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Microwave Assisted Glycerolysis Of Neem Oil

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Biodiesel is considered as a viable alternative to diesel fuels since it is renewable and eco-friendly. Edible oils account for majority of feedstock oils used in biodiesel production since their free fatty acids (FFA) levels are below 1%. However, these oils are expensive and compete with food demand. Low cost feedstock oils may be used but they must undergo a pre-treatment process (glycerolysis) to reduce their FFA content to less than 1%. Conventional glycerolysis requires long reaction times so microwave irradiation is used to speed up the process. Neem oil with an initial %FFA of 1.138% was used to determine the effect of microwave irradiation on different factors that would affect the FFA reduction. The following factors are investigated: reaction time (5 and 9 minutes), reaction temperature (100˚C and 120˚C), oil to glycerol molar ratio (1:1 and 1:2) and sulfuric acid catalyst concentration or loading (2% and 4.5%). This study reports that reaction temperature was the only significant factor on FFA reduction. A higher temperature resulted in a higher FFA reduction. The optimum factors achieved are: oil to glycerol molar ratio of 1:1, a catalyst loading of 2%, a time of 5.58 minutes and a reaction temperature of 120°C resulting in a 91.81% FFA reduction.

Keywords: Microwave-irradiation, esterification, glycerolysis, neem oil

INTRODUCTION

Biodiesel has been considered as a viable alternative to diesel fuels as they are derived from plant oils and animal fats, making them a renewable source of fuel (Anya 2013). Despite its advantages in being a cleaner type of fuel, the cost of available feedstock oils that have low free fatty acids (FFA) has remained high (Sims 2008). Edible oils account for the majority of the feedstock oils used in biodiesel production since their FFA levels are below 1%. However, these oils are expensive and compete with food demand. Low-cost feedstock oils would be more efficient to reduce production cost but these oils have high FFA content making it undesirable to use in the production of biodiesel because of soap formation which lowers biodiesel yield (Freedman 1984).

Neem oil is a non-edible oil with a high FFA content (Sanford *et al.* 2009). To reduce its %FFA, it must undergo a pre-treatment process. The most common pre-treatment method to reduce the FFA content of feedstock oil is esterification. Using glycerol for esterification, which will be called glycerolysis from here on, allows the FFAs to be converted to esters, specifically glycerides which can be used in the transesterification process, thus reducing the %FFA of the feedstock (Anderson *et al.* 2016).

Microwave-irradiation has been proven to shorten the required reaction time for the esterification process; However, limited studies have been done to determine the effect on %FFA reduction and the factors affecting glycerolysis if microwaves will be used instead of conventional heating, as well as the comparison of their respective energy requirements. It is essential to determine the factors that affect the process such as the molar ratio, catalyst concentration, temperature, and time to ensure that the reduction of the FFA content of the feedstock oil is optimized. This study determined the effect of different factors on physical properties of neem oil as well as its %FFA using microwave-irradiation.

THEORY

In esterification, the free fatty acid present in the feedstock oil reacts with an alcohol in the presence of a catalyst to produce ester and water. Reacting glycerol with the FFA found in oils converts the FFAs to the esters monoglyceride, diglyceride, and triglyceride as shown in **Figure 1**. The glycerolysis reaction also produces water. However, since the glycerolysis reaction requires high temperatures, the water formed is immediately vaporized (Gole & Gogate 2014).

Properties of Feedstock Oil

%FFA

The reduction of FFA content of the biodiesel feedstock results in higher biodiesel yield. Concerns with the high FFA content of biodiesel focus on the possibility that FFA may cause engine deposits, notably in fuel injectors, by catalyzing polymerization in hot recycling fuel loops (Mahajan 2006).

The FFA content of a sample is based on the acid value (Banani 2015). Eq. (2) is used to determine the %FFA (Felizardo *et al.* 2011).

$$\%FFA = \frac{mg_{KOH}}{g_{oil}} x \frac{282\frac{mg_{oleic\ acid}}{mmol_{oleic\ acid}}}{56.10\frac{mg_{KOH}}{mmol_{KOH}}} x \frac{1mmol_{oleic\ acid}}{1mmol_{KOH}} x \frac{1g_{oleic\ acid}}{1000\ mg} x100\% \quad (2)$$

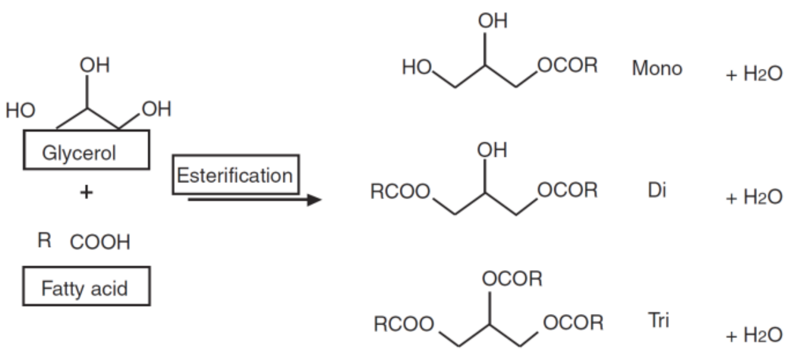

Fig. 1: Glycerolysis Esterification (Wang 2012)

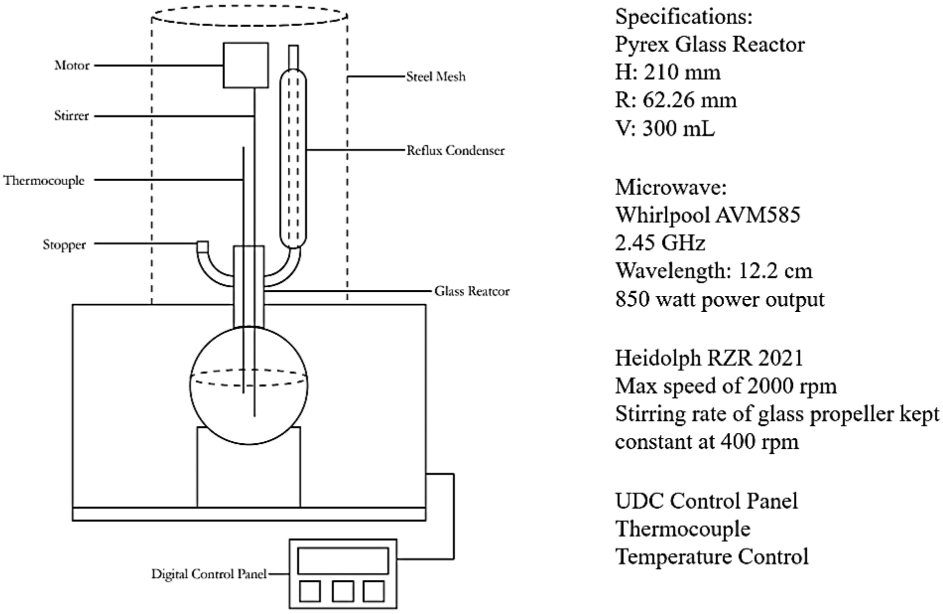

Fig. 2: Reactor

Microwave Heating

Microwaves are electromagnetic radiations which have a magnetic field component and an electric field component (Kumar 2011). Upon the application of microwaves, the dipoles align with the changing direction of the electric field. Both the dipole and the electric field "rapidly oscillates" and the dipole tries to "realign itself with the field as fast as possible by rotation" (Mazubert *et al.* 2014). As a result, there is molecular friction and collisions which give rise to intense localized heating, thus generating heat (Lidstrom *et al.* 2001), allowing the chemical reaction to proceed in a shorter amount of time (Gole & Gogate 2014).

EXPERIMENT

Neem oil was the feedstock oil used. Sulfuric acid was used as the catalyst. Potassium hydroxide was used as the standard solution for the determination of the acid value of the feedstock oil. The indicator used in the acid-base titration is phenolphthalein.

Figure 2 shows the reactor and its specifications used in this study. The Pyrex glass reactor was made by ChemLab Scientific Glass Blowing.

Design of Experiment

A two-level full factorial design was used in this study. Four factors, namely oil to glycerol molar ratio, catalyst amount, reaction temperature and reaction time were studied by varying each of the factors. The stirring speed was constant at 400 rpm and two trials were performed per variable factor. The different factors that were investigated in this study are as follows: oil to glycerol molar ratio (1:1, 1:2), catalyst loading in wt % (2%, 4.5%), reaction temperature (100°C, 120 °C), and reaction time (5 mins, 9 mins).

Experimental Procedure

For the esterification of the Neem oil, glycerol and sulfuric acid (H_2SO_4) was mixed before it was added to the feedstock oil. Sixty (60) g of Neem oil with the glycerol and sulfuric acid mixture was heated in the microwave oven. After heating the mixture, it was cooled to room temperature and transferred into vials for centrifugation. After centrifugation, the excess glycerol and sulfuric acid (bottom layer) was then separated from the esterified oil (top layer). The properties of the esterified oil were then determined using the analytical techniques in **Table 2**.

Table 2. Analytical Techniques

Property	Technique
Density	ASTM D1217: Bingham pycnometer
Viscosity	Falling Ball Viscometer
Moisture Content	Drying Method
FFA Content	ASTM D664: Acid-Base Titration

RESULTS AND DISCUSSION

Physical Properties

Initial properties of neem oil were determined before the glycerolysis reaction was carried out. All tested values from the esterified Neem oil complied with the standard values of biodiesel requirements as per ASTM D6751 as shown in **Table 3**.

FFA

Effect of Oil to Glycerol Molar Ratio on FFA Conversion

Figure 3 shows the effect of varying the oil to glycerol molar ratio while keeping the other three factors constant. Since the difference in %FFA reduction did not vary when the molar ratio was varied, this factor did not have any effect on %FFA reduction.

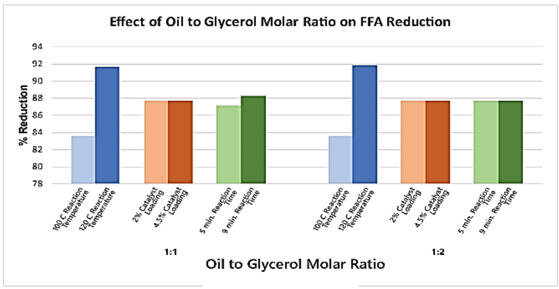

Fig. 3: Effect of Oil to Glycerol Molar Ratio on %FFA Reduction

Effect of Catalyst Loading on FFA Conversion

Figure 4 shows the effect of varying the catalyst loading on %FFA reduction. Since the values in %FFA reduction did not differ significantly, catalyst loading has no effect on %FFA reduction.

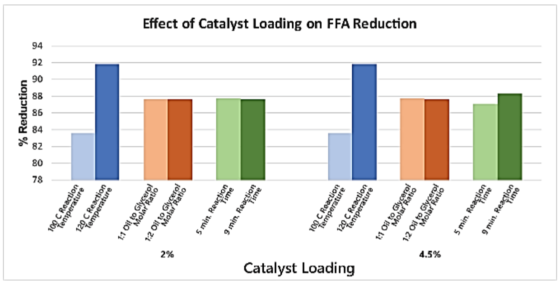

Fig. 4: Effect of Catalyst Loading on %FFA Reduction

Table 3. Comparison with ASTM D6751 Standards for Pure Biodiesel

Physical Properties	Initial Values	Esterified Oil Values	ASTM Standards
Density (kg/m^3)	0.9137	860-896	860-900
Viscosity (cS)	4.12	2.21-3.16	1.9-6.0
Moisture Content (dry basis)	0.6754%	0.009%-0.054%	0.05%
%FFA	1.138	0.093-0.188	<1%

Effect of Reaction Temperature on FFA Conversion

Figure 5 shows that varying the temperature from 100°C to 120°C had a significant effect in %FFA reduction. This is supported by the ANOVA analysis, where the effect of temperature in %FFA reduction was significant and is the only factor that was significant in this study. A similar trend was observed in the study of the effect of temperature, glycerin excess, stirring velocity and type of catalyst by on acidulated soap stocks (Lidstrom *et al.* 2012).

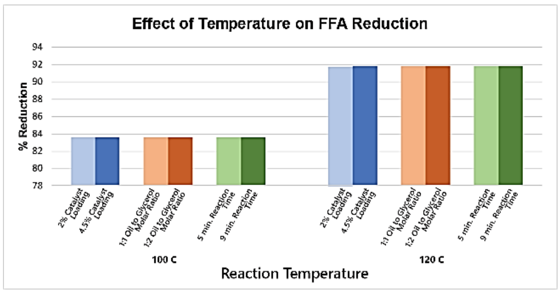

Fig. 5: Effect of Temperature on %FFA Reduction

Effect of Reaction Time on FFA Conversion

Figure 6 shows the effect of varying the reaction time from 5 minutes to 9 minutes. It was shown that an increase in reaction time produced a slight increase in FFA reduction.

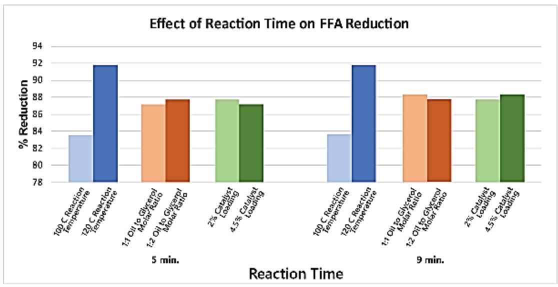

Fig. 6: Effect of Time on %FFA Reduction

Statistical Analysis of Data

The following figure shows the combined effects plot for each factor based on statistical analysis. Temperature was the only significant factor in %FFA reduction.

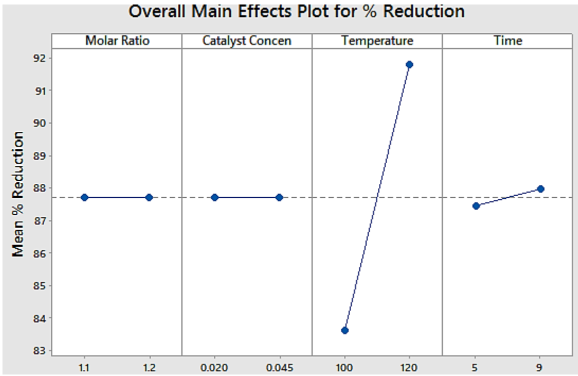

Fig. 7: Overall Main Effects Plot for % Reduction

Model Equation

The data was used to develop a model equation describing the %FFA reduction as a function of the investigated factors.

In terms of Coded Factors:

$$\%FFA\ Reduction = 87.71 - 8.049x10^{-3}B + 4.10C - 2.026x10^{-3}D \quad (7)$$

where: A is the code for oil to glycerol molar ratio, B for catalyst concentration, C for temperature and D for time.

In terms of Actual Factors:

$$\%FFA\ Reduction = 42.78227 - 0.16098(Molar\ Ratio) + 0.39642(Catalyst\ Concentration) + 0.41006(Temperature) - 1.01317x10^{-3}(Time) \quad (8)$$

where: molar ratio is the molar ratio of oil and glycerol, catalyst concentration is in wt%, temperature is in °C, and time is in minutes. In order to get the actual equation, Design Expert replaced each term in the coding equation with its coding formula.

Optimum Conditions

The following optimum conditions were achieved based on the model generated by Design Expert.

Table 4. Optimum Conditions

Factors	Optimum Value
Molar Ratio	1:1
Catalyst Concentration	2%
Temperature (°C)	120
Time (min.)	5.58
Yield (% Reduction)	91.81%

Power Calculations

The power calculations show that based on optimal factors with a 91.81% FFA reduction, 51.33kJ of energy was used for every gram of glycerin. Comparing this with previous studies (Gole & Gogate 2014, Patil *et al.* 2011, 2012), the energy requirement for microwave-assisted esterification is lower than the energy requirements of conventional heating esterification.

CONCLUSIONS

The %FFA of Neem oil with an initial %FFA of 1.138 was successfully reduced to values ranging from 0.093 to 0.188 which is the acceptable %FFA of biodiesel feedstock oil using microwave-assisted glycerolysis. Experimentally, the highest %FFA reduction at 91.88% was achieved with 1:2 Oil to Glycerol Molar Ratio, 4.5% catalyst, a temperature of 120°C and a reaction time of 5 minutes.

The determination of the significant factors in this study was achieved with the use of ANOVA. Out of the four factors, only the reaction temperature was found significant in %FFA reduction. Physical properties of the oil, namely density, viscosity and moisture content determined after glycerolysis, all fell within the ASTM D6751 standards for biodiesel. Power calculations show a 51.33kJ/g energy requirement. Comparison with previous studies on conventional heating esterification showed that using microwave heating required less energy. In general, higher %FFA reduction was achieved even with lower power requirements with the use of microwaves, thus, proving that using microwave heating is favorable as compared to conventional heating.

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