks.

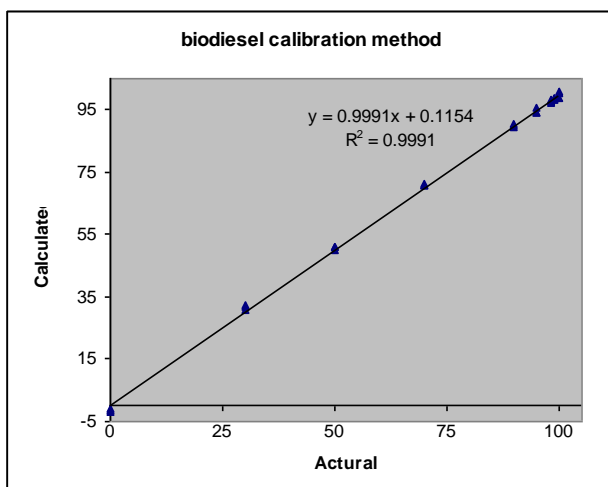


Figure 5. Plots of estimated (calculated) vs. specified value (Actual) of the simple beer's law method in quantitating biodiesel.

With the aid of the on-line dynamic monitoring of the biodiesel transesterification process, the variances impacting canola oil transesterification reaction such as reactant ratio of canola oil to methanol and amount of catalyst in canola transesterification process were investigated. Methanol amount, from 20% to 35% (g/g) in 60 gram canola oil respectively, with a constant catalyst amount 0.6 ml (50% NaOH), were evaluated and their corresponding reaction curves at 1436 cm^{-1} are illustrated in Figure 6. These reaction curves demonstrated that more methanol results in a higher plateau in the reaction curve, which means that increasing methanol facilitates the biodiesel yield. From

30% to 35% of methanol increase, the reaction system has no significant increase on biodiesel yield as from 25% to 30% and 20% to 25%.

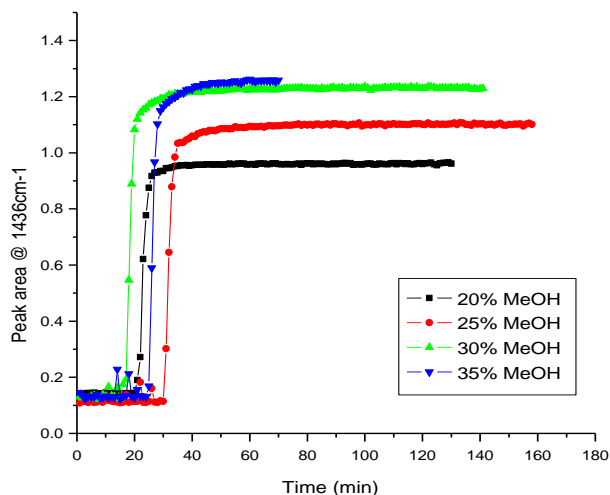


Figure 6. Reaction curves of canola transesterification at 1436 cm^{-1} with various methanol concentrations in 60g canola oil at $65\text{ }^{\circ}\text{C}$.

The catalyst amount in the transesterification process does not affect biodiesel yield but impacts the time of the reaction to the equilibrium. The reaction curves of canola transesterification process with various catalyst amount (50% NaOH) from 0.2 ml to 1.0 ml in 60 gram of canola oil with constant methanol to canola ratio at $65\text{ }^{\circ}\text{C}$ are illustrated in Figure 7. Even though the transesterification reactions at the tested conditions were generally fast processes, 0.6 ml or more catalyst in the system resulted more sharp and rapid turns to the plateau (reaction equilibrium) in the reaction after catalyst addition. While with 0.2 ml and 0.4 ml catalyst in the system, the processes took much longer time to reach the similar plateau level (reaction equilibrium, longer time not shown in the process monitoring).

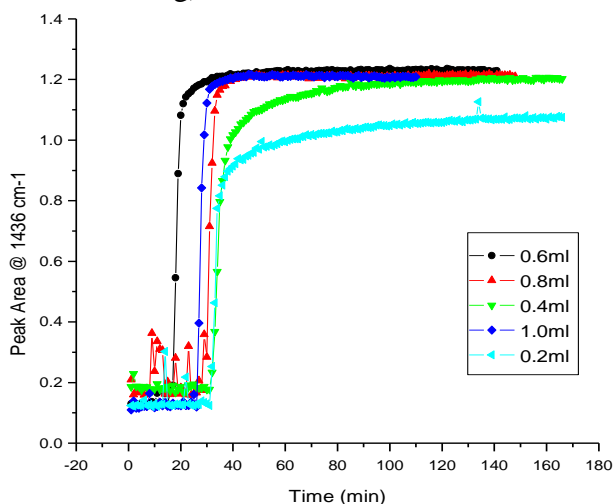


Figure 7. Reaction curves of canola transesterification at 1436 cm^{-1} with various amount of catalyst (50% NaOH) addition with a 60g canola oil and 18g methanol at $65\text{ }^{\circ}\text{C}$.

A partial least square (PLS) calibration model using TQ analyst (Thermo Electron Corp.) was established for quantification of FAME, canola oil, methanol and glycerol using $1060\text{-}1135$, $1180\text{-}1455$, $3100\text{-}3700\text{ cm}^{-1}$ Mid-IR regions and $4220\text{-}4500\text{ cm}^{-1}$ NIR region. The calibration used 3 factors for each component calculation except glycerol with 5 factors. The correlations between actual values and predict values for FAME, canola, methanol and glycerol are shown in Figure 8.

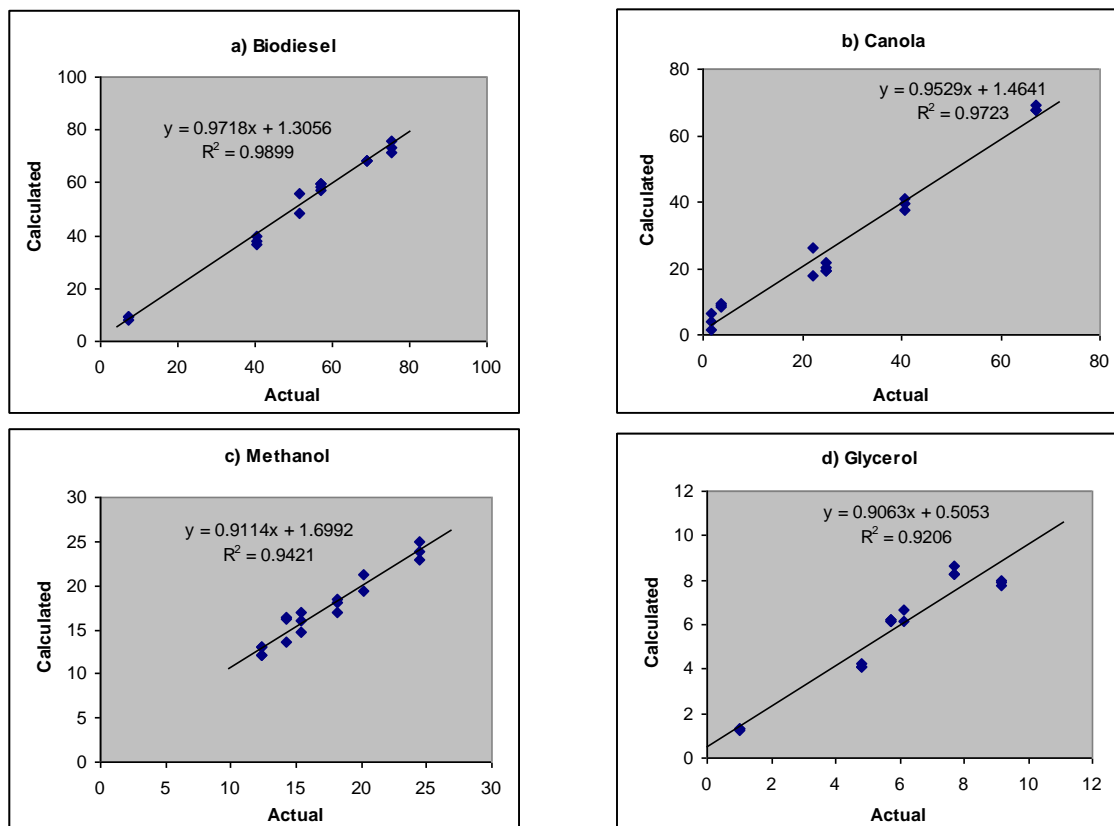


Figure 8. Plots of estimated (calculated) vs. specified value (Actual) of the PLS method in quantitating a) biodiesel, b) Canola oil; c) Methanol; and d) Glycerol.

These calibrations demonstrate good correlations in the analysis of FAME, canola oil, methanol and glycerol without taking account of the intermediates such as mono- and di-glycerides. Given that methanol has a limited miscibility in canola oil and glycerol does not miscible with biodiesel during the reaction, the quantifications of these components in the reaction based on these PLS calibrations are still a rough quantitative method. It should be noted that the quantification based on FTIR method can not distinguish the intermediate residues of mono- and di-glycerides from FAME in the process. Nevertheless, the calibrations are good enough for the purpose of monitoring the course of the biodiesel process and making the judgement of the endpoint of the

transesterification reaction. Furthermore, a GC analysis of the final biodiesel eventually confirmed the reaction endpoint based on the FTIR analysis. Under the optimized conditions of transesterification process (about the 90 min reaction), the plateau in the reaction curve represents more than 98% of canola oil converted to its FAME and no mono- and di- glycerides were detected in GC analysis at this reaction endpoint. The established reaction curves based on the FTIR transmission cell analysis can be confidently applied to the biodiesel production monitoring and reaction endpoint determination.

A FTIR monitored transesterification process with 200 μm CaF_2 cell was investigated as well based on above described methodology. With the increased pathlength, most signals of FAME in Mid-IR region are saturated and the only quantification region used for FAME analysis was at 4430 cm^{-1} , where biodiesel shows a peak but canola oil displays a shoulder. The signals at NIR IR region are less sensitive compared with those utilized in mid-IR region. However, a bigger pathlength cell has the advantage of the increased movability of the analyzed sample in tubing system. Most importantly, it intensively reduces the risk of cell clogging caused by more complicated feedstocks such as animal fats, which extends the potential of FTIR biodiesel monitoring to most industrial applications.

Conclusion

FTIR with a transmission cell provided a rapid and easy way to monitor the biodiesel process in real-time. The collected spectra of the transesterification reaction, confirmed with GC analysis, provided solid information on the determination of the reaction endpoint when monitoring the biodiesel production dynamically.

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References

Arzamendi, G., E. Arguiñarena, et al. (2006). "Monitoring of biodiesel production: Simultaneous analysis of the transesterification products using size-exclusion chromatography." Chemical Engineering Journal **122**(1-2): 31-40.

Bondioli, P. (2004). "The Preparation of Fatty Acid Esters by Means of Catalytic Reactions." Topics in Catalysis **27**(1): 77-82.

Divya BAJPAI and V.K. TYAGI (2006). "Biodiesel: Source, Production, Composition, Properties and Its Benefits." J. Oleo Sci. **55**: 487-502

Dubé, M., S. Zheng, et al. (2004). "A comparison of attenuated total reflectance-FTIR spectroscopy and GPC for monitoring biodiesel production." Journal of the American Oil Chemists' Society **81**(6): 599-603.

Ellis, N., F. Guan, et al. (2008). "Monitoring biodiesel production (transesterification) using in situ viscometer." Chemical Engineering Journal **138**(1-3): 200-206.

Gerpen, J. V. (2005). "Biodiesel processing and production." Fuel Processing Technology **86**(10): 1097-1107.

Holcapek, M., P. Jandera, et al. (1999). "Analytical monitoring of the production of biodiesel by high-performance liquid chromatography with various detection methods." Journal of Chromatography A **858**(1): 13-31.

Karel Komers, R. S. J. M. F. S. (2001). "Biodiesel from rapeseed oil, methanol and KOH. 3. Analysis of composition of actual reaction mixture." European Journal of Lipid Science and Technology **103**(6): 363-371.

Knothe, G. (1999). "Rapid monitoring of transesterification and assessing biodiesel fuel quality by near-infrared spectroscopy using a fiber-optic probe." Journal of the American Oil Chemists' Society **76**(7): 795-800.

Knothe, G. (2005). "Dependence of biodiesel fuel properties on the structure of fatty acid alkyl esters." Fuel Processing Technology **86**(10): 1059-1070.

Knothe, G. (2006). "Analyzing biodiesel: standards and other methods." Journal of the American Oil Chemists' Society **83**(10): 823-833.

Ma K, v. d. V. F., Sedman J, Ismail AA (1997). "Stoichiometric determination of hydroperoxides in fats and oils by FTIR spectroscopy. ." J Am Oil Chem Soc **74**(8): 897-906.

Meher, L. C., D. Vidya Sagar, et al. (2006). "Technical aspects of biodiesel production by transesterification--a review." Renewable and Sustainable Energy Reviews **10**(3): 248-268.

Oliveira, J. S., R. Montalvão, et al. (2006). "Determination of methyl ester contents in biodiesel blends by FTIR-ATR and FTNIR spectroscopies." Talanta **69**(5): 1278-1284.

Türkan, A. and S. Kalay (2006). "Monitoring lipase-catalyzed methanolysis of sunflower oil by reversed-phase high-performance liquid chromatography: Elucidation of the mechanisms of lipases." Journal of Chromatography A **1127**(1-2): 34-44.

van de Voort F, S. J., Ismail AA (1996). "Edible oil analysis by FTIR spectroscopy."
." Lab Robot Autom(8): 205-212.

Zagonel, G. F., P. Peralta-Zamora, et al. (2004). "Multivariate monitoring of soybean oil ethanolysis by FTIR." Talanta **63**(4): 1021-1025.

Al-Alawi, A., Van de Voort, F. and Sedman, J. (2005)"A new Fourier Transform Infrared Method for the Determination of Moisture in Edible Oils" Applied Spectroscopy **59**(10) 1295-1299.

Al-Alawi, A., Van de Voort, F. and Sedman, J. (2006)"Automated FTIR Analysis of Free Fatty Acids or Moisture in Edible Oils" JALA (11) 23-29.