Biodiesel production optimization using γAl_2O_3 based catalysts

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ABSTRACT

Abstract: The transesterification reaction of soybean oil with methanol is studied with different γAl_2O_3 heterogeneous catalysts. The catalysts used are K-γAl_2O_3, Na-γAl_2O_3, Li-γAl_2O_3, Ca-γAl_2O_3 and Ba-γAl_2O_3 both 5% and 10% in metal content are prepared by impregnation. The first study concluded that only two of the ten catalysts studied (K-γAl_2O_3, Na-γAl_2O_3 with 10% content in metal) gave a FAME (Fatty acid methyl esters) yield result higher than 90%. A mixed-level design of experiments is used to know which the best catalyst is between the K-γAl_2O_3 and the Na-γAl_2O_3 with 10% content in metal. Also, a factorial design of experiments and central composite designs have been used with K-γAl_2O_3 with 10% content in metal, which resulted the most active catalyst. The chosen variables are reaction time, initial catalyst percent and methanol:oil ratio, while the response is the biodiesel yield. Soybean heterogeneous transesterification is strongly affected by the methanol:oil ratio and it is slightly affected by the catalyst percent. Nevertheless, reaction time has no important effects in the biodiesel yield. Finally, the industrial application of the soybean biodiesel as determined through the study of the quality control of the biofuel and the reuse of K-γAl_2O_3 with 10% content in metal.

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1. Introduction

Nowadays, one of the main objectives of mankind is to search how to improve clean and environmentally-friendly energy sources. Biodiesel, the valued product of the transesterification of tri-glycerides, is one of these sources and keeps maintaining the promise to substitute part of the petroleum diesel consume [1]. Transesterification can be carried out with different short-chain alcohols, although the most used alcohol is methanol due to its reactivity [2].

Transesterification involves three consecutive and reversible reactions [3]; where monoglycerides, diglycerides and glycerol are also produced. If the used catalyst is homogeneous, it will be within the mixture of the reaction. However, the heterogeneous solid catalyst can be removed easily from the product, making the overall purification much more feasible. Moreover, there are more advantages when a heterogeneous catalyst is used in the

transesterification: catalyst reusability, easy separation of glycerol and much simpler handling and management of waste [4]. On the other hand, there are two important drawbacks in the use of heterogeneous catalysts which are the slow transesterification reaction rate and the viscosity increase of the biodiesel [4]. However, the entire process is still feasible using heterogeneous catalysts due to the advantages mentioned before.

Currently, transesterification reaction can be carried out by five different kinds of catalysts. The first type of catalyst is the alkali homogeneous which is very active and inexpensive but the purification steps are more tedious [5–18]. Secondly, acid homogenous catalysts are suitable for oils with a high content in FFA (Free fatty acids) but the reaction rate is usually low and their separation is difficult [5,6,10,13,19]. Thirdly, there are also alkali heterogeneous catalysts which require high alcohol:oil ratio to be effective but are more environmentally-friendly because they reduce waste emissions [5,6,11,20–22]. The fourth kind of catalysts is the acid heterogeneous which are less corrosive and toxic but is more costly and presents more diffusional problems than the homogeneous catalyst [5,9,20,23]. The last kind of catalyst is the enzyme which can be easily separated, regenerated and reused but, on the other hand, has a low reaction rate and easily loses activity [5,8,12,13,24–30].

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Heterogeneous catalysts have been largely used in the last few years in different fields of research. These catalysts are alkali metal oxides and derivatives [31,32], alkaline earth metal oxides and derivatives [33,34], transition metal oxides and derivatives [35], mixed metal oxides and derivatives [36], ion exchange resins type acid heterogeneous catalyst [37], sulfated oxides as an acid heterogeneous catalyst [38], carbon based heterogeneous catalysts [39], waste material used [40] as catalysts and enzymes [30].

The main objective of this study is to know how the transesterification reaction of soybean oil behaves with different γAl_2O_3 based catalysts. Once the discrimination between the 10 catalysts studied is done the next step is the optimization of the transesterification process with the two better catalysts. This behavior is evaluated thanks to factorial design and response surface methodology. Also, according to the statistical analysis, the influences of methanol:oil ratio, reaction time and catalyst percent on biodiesel yield have been studied and the maximum value of biodiesel yield is reached with these conditions for both potassium and sodium based catalysts: 4 h, 7.28 methanol:oil ratio, 6% of catalyst.

2. Materials and methods

2.1. Reagents and materials

Refined soybean oil is supplied by Gracomsa Alimentaria (Valencia, Spain). The characteristics of the soybean oil are determined according to AOCS official method and UCM method. The main properties and the composition of the oil used as raw material can be found in Table 1. Certified methanol of 99.8% purity is supplied by COR (Madrid, Spain). GC (Gas chromatography) standards were supplied by Sigma Aldrich. The catalysts are K-γAl_2O_3, Na-γAl_2O_3, Li-γAl_2O_3, Ca-γAl_2O_3 and Ba-γAl_2O_3 (5% and 10% in metal) from La Plata University (Argentina).

KOH, NaOH, LiOH, Ba(OH)$_2$ and Ca(OH)$_2$ based catalyst supported on γ-Al$_2$O$_3$ were prepared, which will be designated as K-γAl_2O_3 Na-γAl_2O_3, Li-γAl_2O_3, Ca-γAl_2O_3 and Ba-γAl_2O_3. The γ-Al$_2$O$_3$ (*Air Products*) was ground to a particle size of 60–100 mesh and then calcined for 1 h at 450 °C. The precursor solutions were prepared by dissolving the calculated mass of the hydroxide in 250 mL of distilled water. The impregnation was carried out in a rotary evaporator at 50 °C, 60 rpm and a pressure of 22 mm Hg which corresponded to the same molar concentration as that of the potassium-based catalyst. Before being used, the catalyst was calcined at 350 °C for 3 h. The surface characteristics of the samples were determined by N$_2$ adsorption (77.4 K) in a Micromeritics Accusorb 2100E instrument. SEM micrographs were obtained with

a scanning microscope Philips SEM 505. X-ray diffraction (XRD) was conducted using Cu Kα ($\lambda = 0.154$ nm) as a radiation source in an automatic X-ray Diffractometer (Philips PW 1740). The samples were scanned in the range of $2\theta = 5–75°$ at a scanning speed of 1 min^{-1}. CO$_2$ adsorption/desorption studies were conducted to quantify the basic site density of the catalysts, which were carried out with a Shimadzu TGA-50 instrument. The samples were pretreated at 100 °C in a 100 mL min^{-1} N$_2$ flow. Subsequently, CO$_2$ (purity 99.8%) was introduced at a flow rate of 100 mL min^{-1}. The variation of the sample weight was followed to determine the adsorption/desorption performance at 75 °C. The results associated to K/γ-Al$_2$O$_3$ and Na/γ-Al$_2$O$_3$ with 10% in metal are depicted in Table 2.

2.2. Experimental setup

Experiments have been carried out in a 500 cm^3 three necked batch reactor, where the total volume of soybean oil is 170 cm^3. The reactor is equipped with a reflux condenser to return the evaporated methanol back to the reactor, a mechanical stirrer and a stopper to remove samples. The reaction temperature was achieved immersing the reactor into a thermostatic bath (HETO) with an electrical device connected to a PID controller which allows a temperature control of ±0.1 °C [3].

Experiments have been performed according to the following procedure: Soybean oil is added to the reactor. When the set temperature is reached the catalyst and the methanol are introduced in the reactor, and just at that moment the reaction time is considered zero. The mixture is refluxed at 60 °C at 400 rpm to avoid mass transfer limitations. The temperature is set at 60 °C because of the partial evaporation of the methanol. During the experiments the pressure and impeller speed are maintained constant. After the reaction, the solid catalyst is removed by filtration. The mixture is transferred to a separatory funnel, allowing glycerol to separate by gravity for 1 h. When the layer of glycerol removed, the methyl ester product is washed with two volumes of water. Finally, the methanol is eliminated from the product through a vacuum distillation at 10 mm Hg. Samples have been taken according to the prepared design of experiments and analyzed by gas chromatography.

2.3. Product analysis

GC (Gas chromatography): FAME (Fatty acid methyl esters), monoglycerides, diglycerides and tryglycerides were monitored using a Hewlett–Packard 5890 series II cromatograph, connected to a Hewlett–Packard 3396SA integrator, equipped with a FID (flame ionization detector) using a fused silica capillary column The injection system was split–splitless and the carrier gas was helium at a flow of 1 ml/min. The injector and detector temperatures were 275 and 325 °C, respectively. A temperature program was used starting with a 1 min hold at 120 °C; followed by a ramp rate of 5 °C min^{-1} to 320 °C. The analysis of the standards and the reaction products were prepared dissolving the samples in CS$_2$ and 1 µl was injected into the GC equipment. The used procedure to characterize

Table 1
Fatty acid composition (wt%) and properties of soybean oil.

Fatty acid (wt%)	
Lauric C12:0	0.1
Miristc C14:0	0.3
Palmitic C16:0	10.9
Estearic C18:0	3.2
Oleic C18:1	24
Linoleic C18:2	54.5
Linolenic C18:3	6.8
Properties	
Viscosity (cSt)	35.4
Iodine (I$_2$/100g)	134
Oxidation stability (*h*)	6.7
Flash point (°C)	215
PP (°C)	−9
Acidity (mg/g)	0.1
Moisture (%)	0.04
Density (g/cm^3)	0.915

Table 2
Textural characteristics and CO$_2$ adsorption percentage of the studied catalyst.

Catalyst	Surface area (cm^2/gr)	Pore volume (cm^3/gr)	CO$_2$ adsorption(g/g) $\times$ 100
γ−Al$_2$O$_3$	252.13	0.36	0.70
K/γ−Al$_2$O$_3$ (10%)	168.92	0.29	2.70
Na/γ−Al$_2$O$_3$(10%)	172.0	0.43	–

the samples was the internal standard. N-Octyl octanoate was used as internal standard.

Acid value: Acid value for the soybean biodiesel obtained in this study was determined following the method specified in ASTM Method D 664, using a Metrohm Swiss model 702 SM Titrino.

Iodine value: Iodine value in this study was determined following the method specified in AOCS Official Method Cd 1-25, using a Metrohm Swiss model 702 SM Titrino.

Kinematic viscosity: The kinematic viscosisy of the soybean oil was determined by the method ASTM D445 using a Cannon-Fenske Viscosimeter.

Oxidation stability: Oxidation Stability in this study was determined following the method specified in AOCS Official Method Cd 12b-92, using a model 743 Rancimat instrument.

CFPP (Cold filter plugging point): Soybean biodiesel CFPP was determined by the method ASTM D6371, using a CFFP tester (ISL CPP 97-2).

CP (Cloud point): Soybean biodiesel CP was determined by the method ASTM D2500, using a CFFP tester (ISL CPP 97-2).

PP (Pour point): Soybean biodiesel PP was determined by the method ASTM D97, using a CFFP tester (ISL CPP 97-2).

Water content: Water content in this study was determined following the method specified in ISO EN12937, using a Metrohm Swiss model 702 SM Titrino.

Flash point: Flash point in this study was determined following the method specified in ASTM D93, using a Petrotest PM4 (Instrumentación Analítica S.A.).

Cetane number: Iodine value in this study was determined following the method specified in ASTM D613, using an automatic IROX DIESEL (Grabner Instruments).

2.4. Statistical analysis

These techniques have been largely used to optimize chemical, physical and physic-chemical processes. In this study, two different kinds of experimental designs have been used. Firstly, a mixed level factorial design in order to know which the best catalyst between K-γAl$_2$O$_3$ and Na-γ-Al$_2$O$_3$ with 10% of metal content is and secondly, a standard Response Surface Methodology, called a CCD (Central composite design), to study the heterogeneous transesterification process with the best catalyst.

Mixed-level factorial design: A mixed-level factorial design $3 \cdot 2^3$ with four factors and one response (24 experiments) to know how the transesterification reaction is carried out with K-γAl$_2$O$_3$ and Na-γ-Al$_2$O$_3$ with 10% of metal content, was done. The four factors are the reaction time (X_t), the methanol:oil molar ratio (X_R), the catalyst percent (X_t), and the used catalyst, K-γAl$_2$O$_3$ or Na-γ-Al$_2$O$_3$, (X_{K-Na}) while the response is the FAME yield. In Table 4 is charted the design of experiments used for the preliminary study with the two chosen catalysts.

Full factorial design: A Central Composite Design and response surface methodology were applied. The Full Factorial Design is made for K-γAl$_2$O$_3$ catalyst with a 10% of metal content because it is the best catalyst proved as it was tested in the preliminary experiments. The application of this method requires the adequate selection of responses, factors and levels. The response selected is the molar yield of biodiesel while the factors are the reaction time (X_t), the initial catalyst percent (X_C) and the methanol:oil ratio (X_R).

3. Results

The first step in this study is the discrimination among the ten γ-Al$_2$O$_3$ based catalysts through a transesterification reaction. Secondly, the heterogeneous transesterification of soybean oil using γAl$_2$O$_3$ based catalysts as catalysts was carried out by two different factorial designs of experiments to determine the best catalyst and to optimize the heterogeneous transesterification process.

3.1. Preliminary experiments

The ten studied catalysts are K-γAl$_2$O$_3$, Na-γAl$_2$O$_3$, Li-γAl$_2$O$_3$, Ca-γAl$_2$O$_3$ and Ba-γAl$_2$O$_3$ with a 5% metal content and K-γAl$_2$O$_3$, Na-γAl$_2$O$_3$, Li-γAl$_2$O$_3$, Ca-γAl$_2$O$_3$ and Ba-γAl$_2$O$_3$ with a 10% metal content. The operation conditions are 6 h of reaction time, a 5% of the catalyst percent and a methanol:soybean oil ratio of 6. The obtained results by the transesterification reaction for each catalyst are depicted in Fig. 1. A previous work quantified the catalytic activity of the blank γAl$_2$O$_3$ for the transesterification of the rapeseed oil at 60 °C for 1 h and 9:1molar ratio, obtaining a FAME yield of 3.17% [41]. In addition [42], studied the transesterification of soybean oil with K-γAl$_2$O$_3$ and Na-γAl$_2$O$_3$ with a metallic charge of 8% at 120 °C, 6 h of reaction time and 1% of catalyst percent obtaining a FAME yield of 98.9 and 97.1, respectively. As stated before, this paper deals with the optimization of the process using Design of Experiments and Response Surface Methodology while [42] is more focused on the characterization of the catalysts. Therefore, there is a clear increase in the catalytic activity when alkaline or earth alkaline metals are added in the blank γAl$_2$O$_3$.

According to the results, the most active catalysts are K-γAl$_2$O$_3$, Na-γAl$_2$O$_3$ with a 10% metal content. Also, Li-γAl$_2$O$_3$, Ca-γAl$_2$O$_3$ and Ba-γAl$_2$O$_3$ either 10% metal content or 5% metal content transesterification experiments give poor results in the FAME yield. As it was stated in previous researches, the surface Al-O-Metal group is the active site in the γAl$_2$O$_3$ based catalysts [34,41–43]. These active sites can extract protons from the methanol and thereby methoxide ions are produced to carry out the transesterification reaction [41]. Therefore, the catalysts with the highest capacity to produce the methoxide ion are the most active because they have more base strength [44]. The stability of the aluminate groups are KAlO$_2$ > NaAlO$_2$ > LiAlO$_2$ > Ca$_{0.5}$AlO$_2$ > Ba$_{0.5}$AlO$_2$ [45] which coincides with the activity of the catalysts studied. In addition, the catalysts with the higher content in metal are the most actives because there are more Al-O-Metal groups on the surface of the catalysts. These are the reasons why the chosen catalysts for the design of experiments are K-γAl$_2$O$_3$, Na-γAl$_2$O$_3$ with 10% metal content. The results associated to the chosen catalysts are depicted in Table 2.

3.2. Choice of the best catalyst

The results in the design of experiments proposed for the two most active heterogeneous catalysts are charted in Table 3. The
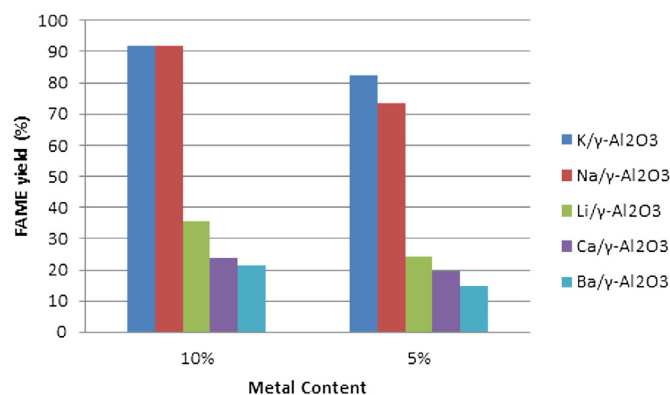

Fig. 1. FAME yield obtained in the γ-Al$_2$O$_3$ based catalysts.

Table 3
Mixed-level design of experiments.

Run number	Time (h)	Catalyst percent (%)	Ratio (−)	Catalyst	X_t	X_c	X_R	X_R	Yield (%)
1	2	4	6	K/γ-Al$_2$O$_3$	−1	−1	−1	−1	90.6
2	2	4	6	Na/γ-Al$_2$O$_3$	−1	−1	−1	1	85
3	2	5	6	K/γ-Al$_2$O$_3$	−1	1	−1	−1	90.7
4	2	5	6	Na/γ-Al$_2$O$_3$	−1	1	−1	1	91
5	2	4	9	K/γ-Al$_2$O$_3$	−1	−1	1	−1	91.4
6	2	4	9	Na/γ-Al$_2$O$_3$	−1	−1	1	1	89.4
7	2	5	9	K/γ-Al$_2$O$_3$	−1	1	1	−1	93.2
8	2	5	9	Na/γ-Al$_2$O$_3$	−1	1	1	1	91.7
9	4	4	6	K/γ-Al$_2$O$_3$	0	−1	−1	−1	91.1
10	4	4	6	Na/γ-Al$_2$O$_3$	0	−1	−1	1	91.1
11	4	5	6	K/γ-Al$_2$O$_3$	0	1	−1	−1	91.5
12	4	5	6	Na/γ-Al$_2$O$_3$	0	1	−1	1	91
13	4	4	9	K/γ-Al$_2$O$_3$	0	−1	1	−1	91.5
14	4	4	9	Na/γ-Al$_2$O$_3$	0	−1	1	1	91.7
15	4	5	9	K/γ-Al$_2$O$_3$	0	1	1	−1	92.9
16	4	5	9	Na/γ-Al$_2$O$_3$	0	1	1	1	92
17	6	4	6	K/γ-Al$_2$O$_3$	1	−1	−1	−1	91.6
18	6	4	6	Na/γ-Al$_2$O$_3$	1	−1	−1	1	91.6
19	6	5	6	K/γ-Al$_2$O$_3$	1	1	−1	−1	91.7
20	6	5	6	Na/γ-Al$_2$O$_3$	1	1	−1	1	91.7
21	6	4	9	K/γ-Al$_2$O$_3$	1	−1	1	−1	91.6
22	6	4	9	Na/γ-Al$_2$O$_3$	1	−1	1	1	91.9
23	6	5	9	K/γ-Al$_2$O$_3$	1	1	1	−1	93
24	6	5	9	Na/γ-Al$_2$O$_3$	1	1	1	1	92.7

main conclusion is that K-γAl$_2$O$_3$ has a slightly better performance in the transesterification reaction than the Na-γAl$_2$O$_3$, especially at lower catalyst percent, soybean oil: methanol molar ratio and reaction time levels. According to the obtained results in Table 4 of the main influences among factors and interactions, K-γAl$_2$O$_3$ is a better catalyst compared to Na-γAl$_2$O$_3$ because higher FAME yields are reached sooner and in more moderated conditions. That is why the chosen catalyst in order to do a Central Composite Design is K-γAl$_2$O$_3$ with 10% in metal content. Nevertheless, the overall activity of these two heterogeneous catalysts is pretty similar. Therefore, the heterogeneous potassium and sodium catalysts have the same behavior as the homogeneous potassium and sodium hydroxides in terms of similarity [6]. For each design of experiments the biodiesel yield results are fitted to a linear model and the statistical models are obtained for K-γAl$_2$O$_3$ and Na-γAl$_2$O$_3$ with 10% in metal content experiments (Table 4 and Equations (1) and (2)).

3.3. Optimization of the heterogeneous biodiesel process

According to the preliminary experiments and the mixed-level factorial design previously applied the best catalyst among the ten catalysts tested is the K-γAl$_2$O$_3$ with 10% in metal content. For this reason, the full factorial design is used with K-γAl$_2$O$_3$ with 10% in metal content to optimize the biodiesel process.

The levels of the chosen factors are given in Table 5, including the center and star points. The center points together with the factorial points make the evaluation of the curvature effect possible. The star points are additional and necessary experiments to the factorial design in order to determine the nonlinear model.

Table 4
Main influences and interaction of the proposed mixed-level designs of experiments.

	$\bar{y}$	I_t	I_C	I_R	$I_{K/Na}$	I_{tC}	I_{tR}	$I_{t-K/Na}$	I_{CR}
Global	91.32	1.61	1.21	1.2	−0.84	−0.98	−0.71	1.09	—
K-γ-Al$_2$O$_3$	91.73	0.5	1.07	0.97	—	−0.5	—	—	0.67
Na-γ-Al$_2$O$_3$	90.9	2.7	1.33	1.57	—	−0.95	−1.85	—	−0.44

Table 5
Levels of factors for the central composite design.

Factor	Levels				
	$-\alpha$	−1	0	1	α
Time (h)	1.32	2	3	4	4.68
Met:oil ratio (−)	4.6	5.28	6.28	7.28	7.96
Catalyst percent (%)	3.32	4	5	6	6.68

Fixed variables: $T = 60\ °C$, pressure = 710 mm Hg.
Note: $-\alpha$ low start point level; −1: low factorial point level; 0: central point level; +1: high factorial point level; $+\alpha$: high star point level.

3.3.1. Linear stage

First of all, a linear stage is made through 8 experiments because a 2^3 factorial design is studied. Also, six more experiments are carried out in order to evaluate the experimental error (center points). Coded factor and natural factor levels with the biodiesel yield results corresponding to each experiment are charted in Table 6. Experiments are carried out randomly. The biodiesel yield is determined from the initial volume of soybean oil poured in the reactor.

For determining the main effects and interaction effects of the reaction time, the methanol:oil ratio and the catalyst percent a statistical analysis is made using the coded and natural factors levels and their response. The results of this analysis are charted in Table 7. Confidence interval and main effects and interactions are used for determining the effect of the factor in the response. Thus, the conclusion is that, on one hand, the reaction time is not significant because its influence is a bit lower than the confidence interval and, on the other hand, the methanol:oil ratio and the catalyst percent have influence on biodiesel yield.

Finally, the biodiesel yield results are fitted to a linear model and, therefore; the statistical model and industrial model are obtained (Equations (1) and (2)).

Statistical model:

$$\text{Biodiesel yield} = 90.57 + 1.73X_R + 0.98X_C - 0.80X_{tC} - 1.275X_{RC} + 0.80X_{tRC} \quad [1]$$

$(r = 0, 97)$

Industrial model:

$$\text{Biodiesel yield} = 34.83 + 6.23X_R + 8.98X_C + 0.61 X_{tC} - 0.96X_{RC} - 0.10X_{tRC} \quad [2]$$

$(r = 0, 93)$

The difference between the statistical and the industrial analysis is that the factors used in statistical model are coded and in the industrial model are natural. These equations are only valid within the experimental range studied.

Since the curvature has no significance in the FAME yield for the studied variables, the linear model predicted in this section is the equation used for the surface response (Fig. 2). In Fig. 2, the time chosen is 3 h because it is the value that corresponds to the center point ($X_t = 0$). The contour plot is represented in Fig. 3 and the same way the reaction time is fixed at 3 h in the surface response and the axes are the methanol:oil ratio and the catalyst percent. On one hand, the linear fitting and its residual distribution of the predicted data to the experimental data are observed in Fig. 4 and Fig. 5, respectively. On the other hand, the curve fitting and its residual distribution are represented in Fig. 6 and Fig. 7. As seen in Figs. 4–7, the linear fitting is more correct than the curve fitting because there is no tendency in the residual distribution as seen in Fig. 5.

Table 6
Experimental matrix and results.

Stage/type of experiment	Run number	Time (h)	Ratio (−)	Cat (%)	X_t	X_R	X_C	Yield (%)
Linear stage	1	2	5.28	4	−1	−1	−1	84.1
	2	4	5.28	4	1	−1	−1	89.1
	3	2	7.28	4	−1	1	−1	92.3
	4	4	7.28	4	1	1	−1	92.9
	5	2	5.28	6	−1	−1	1	91.8
	6	4	5.28	6	1	−1	1	90.4
	7	2	7.28	6	−1	1	1	91.7
	8	4	7.28	6	1	1	1	92.3
Center points	9	3	6.28	5	0	0	0	92.4
	10	3	6.28	5	0	0	0	92.0
	11	3	6.28	5	0	0	0	89.0
	12	3	6.28	5	0	0	0	90.9
	13	3	6.28	5	0	0	0	90.2
	14	3	6.28	5	0	0	0	91.8
Non-linear stage								
Star points	15	1.32	6.28	5	−1.68179	0	0	91.2
	16	4.68	6.28	5	1.68179	0	0	91.4
	17	3	4.6	5	0	−1.68179	0	90.8
	18	3	7.96	5	0	1.68179	0	92.5
	19	3	6.28	3.32	0	0	−1.68179	91.7
	20	3	6.28	6.68	0	0	1.68179	91.6

Note: t: time; R: methanol to vegetable oil molar ratio; C: catalyst percent; X: coded value; Yield: biodiesel yield.

3.3.2. Non-linear stage

A full central composite design, according to Box and Wilson [46], incorporates factorial points, star points and center points, as is shown in Table 6. Therefore, six more experiments, called star points, are included in the two-level factorial design for the reaction time, the methanol:oil ratio and the catalyst percent. Additionally, star points are coded as $\pm\alpha$, where α is the distance between the origin to the star point, and it can be calculated with the expression $\alpha = 2^{n/4}$ (in this case, $n = 3$ and $\alpha = 1.681$).

In the linear stage section, the results related to the significance of the curvature are charted in Table 7. The main conclusion of Table 7 is that the confidence curvature interval is higher than the curvature, and therefore, the curvature has no significance and it is not necessary to obtain a quadratic model for predicting how the biodiesel yield changes with the factors.

4. Discussion

In this section, the influence of the studied variables, which are the reaction time, the methanol:oil ratio and the catalyst percent, are discussed. Also, the influence of the interactions will be discussed from the statistical model.

4.1. Reaction time influence

The experimental range studied for the reaction time is from 2 to 4 h as is mentioned before. The most important conclusion about the influence of the reaction time on the FAME yield in the heterogeneous transesterification using K-γAl$_2$O$_3$ as catalyst is that it has no importance in the experimental range studied. Although reaction time is not a significant variable it affects the transesterification in a slightly positive way. Therefore, 4 h of reaction time gives the highest value of FAME yield, although it is not the best value when scaling up the heterogeneous process because of the slight alteration of the yield when the reaction time is increased.

Table 7
Statistical analysis of 2^3 factorial design.

	Response biodiesel yield (%)
Main effects and interactions	$\bar{y} = 90.57$
	$I_t = 1.2$
	$I_R = 3.45$
	$I_C = 2$
	$ItR = -0.6$
	$ItC = -1.6$
	$IRC = -2.55$
	$ItRC = 1.6$
Significance test: c confidence level: 95%	
Mean response	90.57
Standard deviation	$t = 2.571$ $s = 1.28$
Confidence interval	±1.35
Significant variables	R, C, tC, RC, tRC
Significance of curvature	
Curvature	−0.475
Confidence curvature interval	±1.78
Significance	No

Note: t: time, R: methanol to vegetable oil ratio, C: catalyts concentration, I: main effect: $s =$ standard deviation.

Fig. 2. Response surface of ester yield vs. methanol:oil ratio and catalyst percent. Reaction time: 3 h.

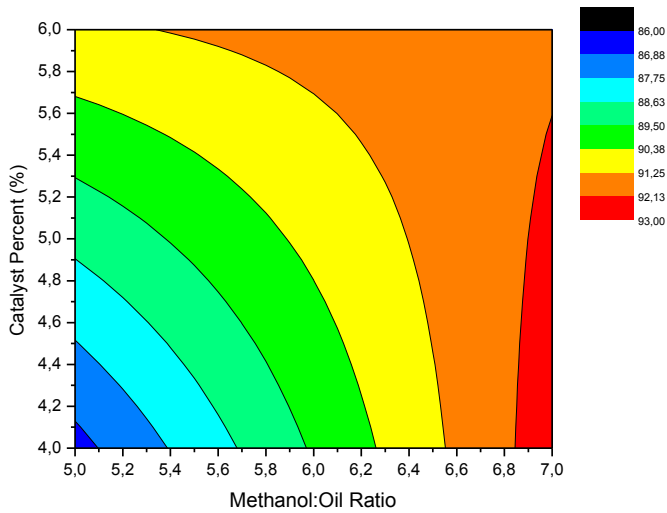**Fig. 3.** Contour plot of ester yield vs. methanol:oil ratio and catalyst percent. Reaction time: 3 h.

Fig. 5. Linear fitting residual distribution.

4.2. Methanol/oil molar ratio influence

The experimental range studied for the methanol:oil ratio is from 5.28 to 7.28 as is mentioned before. According to the statistical analysis, this variable has the most important effect on heterogeneous transesterification using K-γAl$_2$O$_3$. Therefore, the higher the methanol:oil ratio is the higher FAME yield will be obtained. Logically, the transesterification chemical equilibrium is displaced towards the formation of more products when the value of the methanol:oil ratio is increased. This reaction behavior is the same as the KOH homogeneous catalyst [4].

4.3. Influence of the catalyst percent

The experimental range studied for the reaction time is from 4 to 6% wt as is mentioned before. From the statistical analysis, the main conclusion about this variable is that it has a positive effect on the FAME yield but is lower than the methanol:oil ratio. Therefore, the higher the catalyst percent is in the transesterification reactor, the higher the FAME yield will be. The catalyst percent value which
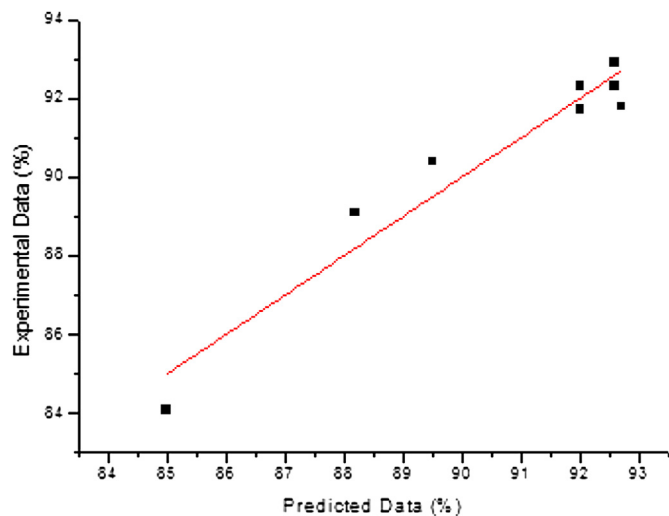
gives the best result is 6%. However, there is an optimum catalyst concentration where the reaction reaches its maximum. Starting from this optimum catalyst, mass transport limitation influences the transesterification reaction, thus, adding more catalyst in the middle of the reaction does not mean a higher FAME yield [40]. In this experiment, the catalyst content range studied does not permit identifying where the mass transport limitation starts, but it can be guaranteed through the studied design of experiments this value is higher than 6%.

4.4. Influence of the interaction

First of all, the t-R interaction has a slight positive effect on the transesterification reaction, although it has no significance according to the statistical analysis. Secondly, the $t-C$ interaction has a negative effect on the FAME yield and does not have significance. Thirdly, the $t-R$ interaction has the highest negative effect on this heterogeneous reaction regarding all the studied interactions. Finally, the $t-R-C$ interaction has a positive effect and it has importance.

Fig. 4. Experimental data vs. predicted data for biodiesel yield according to statistical model linear fitting.

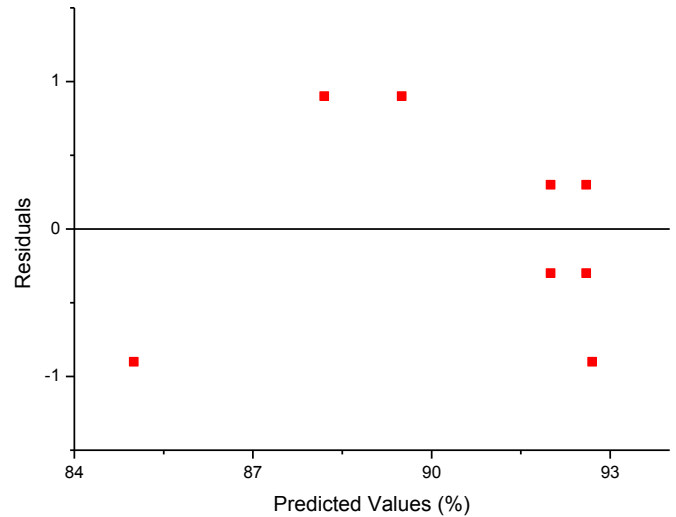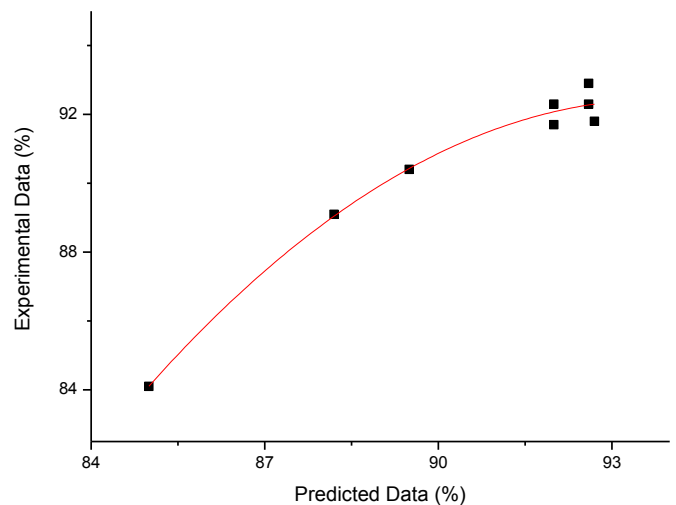**Fig. 6.** Experimental data vs. predicted data for biodiesel yield according to statistical model curve fitting.
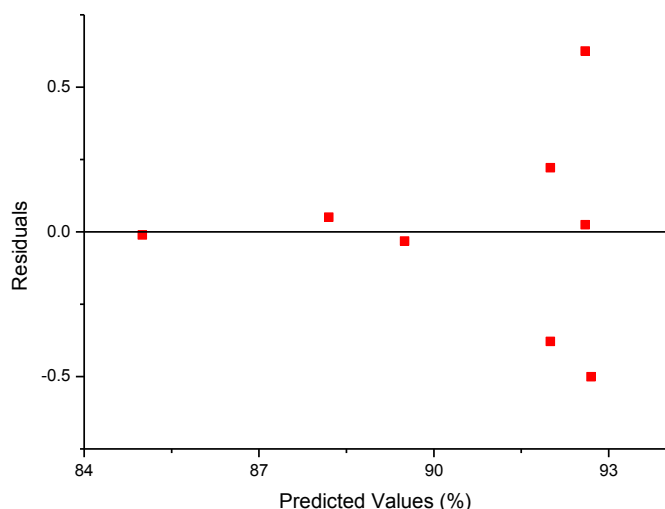
Fig. 7. Curve fitting residual distribution.

4.5. Analysis of the response: FAME yield

The surface response obtained by the statistical model can be seen in Fig. 1. This Figure represents the variation in the FAME yield when the methanol:oil ratio and the catalyst percent change in the studied experimental range. The reaction time has no significance, as it is proved in the results section, and is fixed at 3 h (center point). According to the surface response the maximum value for the FAME yield is reached when the methanol:oil ratio is at its maximum value and when the percent of solid catalyst is about 5%. Moreover, in Fig. 2 can be seen that the experimental results are fitted correctly and there are no tendencies in the linear regression fit.

5. Industrial application of γAl_2O_3 based cataysts

5.1. Recycling of K-γAl_2O_3

From an economic point of view, the more cycles the catalyst is used the better the performance is. The reuse of K-γAl_2O_3 is studied by two recoveries of the catalyst. Once the reaction is completely finished, the product is filtered and the solid is recovered. Next, the catalyst is cleaned with 100 ml of methanol and dried in the oven at 150 °C. Part of the byproduct, glycerol, is retained in the catalyst and the washing with a polar solvent is required for the reuse of the

Table 8
Quality control of biodiesel from soybean oil.

Property	Value	EU standard EN 14214
Viscosity at 40°C (mm^2/s)	4.8	3.50–5.00
Water content (%)	0.03	Max. 0.05
Ester content (%wt)	99.2	Min. 96.5
MG content (%wt)	0.8	Max. 0.8
DG content (%wt)	−	Max. 0.2
TG content (%wt)	−	Max. 0.2
Acid value (mg KOH/g)	0.14	Max. 0.5
Iodine value (mg I2/g)	130.4	Max. 120
Oxidation stability (h)	6.3	Min. 6
Flash point (°C)	161	Min. 120
Cetane number	49	Min. 51
CFPP (°C)	−3	Summer $\leq$ 0
European zone 3		Winter $\leq$ −10
PP (°C)	−3	−
CP (°C)	1	−

catalyst. In this experiment, the used soybean is refined and therefore, there are no traceable amounts of soap.

There are several factors which have contribution on the deactivation of these catalysts. Previous studies have proved the negative effect of the soap on the reusability of different heterogeneous catalysts, such as CaO [1]. Another source of deactivation is the water presence or CO_2 either in the middle of the reaction or environmentally. Wan et al. [47] demonstrated that removing water and carbon dioxide was an effective way to elevate the catalyst stability in methanol when sodium aluminate is used as catalyst. But, the most likely deactivation reason is the leakage of potassium in the glycerol phase, losing the active part of the solid catalyst [48]. In a previous research the leaching process for K-γAl_2O_3 has been described (Equation (3)) assuming that KAlO2-like (or K−O−Al) species would be formed at the surface of the solid [43].

$$KAlO2 + CH_3OH \rightarrow AlOOH + K^+ + CH_3O^- \qquad [3]$$
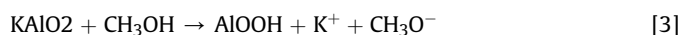
There is a marked drop of the FAME yield in the transesterification with the catalyst obtained in the first and the second recoveries with respect to the fresh catalyst. The FAME yield is reduced in the transesterification with the catalyst recovered in the first and in the second cycles by 28.5% (63.8% for the first cycle and 35.3% for the second cycle) which means the same deactivation has been produced. In conclusion, this catalyst did not show good recycling ability in either the second or third recoveries.

5.2. Quality control of biodiesel

Once the optimum conditions for the heterogeneous transesterification using K-γAl_2O_3 with 10% of metal content as catalyst have been determined (4 h, 7.28 methanol: ratio and 4% wt catalyst), some properties of the purified biodiesel have been measured. The quality parameters quantified were: Kinematic Viscosity, water content, ester content, monoglyceride content, diglyceride content, triglyceride content, acid value, iodine value, flash point, oxidation stability (h), CFPP (Cold filter plugging point), CP(Cloud Point), PP (Pour Point) and cetane number. The results have been compared with the European Union Standard EN 14214 and are charted in Table 8.

Since ester content, kinematic viscosity and water content are within the Standard EN 14214, the transesterification reaction using K-γAl_2O_3 with 10% of metal content is completed and the obtained product has been separated and purified correctly. Monoglyceride, diglyceride and triglyceride contents also fulfill the European requirements, therefore, the reaction is completed as aforementioned. The iodine value is higher than the minimum value requested in the European Standard because of the composition of the soybean oil (high proportion of unsaturated acids), however the acid value and the flash point are within the Standard. The cetane number is slightly lower than the specified limit and the CFPP only is valid according the standard in summer time. A possible solution is the use of blends from different raw materials in order to produce a biodiesel which fulfill all the requirements according to UNE EN 14214 [49–51].

6. Conclusions

The main conclusions obtained in this study are:

- Among ten different heterogeneous catalysts supported on γ-Al_2O_3 the most actives are K-γAl_2O_3 and Na-γAl_2O_3 with a 10% content in metal. The FAME yield is close to 92% in both cases after 6 h of reaction time.

- A portion of the decanted glycerol is retained in the catalyst, and this fact lowers the activity of the catalyst in its reuse. In addition, the washing steps of the catalyst become more difficult.
- A mixed-level design of experiments is made for K-γAl$_2$O$_3$ and Na-γAl$_2$O$_3$ with 10% metal content and the results show that their activity is pretty similar at high reaction times; however the potassium based catalyst needs more mild conditions to reach the maximum yield. The studied variables in the experiment are the catalyst content, the methanol:oil ratio and the reaction time.
- A K-γAl$_2$O$_3$ Full Factorial Design is made by studying the same variables as in the previous design of experiments: catalyst content, methanol:oil ratio and reaction time. Reaction time is no significant in the experimental range studied, nevertheless; the catalyst content and the methanol:oil ratio are significant in the transesterification process.
- The most influential variable in this heterogeneous transesterification is the methanol:oil ratio.
- K-γAl$_2$O$_3$ reuse is studied and the catalyst loses its efficiency in the first and in the second cycles proportionally. K-γAl$_2$O$_3$ is not ideal for being used in biodiesel plants because it does not give high FAME yields and it can't be reused in many cycles. According to previous papers, the most probable cause of the catalyst deactivation is the loss of potassium in the solid because the metal is retained in the glycerol phase due to a partial leakage.

Acknowledgments

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