# TRANSESTERIFICATION OF VEGETABLE OILS TO BIODIESEL IN A FIXED BED CATALYST REACTOR: EXPERIMENTAL AND MODELLING

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***Abstract***

*Continuous transesterification of fresh sunflower oil with methanol (1/6 molar ratio) to fatty acid methyl esters (FAME) and glycerol was conducted for 1 h in a fixed-bed catalyst reactor (1.6 cm internal diameter and 55 cm height). A base catalyst was prepared by impregnation of activated carbon with a KOH solution followed by thermo-chemical activation (at 750 °C under* $CO_2$ *atmosphere) of impregnated precursor.*

*Fixed bed catalyst height (20, 40 cm), operating temperature (55, 65 °C), and reactant superficial velocity (0.14, 0.28 cm/s) were selected as transesterification process factors. 8 experiments were performed according to a* $2^3$ *factorial plan. The effects of process factors on FAME yield (91.60-95.74%), glycerol yield (73.31-90.48%), and time of glycerol forming (6-23 min) were predicted. Regression equations obtained in this study could be used to evaluate the transesterification performances for factor levels within the ranges considered in the experimental runs.*

**Key words:** biodiesel, factorial experiment, fixed bed reactor, heterogeneous catalyst, transesterification, vegetable oil

## 1. Introduction

Transesterification of vegetable oils or animal fats with short chain alcohol (*e.g.*, methanol, ethanol) in the presence of a catalyst (homogeneous or heterogeneous, acid, base or enzyme) leads to fatty acid alkyl esters (biodiesel) and glycerol [1-10]. Biodiesel is a clean, non-toxic, renewable, and biodegradable fuel as compared to petroleum diesel [5-9,11].

Vegetable (edible and non-edible) oils are extensively used for developing alternative fuels including biodiesel [7]. Its yield depends on various transesterification parameters, *e.g.*, catalyst type, preparation method, and quantity, reactor type, contacting mode between reactants and catalyst, oil type as

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well as its content of free fatty acids (FFA) and water, oil/methanol ratio, reaction time and temperature [1-13].

At present, most of the biodiesel is produced from edible oils and methanol in the presence of base catalysts in batch reactors [1,7,8,13].

Heterogeneous catalysts are widely used due to their advantages over homogeneous ones, *e.g.*, they can be easily separated by filtration of the reaction mixture, do not involve a neutralization step, are reusable, non-corrosive, environmentally friendly, and less sensitive to the presence of water in the oil, which can lead to a significant decrease in the process cost [1-3,5,6,9-14]. Solid catalysts involve a suitable catalytic support that can "host" chemical compounds characterized by acid or base properties needed to catalyze the conversion of oil or fat to biodiesel.

This paper aims at studying the biodiesel production from fresh sunflower oil and methanol in a fixed-bed catalyst reactor with product recirculating. A supported catalyst was prepared by impregnation of activated carbon with a KOH solution followed by thermo-chemical activation of impregnated precursor. The effects of transesterification factors (fixed-bed catalyst height, operating temperature, and reactant superficial velocity) on process responses (biodiesel yield, glycerol yield, and time of glycerol forming) were evaluated.

## 2. Experimental

### *2.1. Materials*

Refined sunflower oil (ARGUS SA, Constanta) and methanol (99%, Merck, Germany) were used as reactants for biodiesel production. KOH pellets (99%, Merck, Germany) and granular activated carbon (Chemviron Carbon Corporation, Belgium) were employed for heterogeneous catalyst preparation.

### *2.2. Procedure*

#### *2.2.1. Catalyst preparation*

Heterogeneous catalyst preparation consisted of two main stages, *i.e.*, impregnation of catalyst support and thermo-chemical activation of catalyst precursor obtained by impregnation. Activated carbon (AC) was firstly sieved, keeping only particles with a size larger than 1 mm for avoiding fine carbon powder to contaminate reaction products and thus eliminating ultrafiltration as a supplementary process stage.

Sieved AC was further impregnated with KOH as follows: it was heated at 130 ºC in a drying stove, then immersed in 2M KOH solution, kept under stirring for 2 h at 80 ºC, left for 24 h, filtered, and dried at 130 ºC.

Thermo-chemical activation of dried impregnated AC (KOH/AC) was conducted in an experimental set-up presented in Fig. 1. KOH/AC granules were packed into a ceramic furnace (1) heated by an electric resistance fed by an autotransformer (2). The heating was performed up to 750 °C at a heating rate of 15 K/min. The temperature was measured by a K thermocouple (3) connected to a voltmeter (4). $CO_2$ from a tank (5), whose flow rate (5 L/h) was controlled by a valve (6) and measured by a flow-meter (7), was bubbled into distilled water contained in a flask (8). The mixture of $CO_2$ and water vapour exiting the bubbler (8) was fed into the furnace (1) and up-flowed through the fixed bed catalyst. KOH/AC supported catalyst was thermo-chemically activated for 1 h at 750 °C.

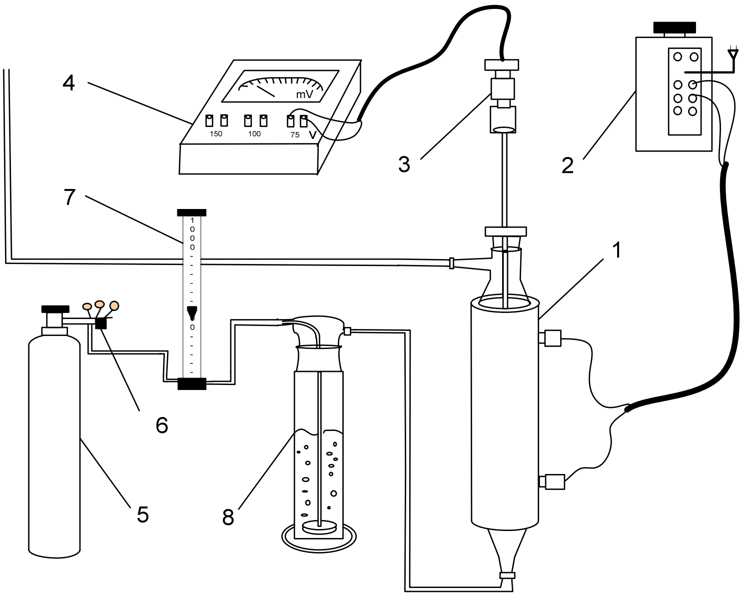

**Fig. 1.** Catalyst activation experimental set-up:
(1) furnace; (2) autotransformer; (3) thermocouple; (4) voltmeter; (5) $CO_2$ tank; (6) valve; (7) flow-meter; (8) bubbler.

### *2.2.2. Biodiesel synthesis*

Catalytic synthesis of biodiesel from fresh sunflower oil was conducted in an experimental set-up shown in Fig. 2. Activated catalyst granules (1) were packed in a reactor (2) consisting in a water-jacketed glass column (1.6 cm internal diameter and 55 cm height). The control of reaction temperature was performed by a thermostat water bath (3) with an error of ±0.5 °C.

Fresh oil (200 g) and methanol (43.2 g) at a 1/6 oil to methanol molar ratio were fed into a four-neck round-bottom flask (4) forming two separate layers. A part of upper layer of methanol was pumped for 2 min by a dosing pump (5) into the reactor (2), down-flowed through the fixed bed catalyst (1) producing potassium methoxide, and further was collected into the funnel (6). After that, the oil and the rest of methanol were stirred and heated using a heating magnetic stirrer (7) fitted with a contact thermometer (8) to control the temperature and a water-cooled condenser to avoid methanol losses (9). Mixed and heated reactants were pumped by the dosing pump (5) for 60 min into the catalytic reactor (2), wherein methyl esters and glycerol were obtained in the presence of potassium methoxide. Reactor effluent entered into the funnel (6) wherein two layers were separated, *i.e.*, a lower layer of glycerol and an upper one consisting mainly of reaction products and methanol. The filling of the funnel (6) determined the mixture recirculation in the mixing flask (4). The process was stopped after 60 min and the reaction mixture was left to separate for 24 h in the funnel (6).

Characteristic factors of transesterification process performed in the catalytic reactor were selected as follows: fixed bed catalyst height ($h$=20, 40 cm), operating temperature ($t$=55, 65 °C), and reactant superficial velocity ($w$=0.14, 0.28 cm/s). According to a $2^3$ factorial plan (3 factors and 2 levels of each factors), 8 experimental runs were conducted. The effects of process factors on its responses in terms of fatty acid methyl ester yield ($Y_{FAME}$), glycerol yield ($Y_G$), and time of glycerol forming ($\tau_G$) were evaluated. $Y_{FAME}$ and $Y_G$ were determined as percentages depending on theoretical values of product masses.

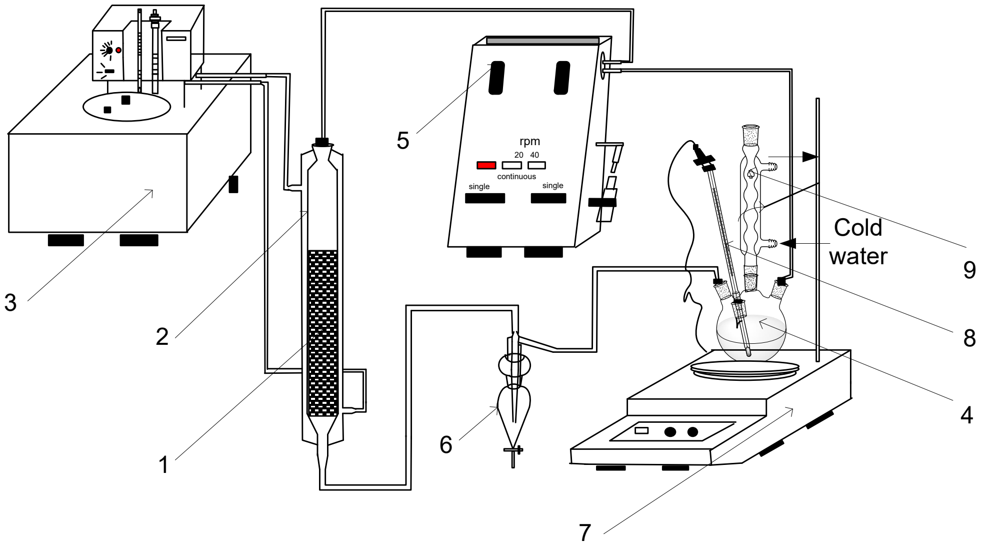

**Fig. 2.** Biodiesel synthesis experimental set-up:
(1) supported catalyst; (2) fixed-bed catalytic reactor; (3) thermostat water bath; (4) mixing flask; (5) micro-dosing pump; (6) separation and recirculation funnel; (7) heating magnetic stirrer; (8) contact thermometer; (9) water-cooled condenser.

## 3. Results and discussions

The process performances in terms of methyl ester yield ($Y_{FAME}$=91.60-95.74%), glycerol yield ($Y_G$=73.31-90.48%), and time of glycerol forming ($\tau_G$=6-23 min) under different operating conditions are specified in Table 1.

A statistical model based on a $2^3$ factorial plan was used to predict the process performances depending on its factors ($h$=20, 40 cm, $t$=55, 65 °C, and $w$=0.14, 0.28 cm/s). Dimensionless values of process factors are given by Eqs. (1)-(3), where $h_{cp}$=30 cm, $t_{cp}$=60 °C, and $w_{cp}$=0.21 cm/s are centre-points. Process factors and responses corresponding to 8 experimental runs are summarized in Table 1 (no. 1-8).

*Table 1*

**Experimentation matrix for $2^3$ factorial experiment**

| No. | $h$ (cm) | $t$ (°C) | $w$ (cm/s) | $x_1$ | $x_2$ | $x_3$ | $Y_{FAME}$ (%) | $Y_G$ (%) | $\tau_G$ (min) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 20 | 55 | 0.14 | -1 | -1 | -1 | 92.40 | 84.97 | 21 |
| 2 | 20 | 55 | 0.28 | -1 | -1 | 1 | 95.02 | 78.97 | 23 |
| 3 | 20 | 65 | 0.14 | -1 | 1 | -1 | 93.57 | 78.73 | 18 |
| 4 | 20 | 65 | 0.28 | -1 | 1 | 1 | 91.60 | 76.36 | 20 |
| 5 | 40 | 55 | 0.14 | 1 | -1 | -1 | 95.41 | 87.14 | 9 |
| 6 | 40 | 55 | 0.28 | 1 | -1 | 1 | 91.88 | 90.48 | 6 |
| 7 | 40 | 65 | 0.14 | 1 | 1 | -1 | 93.56 | 85.31 | 10 |
| 8 | 40 | 65 | 0.28 | 1 | 1 | 1 | 95.74 | 73.31 | 7 |
| 9 | 30 | 60 | 0.21 | 0 | 0 | 0 | 93.73 | 82.55 | 15 |
| 10 | 30 | 60 | 0.21 | 0 | 0 | 0 | 93.68 | 83.83 | 14 |
| 11 | 30 | 60 | 0.21 | 0 | 0 | 0 | 93.61 | 80.84 | 14 |
| 12 | 30 | 60 | 0.21 | 0 | 0 | 0 | 93.63 | 81.48 | 15 |

$$x_1 = \frac{h-30}{10} \tag{1}$$

$$x_2 = \frac{t-60}{5} \tag{2}$$

$$x_3 = \frac{w-0.21}{0.07} \tag{3}$$

Regression coefficients of statistical model described by Eq. (4), *i.e.*, $\beta_{ij}$ ($i$=1..$N$=8, $j$=1..3), which are specified in Table 2, were determined by processing the data summarized in Table 1 (no. 1-8) according to characteristic procedure of a $2^3$ factorial experiment.

$$y_j = \beta_{1j} + \beta_{2j}x_1 + \beta_{3j}x_2 + \beta_{4j}x_3 + \beta_{5j}x_1x_2 + \beta_{6j}x_1x_3 + \beta_{7j}x_2x_3 + \beta_{8j}x_1x_2x_3 \tag{4}$$

*Table 2*

**Significance of regression coefficients of Eq. (4)**

| | $i$ | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|---|
| $j$=1 | $\beta_{i1}$ (%) | **93.65** | **0.5** | -0.03 | **-0.088** | **0.533** | **-0.25** | **0.14** | **1.287** |
| | $y_{1,mn,cp}$ (%) | 93.66 | | | | | | | |
| | $\sigma_{rp,1}$ (%) | 0.052 | | | | | | | |
| | $\sigma_{\beta,1}$ (%) | 0.018 | | | | | | | |
| | $t_{i1}$ | **5089** | **27.17** | 1.630 | **4.755** | **28.94** | **13.59** | **7.608** | **69.97** |
| | $t_{i1}$-3.176 | **>0** | **>0** | <0 | **>0** | **>0** | **>0** | **>0** | **>0** |
| $j$=2 | $\beta_{i2}$ (%) | **81.91** | **2.151** | **-3.481** | **-2.129** | -1.269 | -0.036 | -1.464 | **-2.371** |
| | $y_{2,mn,cp}$ (%) | 82.18 | | | | | | | |
| | $\sigma_{rp,2}$ (%) | 1.31 | | | | | | | |
| | $\sigma_{\beta,2}$ (%) | 0.463 | | | | | | | |
| | $t_{i2}$ | **176.8** | **4.643** | **7.514** | **4.595** | 2.739 | 0.078 | 3.159 | **5.118** |
| | $t_{i2}$-3.176 | **>0** | **>0** | **>0** | **>0** | <0 | <0 | <0 | **>0** |
| $j$=3 | $\beta_{i3}$ | **14.25** | **-6.25** | -0.50 | -0.25 | **1.00** | **-1.25** | 0 | 0 |
| | $y_{3,mn,cp}$ (min) | 14.5 | | | | | | | |
| | $\sigma_{rp,3}$ (min) | 0.577 | | | | | | | |
| | $\sigma_{\beta,3}$ (min) | 0.204 | | | | | | | |
| | $t_{i3}$ | **69.81** | **30.62** | 2.45 | 1.225 | **4.899** | **6.124** | 0 | 0 |
| | $t_{i3}$-3.176 | **>0** | **>0** | <0 | <0 | **>0** | **>0** | =0 | =0 |

In order to determine the significance of regression coefficients using the Student's test [15-17], 4 centre-point runs ($N_{cp}$=4) were performed (no. 9-12 in Table 1). Characteristic parameters of centre-point runs, *i.e.*, mean value of response ($y_{j,mn,cp}$), reproducibility standard deviation ($\sigma_{rp,j}$), and number of degrees of freedom ($\upsilon_1$), as well as standard deviation associated to regression coefficients ($\sigma_{\beta,j}$) and values of Student's random variable ($t_{ij}$), given by Eqs. (5)-(9), are presented in Table 2.

$$y_{j,mn,cp} = \frac{\sum_{k=1}^{N_{cp}} y_{jk,cp}}{N_{cp}} \tag{5}$$

$$\sigma_{rp,j} = \sqrt{\frac{\sum_{k=1}^{N_{cp}} \left(y_{jk,cp} - y_{j,mn,cp}\right)^2}{\upsilon_1}} \tag{6}$$

$$\upsilon_1 = N_{cp} - 1 = 3 \tag{7}$$

$$\sigma_{\beta,j} = \frac{\sigma_{rp,j}}{\sqrt{N}} \tag{8}$$

$$t_{ij} = \frac{|\beta_{ij}|}{\sigma_{\beta,j}} \tag{9}$$

Regression coefficients satisfying the condition $t_{ij} - t_{\alpha,\upsilon_1} > 0$ were considered as significant, where $t_{\alpha,\upsilon_1} = 3.176$ represents the theoretical value of Student's variable corresponding to a significance level ($\alpha$) of 0.05 and $\upsilon_1$=3 [15-17]. Considering only significant coefficients (bold characters in Table 2), the statistical model described by Eq. (4) becomes:

$$y_1 = Y_{FAME} = 93.65 + 0.5x_1 - 0.088x_3 + 0.533x_1x_2 - 0.25x_1x_3 + 0.14x_2x_3 + 1.287x_1x_2x_3 \tag{10}$$

$$y_2 = Y_G = 81.91 + 2.151x_1 - 3.481x_2 - 2.129x_3 - 2.371x_1x_2x_3 \tag{11}$$

$$y_3 = \tau_G = 14.25 - 6.25x_1 + x_1x_2 - 1.25x_1x_3 \tag{12}$$

Referring to the effect of process factors, *i.e.*, fixed bed height ($x_1$), operating temperature ($x_2$), and reactant superficial velocity ($x_3$), on the process responses, regression equations (10)-(12) indicate the following issues: (i) $Y_{FAME}$ increases with $x_1$, $x_1x_2$, $x_2x_3$, and $x_1x_2x_3$, as well as it decreases with an increase in $x_3$ and $x_1x_3$; (ii) $Y_G$ increases with $x_1$ and decreases with an increase in $x_2$, $x_3$, and $x_1x_2x_3$; (iii) $x_1$ and $x_1x_3$ interaction have a negative effect on $\tau_G$, whereas $x_1x_2$ interaction has a positive effect. Statistical model described by Eqs. (10)-(12) could be applied to estimate the performances of transesterification process for factor levels within the ranges considered in the statistical analysis, *i.e.*, *h*=20-40 cm, *t*=55-65 °C, and *w*=0.14-0.28 cm/s.

## 4. Conclusions

Transesterification of fresh sunflower oil with methanol to FAME and glycerol was continuously performed in a fixed-bed catalyst reactor. A supported catalyst was prepared by impregnation of activated carbon (AC) with a 2M KOH solution followed by thermo-chemical activation (at 750 °C under $CO_2$ atmosphere) of impregnated precursor. Activated catalyst (KOH/AC) was packed in a water-jacketed glass column (1.6 cm internal diameter and 55 cm height) and tested in the transesterification.

Fresh oil and methanol (1/6 molar ratio) were mixed, heated, and further passed (for 1 h) through the fixed-bed catalyst. Reactor effluent, consisting mainly of FAME, glycerol, and unreacted methanol, was recirculated in the process.

The effects of process factors, *i.e.*, fixed bed catalyst height (*h*=20, 40 cm), operating temperature (*t*=55, 65 °C), and reactant superficial velocity (*w*=0.14, 0.28 cm/s), on its responses in terms of FAME yield, glycerol yield, and time of glycerol forming were evaluated using a $2^3$ factorial plan. FAME yield (91.60-95.74%) increased with *h*, *ht*, *tw*, and *htw*, whereas it decreased with an increase in *w* and *hw* interaction. Glycerol yield (73.31-90.48%) increased with *h* and decreased with an increase in *t*, *w*, and *htw* interaction. The time of glycerol forming (6-23 min) was negatively influenced by *h* and *hw* interaction, whereas *ht* interaction had a positive effect on it. Regression equations obtained by processing the experimental data could be applied to predict the transesterification performances for factor levels within the ranges considered in the study.

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