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Abstract

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Keywords

Food Science and Human Nutrition, Chemistry, Soybean oil, biodiesel, methanol, transesterification, thermogravimetric analysis, proton nuclear magnetic resonance spectroscopy

Disciplines

Agriculture | Bioresource and Agricultural Engineering | Chemistry | Food Chemistry | Food Science

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Abstract. *The aim of this study was to demonstrate thermogravimetric analysis (TGA) as a potential method for monitoring biodiesel production. Soybean oil and commercial biodiesel were mixed in different proportions by weight. Mixtures of different biodiesel/soybean oil ratios were also created by interrupting a base-catalyzed transesterification process for producing biodiesel at various times. The mixtures produced by both approaches were analyzed with TGA. The results were then compared with data obtained by proton nuclear magnetic resonance spectroscopy (¹HNMR spectroscopy). The relative weight losses in both sets of mixtures we generated correlated well to the proportion of biodiesel present in the sample. The results from both analytical methods were in good agreement and within a deviation of 5%. Thus, TGA is a simple, convenient and economical method for monitoring biodiesel production.*

Keywords. Soybean oil, biodiesel, methanol, transesterification, thermogravimetric analysis, proton nuclear magnetic resonance spectroscopy.

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Introduction

Vegetable oils such as soybean oil have been considered as fuel for diesel engines (Knothe et al., 2005). However, such oils cannot be used directly in standard diesel engines because of their high molecular mass, kinematic viscosity, poor atomization, lubrication problems, and carbon deposits due to incomplete combustion (Hanna and Ma, 1999). These issues can be resolved by: dilution, microemulsification, pyrolysis, and transesterification with methanol (Toda et al., 2005); the latter approach being used most commonly in industry (Srivastava and Prasad, 2004). Biodiesel, a fatty acid methyl ester, (FAMES) is produced by the transesterification of vegetable oils and an alcohol in presence of suitable catalyst (Freedman et al., 1984 and Neto et al., 2004). The triglyceride reacts with three molecules of methanol, to produce three molecules of a fatty acid methyl ester (biodiesel) and a molecule of glycerin (Mushrush et al., 2000).

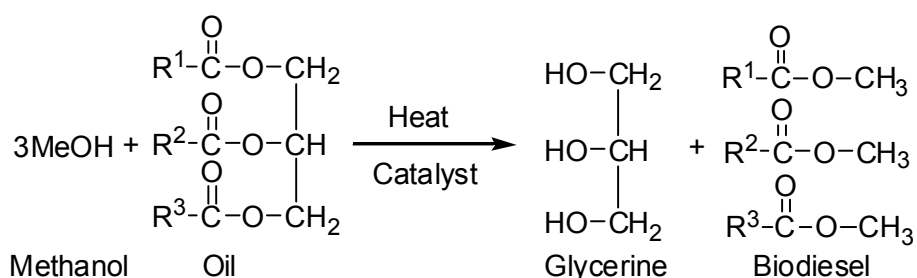


Figure 1. Transesterification reaction of soybean oil with methanol in presence of sodium hydroxide as catalyst produces biodiesel and glycerine.

Commonly used catalysts for the reaction include strong bases such as alkali metal hydroxides and alkoxides, metal oxides and acid catalysts such as HCl and H₂SO₄ (Lotero et al., 2005).

The advantages of biodiesel compared to fossil diesel fuel include: biodegradability, it is biorenewable, has low sulfur content and toxicity, is low volatility/flammability, and storage properties and salutary atmospheric CO₂ balance for production (Srivastava and Prasad, 2004).

Burgeoning demand for biodiesel derived from plant oils has grown significantly over the last decade. Thus biodiesel production has increased from 500,000 gallons in 1999 to 28 million gallons in 2004 in United States alone and it is expected that this growth will continue at a rate of approximately 170% annually (Statement Of Keith Collins Chief Economist, U.S. Department Of Agriculture Before The U.S. Senate Committee On Appropriations Subcommittee On Agriculture, Rural Development, And Related Agencies, Economic Issues Related to Biofuels, August 26, 2006, Northern Plains Research Lab, Sidney, Montana).

There are a variety of standard methods for analyzing biodiesel production including: gas chromatography (GC) (Plank and Lorbeer, 1995), high performance liquid chromatography (HPLC) (Holčapek et al., 1999), gel permeation chromatography (GPC) (Knothe, 2001 and Dube et al., 2004), proton nuclear magnetic resonance spectroscopy (¹H NMR) (Dube et al., 2004), near infrared (NIR) (Knothe, 2000 and Knothe, 1999), spectroscopy and Fourier transform infrared spectroscopy (FTIR) (Dube et al., 2004). Among these, ¹H NMR spectroscopy has been used extensively and is a well established method for the characterization of biodiesel (Reddy et al., 2006).

Thermogravimetric Analysis (TGA) is a characterizing technique that works by measuring the changes in physico-chemical properties as a function of temperature (Coats and Redfern, 1963). That is to say, the change in weight of a substance is measured as a function of

increasing temperature. Thus, TGA can be used to measure the thermal stability of a material. It can also be used to measure the composition of a mixture if the components undergo thermal degradation or valuation at different temperatures. TGA instrument consists of a precision balance which records the initial and instantaneous weight of the sample which are located in furnace which heats a linear fashion (linear increase in temperature with time). The test can be performed in atmospheric gases or in nitrogen depending on the substrate being studied. The results are plotted as mass change and rate of mass rate change as a function of temperature. The typical range of temperature for TGA studies is from 20 °C -1000 °C.

The advantages and disadvantages of TGA as compared to other methods are tabulated in Table 1.

Table 1. Comparison of TGA and other methods for biodiesel characterization

Characterization Method	Advantages	Disadvantages
TGA	No reagent or solvent required. Can easily differentiate between biodiesel and oil due to the large difference in boiling points of both the components. Relatively inexpensive compared to ¹ HNMR and gives acceptable results.	Can not differentiate between different fatty acid methyl esters present in the biodiesel.
¹ H NMR	Relatively high accuracy in determining the biodiesel content.	Different solvents are required (CDCl ₃ in this case). Instrumentation is more expensive.
GC	Can differentiate between mono-, di- and tri-glycerides, methyl esters and glycerol.	Standard solutions of glycerol, monoolein, diolein, triolein, etc in pyridine are first prepared. These are added to biodiesel samples and diluted with heptanes. Extreme caution is required in preparing these solutions and carrying out GC to minimize experimental error.
NIR	No solvent required. Can differentiate between soybean oil, biodiesel and glycerol.	Can not quantify low levels of contaminants.
HPLC	Differentiates between mono-, di- and tri-glycerides, methyl esters and glycerol.	Different solvents such as triolein, trilinolein, trilinolenin, etc. are required to determine particular components of the mixture.

The goal of this work was to compare determinations of biodiesel content in soybean oil using TGA and ^1H NMR spectroscopy.

Experimental Procedures

Known mixtures of commercial biodiesel and soybean oil were created and analyzed by TGA and ^1H NMR spectroscopy respectively. The results were then compared in order to quantify the accuracy of the TGA analysis of biodiesel. In addition, samples for TGA and ^1H NMR analysis were also prepared from reaction mixtures created during the conversion of soybean oil to biodiesel catalyzed by sodium hydroxide.

Materials

The materials used in this study were commercially refined soybean oil obtained from Watkins E. Inc. Sodium hydroxide (NaOH), methanol, anhydrous magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and hexanes were all obtained from Fisher Scientific.

Preparation of standard mixtures of biodiesel and soybean oil:

Ambient temperature conversion of soybean oil to biodiesel catalyzed by nanocrystalline calcium oxides (Reddy et al., 2006) was used for the production of biodiesel for standard mixtures. This biodiesel sample was found to be $\geq 99\%$ pure when analyzed by ^1H NMR spectroscopy. Soybean oil was also analyzed by ^1H NMR spectroscopy and was found to be free of contaminants.

Standard samples of biodiesel and soybean oil were made by manually mixing biodiesel and soybean oil in different proportions by weight. For preparing a 50%: 50% mixture of biodiesel and soybean oil, 10 g of soybean oil was first added to a glass vial using an analytical balance with a least count of 0.0001 gm. Biodiesel was then added to complete the total weight of the mixture to 20 g. The mixture was then mixed thoroughly for 1 minute using a vortex mixer. The remaining standard mixtures were prepared similarly. The following weight proportions of soybean oil to biodiesel were used for the analyses: 25%: 75%, 30%: 70%, 50%: 50%, 75%: 25% and 80%: 20%. These samples were then analyzed by TGA and ^1H NMR spectroscopy.

Preparation of biodiesel/soybean mixtures from transesterification:

These mixtures were prepared by collecting samples from a transesterification reaction mixture at specific times. In these experiments, 5 mL of methanol was added to 0.2 g of sodium hydroxide (0.74 M). This mixture was continuously stirred with a magnetic stirrer at 300 rpm and a temperature of 40 °C for 5 min. This reaction formed a solution of sodium methoxide/sodium hydroxide which was then added to 20 mL of soybean oil. To achieve full conversion of the soybean oil to FAMES, approximately 3 ml methanol (1:3 molar ratio) is required to drive the reaction equilibrium to completion and to account for losses during the reaction. The mixture was allowed to react at 60 °C in a shaker water bath with continuous stirring of the reactants. Soybean oil and methanol react in the presence of the sodium hydroxide/sodium methoxide catalyst mixture to form fatty acid methyl esters (FAMES, biodiesel). The byproducts of this reaction are glycerol and a relatively small amount of soap. The reaction was stopped at a predetermined time by adding water (50 mL) and hexanes (50 mL) to the reaction mixture. That is to say, the water stops the reaction and the biodiesel and residual soybean oil are extracted with the hexanes. Additional hexanes (200 mL) were added to dissolve biodiesel and soybean oil. This mixture is allowed to settle for ten minutes in a separatory funnel for clear separation of the two layers. The top layer contains biodiesel, soybean oil and hexanes, while the bottom layer contains glycerol, water, catalyst and soap. The top layer was then separated, and anhydrous magnesium sulfate was added to remove trace amounts of water. This mixture was

then passed through filter paper to remove the magnesium sulfate and the filtrate was subjected to rotary evaporation to remove the solvent. The remaining sample was then analyzed by TGA and ^1H NMR spectroscopy for the degree of conversion to biodiesel.

Analytical methods:

^1H NMR spectra were recorded at ambient temperature on a Varian VXR-400 MHz spectrometer using standard procedures. The chemical shifts were referenced to the residual peaks of CHCl_3 in CDCl_3 (7.26 ppm). The relevant signals chosen for integration were those of methoxy groups in the FAMES (3.66 ppm, singlet) and those of the α -methylene protons present in all triglyceride derivatives (2.3 ppm, triplet) of the soybean oil. The conversion was calculated directly from the integrated areas of the aforementioned signals (Reddy et al., 2006).

TGA was also used to measure the biodiesel and oil contents in the samples. In this experiment, 10 μL samples of biodiesel and oil mixture were heated at a constant heating rate of 10 $^\circ\text{C}/\text{min}$ in an atmosphere of nitrogen. The temperature range was 25 $^\circ\text{C}$ to 500 $^\circ\text{C}$.

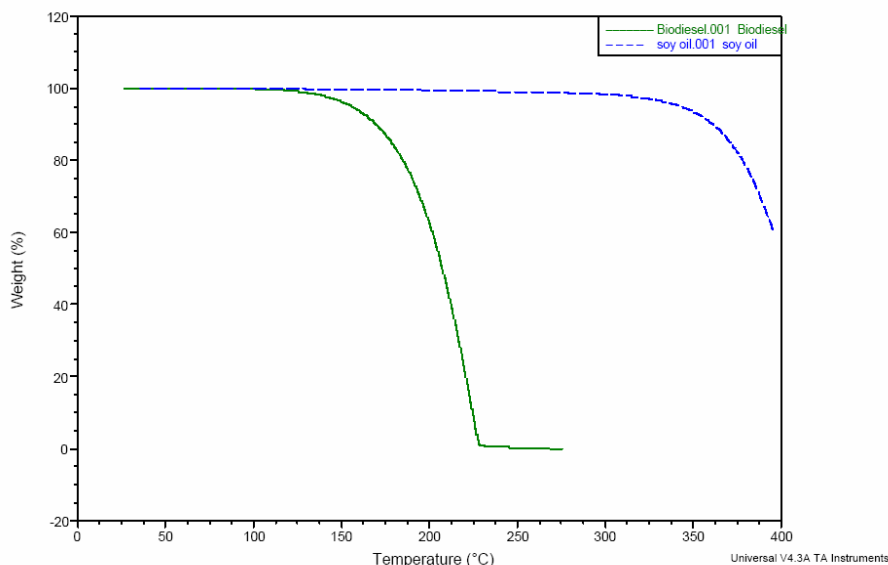


Figure 2. Overlay of thermogravimetric curves for biodiesel and soybean oil (Weight % versus temperature).

Figure 2 shows the thermogravimetric plots for pure biodiesel and pure soybean oil sample. The mass of the biodiesel starts to decrease at approximately 150 $^\circ\text{C}$ and it continues to decrease until all the biodiesel present in the sample is vaporized. Similarly, evaporation of soy oil starts at approximately 350 $^\circ\text{C}$. Figure 3 shows analysis of a standard sample containing 50% biodiesel and 50% soy oil prepared by mixing soybean oil and laboratory grade biodiesel. From this plot the percentage of biodiesel in the mixture is 47.40% which is very similar to the 47.98 % biodiesel value obtained from NMR analysis for the same sample. These estimates are obtained by direct correlation to the weight % from the TGA analysis. It is important to note that the ratio of biodiesel: soy oil in samples obtained by varying the transesterification time was estimated using this same procedure.

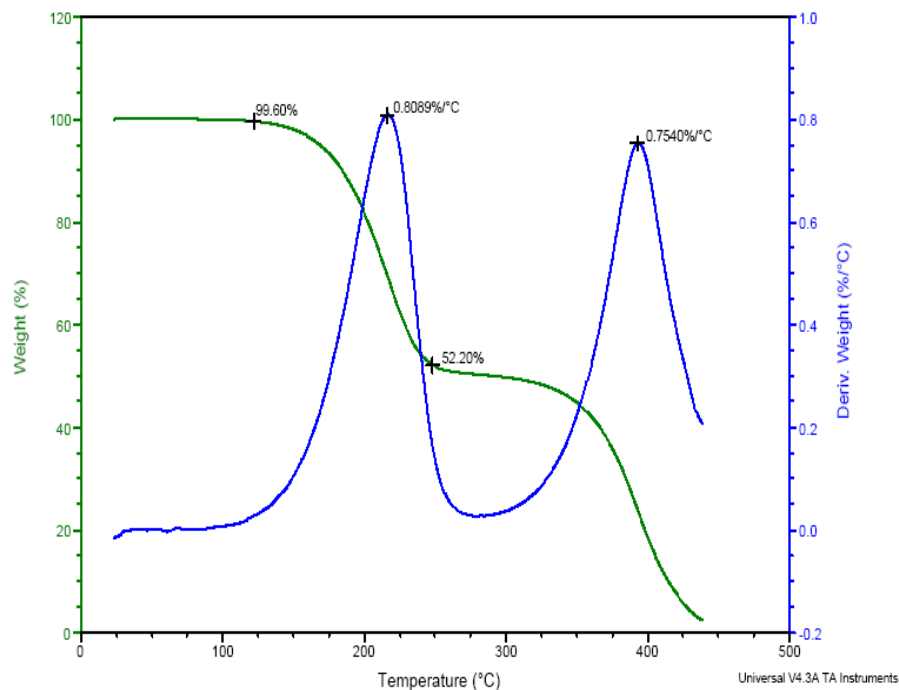


Figure 3. Thermogravimetric curve for a standard mixture containing 50:50 Biodiesel:soybean oil ratio.

It was assumed that the amount of biodiesel present in a given sample is equal to the average weight percentage of over the range where weight starts to drop (at ca. 150 °C) and where all the biodiesel is vaporized. The biodiesel/soybean oil TGA plots were compared with the standard plots, allowing a determination of the percent by weight of biodiesel in the sample.

Results and Discussion

The biodiesel percentages from the TGA analysis of the standard bio-diesel/soybean oil mixtures were very similar to the actual (Figure 4). The linear fit between the two data series gives an R^2 value of 0.9981 which suggest good agreement between the TGA results and actual bio-diesel mixture.

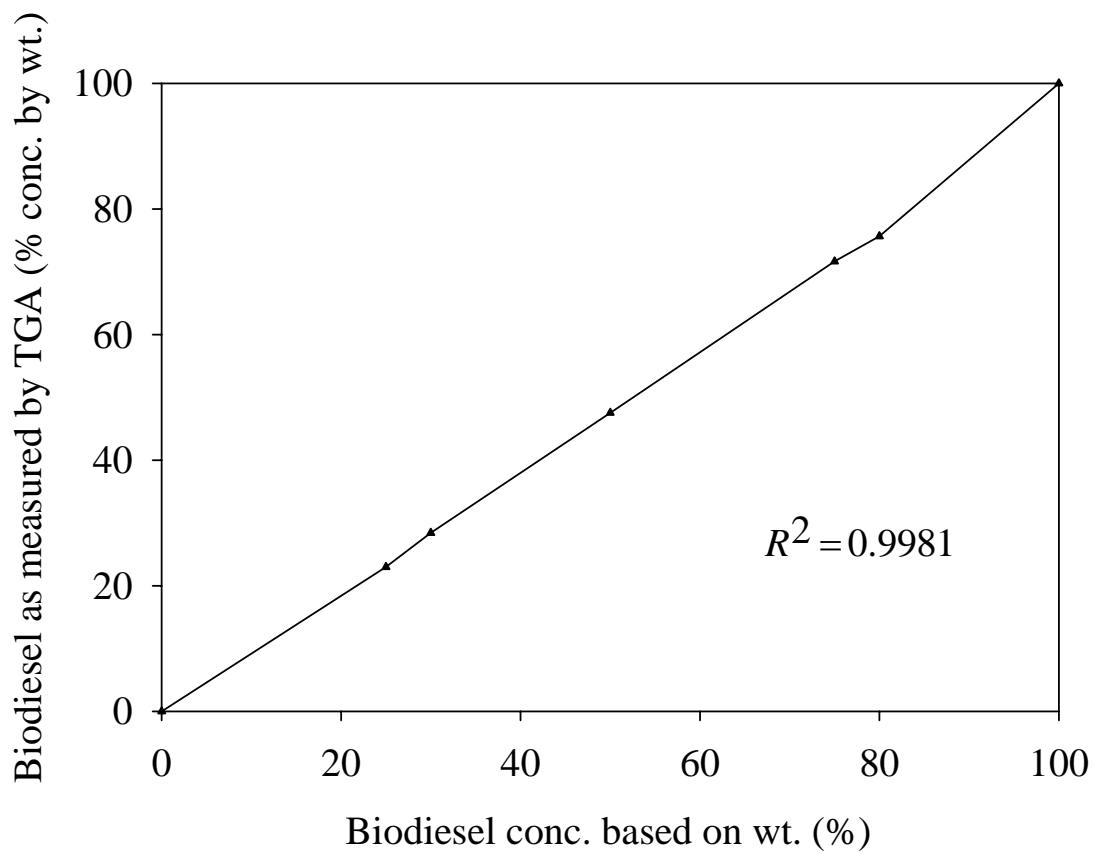


Figure 4. Biodiesel % by wt. obtained from TGA analysis is plotted against the actual biodiesel % in the sample.

The TGA biodiesel analyses were also plotted as a function of the ^1H NMR analyses as seen in Figure 5. The linear fit between the two methods show an R^2 value of 0.9997. Again the linear regression suggests that TGA accurately quantifies the amount of bio-diesel present.

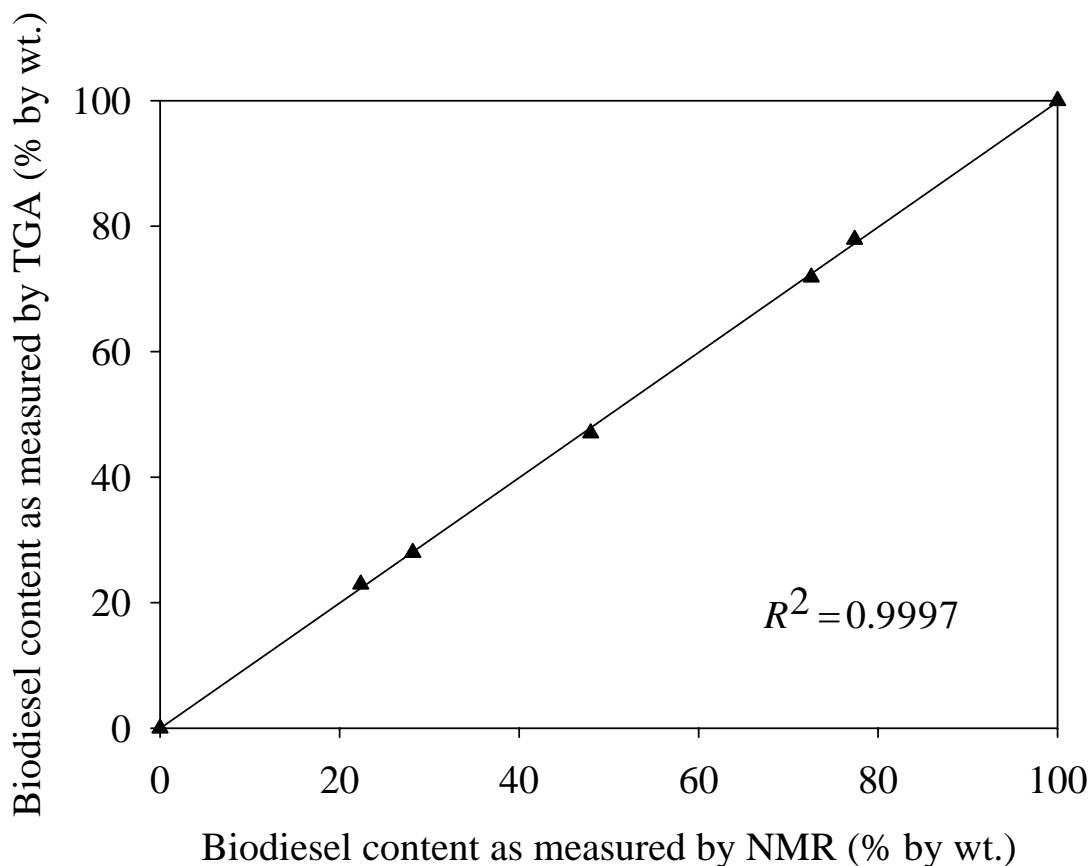


Figure 5. Biodiesel content (%) obtained from TGA and NMR methods.

Figure 6 shows the biodiesel production as a function of esterification time as determined by ^1H NMR spectroscopy and by TGA. It is important to note that in these experiments, there are varying amounts of partially transesterified oil, unlike the previously detailed experiments with the standard mixtures that contained pure bio-diesel and pure soybean oil. Thus, the latter experiments are more representative of actual laboratory or industrial production conditions. It is again seen there is good correlation between the two characterization methods. Statistical regression analysis is used to calculate the variance for this data and it was found that the R^2 value obtained for the data was 0.9994. These results again suggest that TGA can be efficiently used for analyzing biodiesel contents in vegetable oil transesterification reactions.

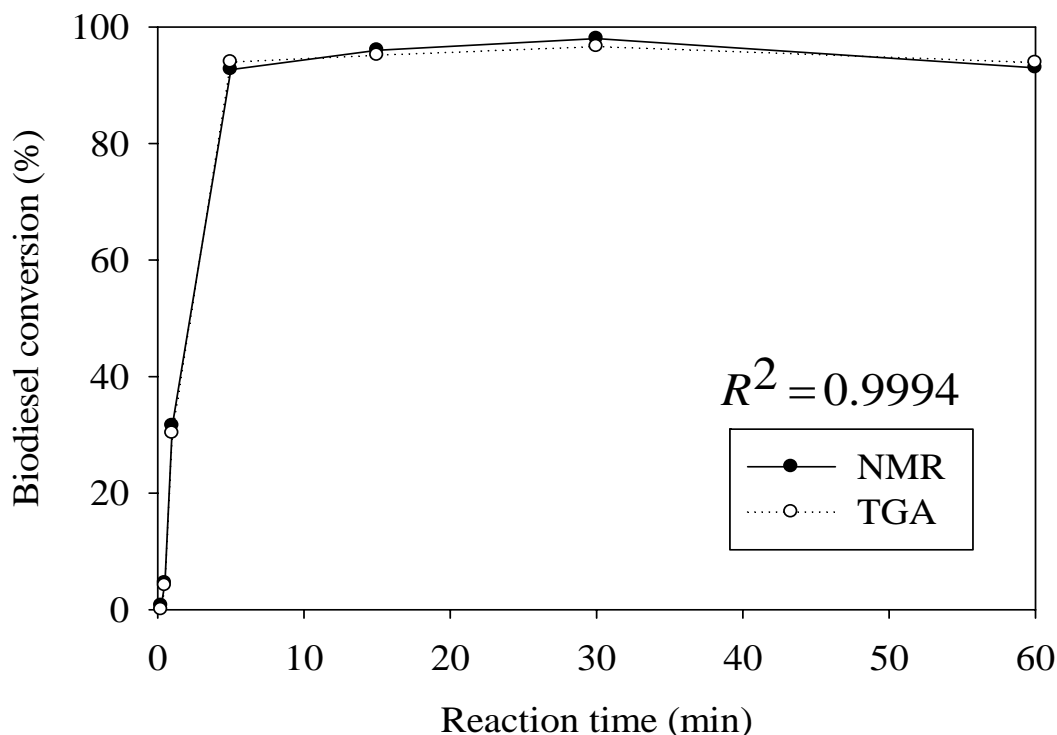


Figure 6. Biodiesel (%) conversion from transesterification of soybean oil determined by TGA and NMR analysis.

Conclusion

Our results suggest that the thermogravimetric analysis (TGA) is an effective method for estimating the percentage of biodiesel in reaction mixtures. This method was carefully validated with existing NMR spectroscopic technique for the determination of biodiesel conversion and found to be comparative to NMR technique. TGA method does not require addition of any reagents or solvents to the sample prior to its analyses, thus reducing the probability of errors.

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