optimising bidiesel production from high acid value waste cooking oil using supercritical methanol

Omar Aboelazayem, Mamdouh Gadalla and Basudeb Saha

CORRESPONDENCE ADDRESSES: Omar Aboelazayem, Ph.D Student, London South Bank University, School of Engineering, 103 Borough Road SE1 0AA, London, United Kingdom, e-mail: aboelazo@lsbu.ac.uk, Mamdouh Gadalla, Ph.D., Associate Professor, The British University in Egypt, Department of Chemical Engineering, Misr-Ismailia Road, El-Sherouk City 11837, Cairo, Egypt, e-mail: mamdouh.gadalla@bue.edu.eg, Basudeb Saha, Ph.D., Professor, London South Bank University, School of Engineering, 103 Borough Road SE1 0AA, London, United Kingdom, e-mail: b.saha@lsbu.ac.uk.

Abstract

In this study, biodiesel production from a typical Egyptian waste cooking oil (WCO) with high acid value content (18 mg KOH/g oil) has been analysed by studying the main factors affecting biodiesel and glycerol yields. Response Surface Methodology (RSM) *via* Central Composite Design (CCD) has been used to analyse the effect of four independent variables, i.e. methanol to oil (M:O) molar ratio, temperature, pressure and time on the reaction responses. A quadratic model for each response has been concluded representing the interrelationships between reaction variables and reaction responses. In addition, the predicted models’ adequacy has been evaluated through Analysis of Variance (ANOVA) method. Numerical optimisation technique has been applied to conclude the optimum reaction conditions for maximum production of biodiesel resulting in 98% and 2.05% for biodiesel and glycerol yields at M:O molar ratio, temperature, pressure and time of 25:1, 265oC, 110 bar and 20 minutes, respectively. Experimental validation has been analysed for the predicted optimum conditions resulting in 98.82% biodiesel yield with 0.83% relative error.

*Keywords*: Biodiesel, Waste cooking oil, Supercritical transesterification, Optimisation, Response surface methodology.

# introduction

The unstable price and depletion of world’s crude oil reserves are the main reasons for searching for alternative fuels, specifically for the transportation sector. Biofuels have been considered as effective replacement for fossil fuels including biodiesel, bioethanol, biohydrogen and biogas. Biodiesel has been observed as an efficient replacement for petroleum based diesel fuel (petro-diesel). It is biodegradable, nontoxic, provide better engine lubricity and produced cleaner combustion compared to petro-diesel with significant reduction in carbon monoxide, unburned hydrocarbons and particulates. Biodiesel could also be blended with petro-diesel in various proportions for cleaner exhaust and to avoid engine modification requirements [1].

Biodiesel is defined as a mono alkyl ester of long chain fatty acid derived from vegetable oil or animal fats. It is mostly produced by esterification and/or transesterification of various feedstock with methanol or ethanol [2]. Biodiesel production form first-generation feedstock including fresh edible oils (palm oil, sunflower oil, corn oil and soybean oil) and animal fats (beef tallow, lamb and chicken fats) has been considered as an intense competition with food industry resulting in the increase of prices for these edible oils and fats due to the high demand from both food and biodiesel industries. Accordingly, researches have been directed towards utilisation of second-generation feedstocks including nonedible oils and waste cooking oils (WCO). Their advantages over the first-generation feedstocks that they are lower in cost and most importantly they do not affect food security [3]. WCO has been considered as an ideal feedstock for biodiesel production since it adds to the benefits of second-generation feedstocks advantages that it contributes in waste reduction and utilisation. Moreover, it reduces the cost of waste water treatment plants since most of the residences get rid of their waste oils through the sewage causing severe problems for the treatment plants [4].

However, WCO has some disadvantages as a feedstock including the high free fatty acids (FFA) and water content results from the cooking process. Accordingly, pre-treatment for the WCO feedstock is essential for alkaline homogenous catalyst processes to avoid saponification reaction by two steps production including esterification of FFA then transesterification of triglycerides [4]. Currently most of the biodiesel production processes use homogenous acidic and/or alkaline catalysts for biodiesel production from WCO. These homogenous catalysts have number of drawbacks including equipment corrosion, generation of significant amount of wastewater, existence of side reactions and the high production cost due to difficulties of catalyst separation and recovery [1].

The use of heterogenous catalyst has proven simpler production and separation processes for biodiesel production compared to homogenous catalysts since they can be easily separated by settling. However, heterogenous catalysts are very sensitive for waste content which then requires effective water removal pre-treatment for the feedstock [5].

Non-catalytic supercritical methanol production technique is a special method for biodiesel production without considering any of the previously mentioned restrictions. This technique has proven efficient production of biodiesel from low quality feedstock with high FFA and water contents. It tolerates esterification and transesterification reactions at the same time resulting in one step production of biodiesel [6].

The main goal of this research is to investigate the applicability of supercritical methanol technique for biodiesel production from a typical Egyptian WCO with high total acid value (18 mg KOH/g oil). In addition, to optimise the reaction conditions including M:O molar ratio, temperature, pressure and time to maximise biodiesel yield.

# materials and methods

## Materials used

WCO collected from Egyptian random local restaurants and industries were exported to the UK. Methanol 99% (MeOH) was purchased from Fisher Scientific, UK. The standard methyl esters used for preparing calibration curves and the heptadecanoic acid methyl ester used as an internal standard were purchased from Sigma-Aldrich, UK. The liquid CO2 cylinder (99.9%) equipped with a dip tube was purchased from BOC Ltd., UK.

## Experimental Setup

WCO have been filtered in order to remove the cooking process residuals. The reaction took place in a 100-mL high pressure reactor made of stainless steel (model 49590, Parr Instrument Company, USA) which washas been fitted with a thermocouple (type J), heating mantle, controller (model 4848) and a mechanical stirrer. Oil was heated to 30oC to convert it to the liquid state. Then, it was weighted and mixed with methanol (based on specific ratio) to the reactor and heated with continuously stirring at constant rate of 300 rpm to the target temperature. Then, supercritical fluid pump (model SFT-10, Analytix Ltd., U.K) was used to compress CO2 to the targeted pressure from the cylinder to the reactor. The reaction time starts when the reactor reaches the required reaction temperature and pressure. After the reaction time, the reactor was quenched using an ice bath to stop the reaction and then the reactor was then depressurised. Unreacted methanol has been recovered using simple distillation. The reaction products were separated using a centrifuge (1500 rpm, 3 min per cycle) to biodiesel and glycerol. Finally, biodiesel and glycerol weights were measured for yields calculations. Yields have been calculated by Equation (1) [6].

*Yield (%) = mass of Product / mass of Oil* (1)



## Experimental Design

RSM has been established to conclude the optimum conditions for biodiesel production by analysing the relationship of reaction parameters with reaction responses. Four independent variables have been chosen for the analysis including M:O molar ratio, temperature, pressure and time, which were labelled as A, B, C, D respectively. Three levels for each variable have been coded as -1, 0, 1 as shown in Table 1. Biodiesel and glycerol yields have been selected as reaction responses. Thirty experiments have been performed in a randomised order where the responses have been calculated for each experiment.

Table 1. Experimental Design Variables

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Factor | Code | Levels | | |
|  |  | -1 | 0 | 1 |
| M:O (molar ratio) | A | 20 | 30 | 40 |
| Temperature (oC) | B | 240 | 260 | 280 |
| Pressure (bar) | C | 85 | 135 | 185 |
| Time (min) | D | 7 | 22 | 27 |

## Statistical Analysis

The general quadratic equation has been used to define the model. Statistical significance has been investigated using ANOVA by calculating the Fisher’s F-test at 95% confidence level. Statistical significance of the results has been presented by p-value, where the result is considered to be significant when p-value is less than 0.05.

Numerical optimisation of the reaction variables has been constructed based on certain goals. The goals were identified by maximising biodiesel yield and minimising glycerol yield at minimum temperature, pressure and time of the reaction.

Design of experiments, regression analysis, graphical analysis and numerical optimisation have been performed using Design Expert 10 software (Stat-Ease Inc., Minneapolis, MN, USA).

## Physicochemical properties analysis

The final pure biodiesel at the concluded optimum conditions has been analysed for investigating its chemical and physical properties. Analysis results have been compared to the European standard of biodiesel, EN14214. The analysed properties have been replicated twice and the final results have been obtained as an average of the two results. Total acid number (TAN), standard density and kinematic viscosity of the produced biodiesel have been calibrated according to ASTM D974, ASTM D4052 and ASTM D445, respectively.

## Gas Chromatography Analysis

Fatty acids composition of the WCO was analysed according to BS EN ISO 12966-2:2011 by converting them to methyl esters as shown in Table 2. WCO and biodiesel samples were analysed using gas chromatograph (GC) (Thermo- Scientific, Trace 1310) equipped with a capillary column (TR-BD 30 m × 0.25 mm × 0.25 μm) and flame ionisation detector (FID). Both injector and detector temperatures have been adjusted at 250oC. Helium was used as the carrier gas. The temperature programme started from 60°C and held for 2 min. Then it ramped with 10°C/min to 200°C and directly ramped with 1°C/min to 210°C. Finally, the temperature was increased to 240°C with a ramp rate of 20°C/min and remained for 7 minutes.

Table 2. Fatty Acids Compositions in WCO

|  |  |
| --- | --- |
| Fatty Acid | Weight (%) |
| Methyl Oleate | 48.2 |
| Methyl Palmitate | 41.6 |
| Methyl Linoleate | 9.3 |
| Methyl Myristate | 0.8 |

# Results and discussion

## Model adequacy checking

After performing the 30 experiments generated using CCD and calculating the responses for each run, two regression equations representing an empirical relationship between reaction variables and each response have been concluded. For simplicity, this paper will represent only the analysis and results for biodiesel yield response. The polynomial model as shown in Equation (2) has been used to fit the experimental results where Y is the dependant variable (biodiesel yield); A, B, C and D are the independent variables (M:O molar ratio, temperature, pressure and time respectively).

*Y = 88.64 – 1.31 A – B – 0.65 C + 0.32 D – 2.34 AB – 0.17 AC – 1.54 AD – 1.04 BC – 0.17 BD – 0.86 CD – 0.18 A2 + 0.32 B2 + 2.23 C2 + 1.28 D2* (2)

The proposed model has been examined for adequacy to identify any errors associated with the normality assumptions. ANOVA has been used to model using F-test and p-value tests, these values have been concluded as 121.52 and <0.0001, respectively which prove that the developed quadratic model is statistically significant with 95% confidence level. Lack-of-fit test has been applied for the model concluding p-value of 0.088, which has successfully represented most of the experimental data. The determination coefficient values, R2 and R2adj, which measure the reliability of the model fitting, have been calculated to be 0.9913 and 0.9831, respectively. These values indicate that only 0.087 of the total variation is not well clarified by the developed model, which ensure the model fitting to the experimental data. Figure 1 illustrates the relation between predicted values generated by the model and actual experimental values.

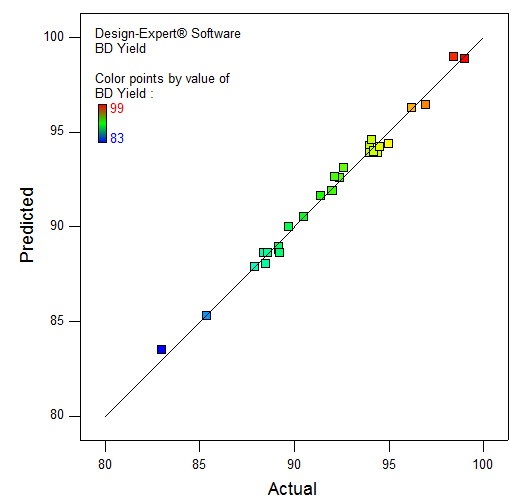


Figure 1. Predicted Data Verses Experimental Actual Data

## Effect of process variables

### Effect of M:O molar ratio

One of the drawbacks of using supercritical methanol technique for biodiesel production is the usage of large excess of methanol where, it is very important to investigate it’s effect of the biodiesel yield for optimisation considerations. Experimental runs have been carried out at M:O molar ratio between 20:1 and 40:1. The ANOVA results for M:O molar ratio with p-value less than 0.0001 indicates that it has highly significant effect on biodiesel yield. Figure 2 illustrates a 3-D plot for M:O molar ratio and temperature verses biodiesel yield where the other two variables, i.e. pressure and time, are kept constant at their centre points. At constant temperature of 250oC, it is clearly shown that there is a direct proportional relationship between M:O molar ratio and biodiesel yield. However, at higher temperatures its effect decreases to constant at 260oC reaching negative effect at higher temperatures.

### Effect of reaction temperature

Reaction temperature is an important parameter for supercritical production of biodiesel. Since the critical temperature of methanol is 240oC, the studied temperatures ranges have been chosen between 250oC and 270oC. It has been concluded from the ANOVA results that reaction temperature has significant effect on biodiesel yield with p-value less than 0.0001. Figure 2 demonstrates the effect of temperature on biodiesel yield where the relation showed increase of biodiesel yield while increasing temperature at low M:O molar ratio range. The temperature has negative effect with an increase M:O molar ratio.



Figure 2. 3-D Plot Showing the Effect of M:O Molar Ratio and Temperature on Yield

### Effect of reaction pressure

Carbon dioxide gas has been used to pressurise the reaction to the targeted pressure using a high-pressure pump. In addition, carbon dioxide acts as a co-solvent where it enhances the solubility of methanol in oil [7]. According to the ANOVA results, reaction pressure showed highly significant effect on biodiesel yield. As shown in Figure 3 the pressure has inversely proportional relationship with the yield from pressure range of 110 bar to 130 bar then, the yield increases slightly by increasing the pressure more than 130 bar.

### Effect of reaction time

According to the ANOVA results, reaction time showed significant effect on biodiesel yield with p-value of 0.005. This significance effect is clearly shown in Figure 3, where increasing time has negative effect on biodiesel yield from time range between 12 min to 16 min. Reaction time more than 16 min has no effect on biodiesel yield.



Figure 3. 3-D Plot Showing the Effect of Pressure and Time on Yield

## Optimisation of reaction conditions

Optimisation of supercritical methanol production of biodiesel has been studied to conclude the optimum values of the independent variables (M:O molar ratio, temperature, pressure and time) affecting the dependant response variables (biodiesel and glycerol yields). Numerical optimisation technique has been carried out using Design Expert software. In order to conclude the optimum conditions, a set of targets must be defined on the software to guide the optimisation process. Targets of the independent variables have been set based on environmental and economic considerations. Reaction temperature, pressure and time have been set to be minimised in order to optimise energy consumption. Responses targets have been set to maximise the biodiesel yield while minimising glycerol yield.

The numerical optimisation technique has concluded that according to the set goals the optimum conditions for production of biodiesel is at 25:1, 265oC, 110 and 20 minutes for M:O molar ratio, temperature, pressure and time, respectively. These optimum conditions has concluded biodiesel yield of 98% and glycerol yield of 2.1%.

## Optimum conditions validation

In order to validate the efficiency of the predicted model and it’s predicted optimum conditions, experiments have been performed at the concluded optimum conditions. The experimental results showed similar response value to the predicted optimal response of 98.82% with relative error of 0.83%. The similarity between the experimental response results and the predicted optimal response confirms and verifies the accuracy and adequacy of the predicted quadratic model.

## Physicochemical properties

The physicochemical properties of the final biodiesel product have been analysed and compared to the European Biodiesel Standard, EN14214. Table 3. shows the concluded properties in comparison with the standard limits of EN14214. The agreement of the biodiesel’s properties with the biodiesel standard properties insures the quality of the produced biodiesel.

Table 3. Produced Biodiesel Properties

|  |  |  |  |
| --- | --- | --- | --- |
| Test | Unit | Produced biodiesel | Biodiesel (EN14214)  Standard |
| Density at 15oC | kg/m3 | 884 | 860 - 900 |
| Kinematic viscosity at 40oC | cSt | 4.62 | 3.5 - 5 |
| TAN | mg KOH/ g oil | 0.3 | < 0.5 |

# Conclusions

Using supercritical methanol technique has been proved to be an efficient technique for biodiesel production from high acidity feedstock in single step reaction. Both esterification and transesterifications reactions have been achieved in parallel through the reaction time. The optimum biodiesel yield has been found to be 98% at M:O molar ratio of 25:1, reaction temperature of 265oC and reaction pressure of 110 bar in 20 minutes. The optimisation results have been validated experimentally resulting in biodiesel yield of 98.82%, which shows the adequacy of the predicted optimum conditions with 0.83% relative error from the experimental results. The main properties of the produced biodiesel have been analysed and compared to the European Biodiesel Standard (EN14214) showing excellent agreement with the standards specified range, which insure the quality of the produced biodiesel.

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