



Trade Science Inc.

ISSN : 0974 - 7443

Volume 6 Issue 2

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ 6(2) 2011 [93-97]

New catalytic solids for biodiesel production. Study of its catalytic activity for vegetable oils transesterification reaction

L.Díaz, M.E.Borges*

Chemical Engineering Department, University of La Laguna, Avda. Astrofísico Fco. Sánchez s/n,
La Laguna, Tenerife, Canary Island, 38200, (SPAIN)

E-mail: eborges@ull.es

Received: 6th May, 2011 ; Accepted: 6th June, 2011

ABSTRACT

The activity of several materials as heterogeneous catalysts for biodiesel production by sunflower oil transesterification reaction at low temperature was studied. Zeolites, natural materials as volcanic ashes, oxides as La_2O_3 and hydrotalcite were evaluated as catalyst. These potentially catalytic materials were subjected to different chemical treatments with the aim to increase their catalytic activity. Transesterification reactions were carried out in a slurry reactor at 60°C, 12:1 methanol/oil molar ratio, 6 wt% catalyst amount and 4 h reaction time. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Biodiesel;
Heterogeneous catalysts;
Transesterification reaction;
Zeolites;
Oxides.

INTRODUCTION

Currently, fossil fuels are used in diesel engines and they are essential in industrialized nation's economy. However, petroleum-based diesel fuels increase environmental pollution. In order to solve this problem, the use of fatty acid methyl esters (FAMES) derived from vegetable oils and animal fats as diesel fuel extenders (biodiesel) has received considerable attention because of its many environmental benefits^[1].

Transesterification reaction is the process by which the glycerides molecules present in fats or oils react with an alcohol in the presence of a catalyst to form esters and glycerol^[2,3]. Biodiesel (FAMES) is usually produced by reacting methanol and vegetable oil in a batch stirred tank reactor using a liquid alkaline catalyst. The catalyst cannot be recovered from the reaction products and it must be neutralized and disposed as a waste water stream from biodiesel product washing. A heterogeneously-catalyzed process instead of a

homogeneous catalyzed process offers a number of advantages over conventional current technology, simplifying and economizing the catalyst removal from biodiesel product step^[4,5]. The development and use of effective heterogeneous catalyst can significantly simplify the downstream purification process by removing the neutralization and washing steps^[6].

Various heterogeneous catalysts have been designed for transesterification reaction^[7,8]. However, most of the tested catalysts require long reaction time while some of them need high reaction temperature conditions. Therefore, it is important to continue searching an effective transesterification reaction catalyst for biodiesel production under moderate reaction conditions, especially at low temperature.

In this paper, different materials with potential catalyst activity for transesterification reaction were studied using them as heterogeneous catalysts in vegetable oils transesterification reaction to produce biodiesel at low temperatures.

Full Paper

EXPERIMENTAL

Catalyst preparation

Several materials were proven as heterogeneous catalysts to carry out the transesterification reaction: (a) Zeolite X (microspheres, 400-800 μm); (b) Zeolite Y (Akzo Nobel); (c) natural volcanic ashes (particles, 1.40-1.80 mm) from volcanic zone soil in Tenerife (Canary Islands); (d) La_2O_3 supplied by Panreac; (e) Hydrotalcite $[\text{Mg}_6\text{Al}_2(\text{OH})_{16}](\text{CO}_3)_4\cdot 4\text{H}_2\text{O}$ supplied by Aldrich. In order to increase their catalytic activity, the potentially catalytic materials were subjected to different treatments related to their individual nature and structure.

In order to increase the basic sites, the zeolitic materials (Zeolite X and Zeolite Y) were ionic exchanged with a KOH aqueous solution. These modified materials were named K-ZX and K-ZY respectively). Previously, zeolites were dried in an oven at 120°C for 2 hours to remove the absorbed water on the surface. Ionic exchange was carried out with 0.5 M KOH aqueous solution for 24 hours. After ionic exchange, solids were only dried at 120°C for 3 hours. Xie et al.^[9] have used a similar treatment to prepare modified NaX zeolite with different KOH loadings. In order to generate acid sites in zeolitic materials studied, Zeolite X and Zeolite Y were exchanged with 1M HCl aqueous solution (H-ZX and H-ZY respectively) for 5 hours. After acid treatment, samples were washed with deionised water until neutrality. Finally, the samples were dried in an oven at 120 °C for 5 hours.

Natural materials as volcanic ashes have demonstrated to be good catalysts or catalyst supports for different kinds of reactions^[10-13]. Black volcanic ashes (VA) particles in the range 1.40-1.80 mm were evaluated as catalyst for sunflower oil transesterification reaction. Natural volcanic ashes modification was carried out by TiO_2 impregnation using a hydrothermal method. TiO_2 (5 g) and natural black volcanic ashes (25 g) were added to a NaOH aqueous solution (1.0 M). The resulting suspension was heated at 140 °C for 22 hours in a teflon container which was backed up by a stainless steel pressurized vessel. After hydrothermal treatment, the impregnated volcanic ash particles (TVA) were washed with a HCl solution (0.1 M) and distilled

water until pH 7. The impregnated material was then dried in air at 100 °C for 15 min and heated at 140 °C for 22 hours in an oven^[13].

La_2O_3 catalyst was prepared by an impregnation method with a NaOH aqueous solution using La_2O_3 as support. Prior to impregnation, 30 g of La_2O_3 were dried at 120°C for 10 hours. Then, a NaOH aqueous solution (2 M) was added to the lanthanum oxide (La_2O_3); the resulting mixture was subjected to stirring for 2 h. After impregnation, the overlying water was removed and the catalyst (Na- La_2O_3) was dried at 120 °C for 12 hours. Part of this catalyst was calcined at 560° C for 5 hours (Na- La_2O_3 calcined). Xie and Yang (2007)^[14] have used a similar treatment to impregnate barium on a commercial zinc oxide.

Catalytic material characterization

The crystalline structure of the catalysts was characterized by X-ray diffraction (XRD). Measurements were performed with a X' Pert Pro diffractometer of Panalytical, using X' Celerator detector and $\text{Cu K}\alpha$ radiation. BET surface area and structural properties of samples were evaluated by nitrogen adsorption-desorption isotherms recorded on a surface pore size analyzer (Gemini V, Micromeritics) and by mercury porosimetry (Autopore IV mercury porosimeter, Micromeritics).

Catalytic activity evaluation

Transesterification reaction was performed in a 250 ml jacketed glass slurry reactor equipped with a reflux condenser and a mechanical stirring (Figure 1). Commercial edible-grade sunflower oil purchased from the market was used as feedstock. Properties of this oil are shown in TABLE 1. Before reaction the system was heated and oil was added. When the oil reached the selected temperature (60°C), methanol (methanol/oil molar ratio 12:1) and solid catalyst (powder, microspheres or particles) (6% wt respect to oil weight) were added with continuous stirring. After 4 hours of reaction, the solid was separated from the reaction mixture by filtration. The liquid product obtained was rotary evaporated to remove methanol in excess, and then settled in a separating funnel. The upper phase consisted of fatty acid methyl esters (biodiesel) and the lower phase contained the glycerol. Viscosity and den-

sity of the obtained biodiesel product was measured using a rotational viscometer Visco Star Plus L and a pycnometer, respectively. Moreover, FAME content in the biodiesel product was quantitatively determined by ^1H Nuclear Magnetic Resonance (NMR) in order to estimate the yield of fatty acid methyl ester obtained from transesterification reaction^[15].

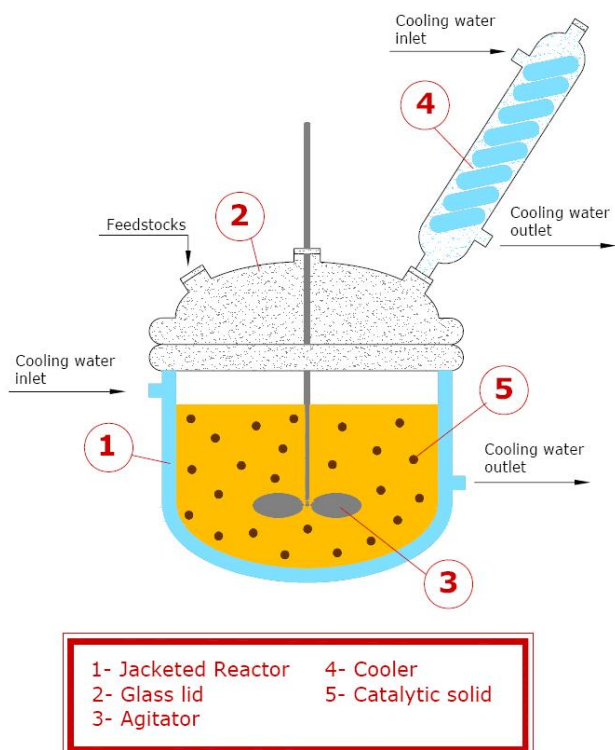


Figure 1 : Scheme of the reaction system.

TABLE 1 : Sunflower oil characteristics

Property	Sunflower oil
Density at 15°C (g/cm ³)	0.924
Kinematic viscosity at 40°C (cSt)	29.4
Acid value (mg KOH/g)	0.17
Iodine index (g Iodine/100 g sample)	138.8
Turbidity (NTU)	2.24

RESULTS AND DISCUSSION

In a first step, as a basis for the catalytic activity evaluation, transesterification reaction was performed using several materials without modification (zeolite X, zeolite Y, natural volcanic ashes, La_2O_3 and hydrotalcite). Results show that a low decrease in sunflower oil viscosity was achieved (from 3.7 to 14.9% related to initial sunflower oil viscosity) and a low

transesterification reaction conversion was obtained (TABLE 2), As the conversion of triglycerides to methyl esters achieved was very low, potential catalytic materials were subjected to different treatments in order to increase their catalytic activity.

TABLE 2 : Transesterification reaction conversion obtained using different unmodified materials as heterogeneous catalysts. (Kinematic initial sunflower oil viscosity: 29.4 cSt)

Catalyst	Product Kinematic viscosity (cSt)	FAME yield (%)
Zeolite X	26.9	4.1
Zeolite Y	26.5	4.4
Volcanic ashes	25.0	5.4
La_2O_3	28.3	3.5
Hydrotalcite	26.7	4.2

The increase of basic sites on the zeolite X enhance its catalytic activity for the transesterification reaction and the material subjected to ionic exchange with KOH (K-ZX) is more active than untreated material reaching a reaction product viscosity decrease of 57.5% and a FAME yield of 30.1%. However, the creation of acid sites on the same zeolitic material does not increase the catalytic activity for the transesterification reaction (Figure 2). In addition, material exchanged with the HCl solution (H-ZX) is less active than unmodified material reaching only a reaction product viscosity decrease of 3.0% and a FAME yield of 3.6%. The same trend was observed with the zeolite Y.

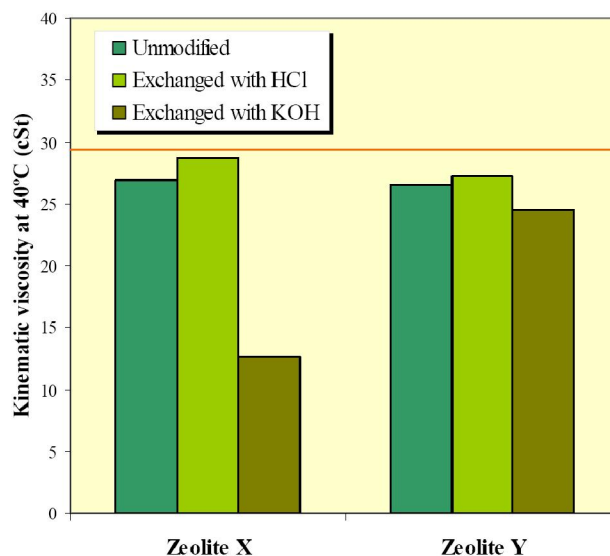


Figure 2 : Reaction product viscosity using zeolite X and zeolite Y as catalyst for sunflower oil transesterification reaction (— commercial sunflower oil viscosity).

Full Paper

Figure 3 shows that the modification of natural volcanic material with TiO_2 (TVA) favors its activity for the transesterification reaction, achieving a significant reduction in biodiesel product viscosity (66.1%) and reaching a FAME yield of about 42% in biodiesel product obtained. However, further studies with the aim of reactor operation conditions optimization could be performed to achieve higher decrease of the viscosity of the reaction products getting better FAME yields and specification values for commercial biodiesel.

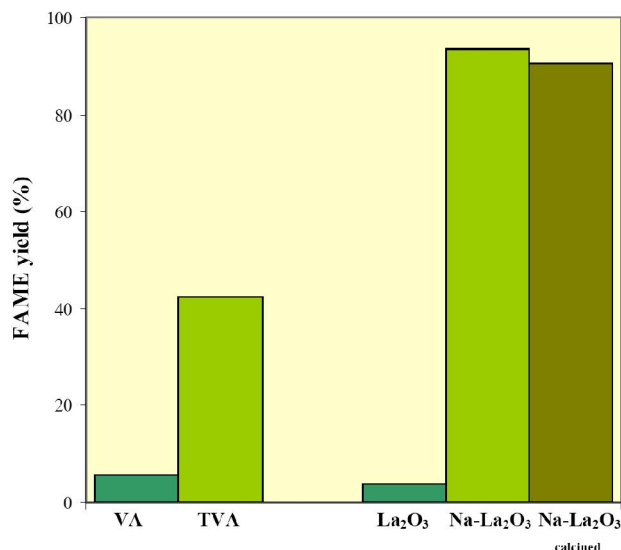


Figure 3 : Catalytic activity of volcanic ashes and lanthanum oxide, FAME yield of the reaction product.

When lanthanum oxide was used as heterogeneous catalysts better conversion was obtained for the transesterification reaction of sunflower oil. It can be observed that the impregnation of lanthanum oxide with NaOH is an effective treatment achieving a viscosity of product obtained into required standards for biodiesel (4.2 and 4.4 cSt for $\text{Na-La}_2\text{O}_3$ and $\text{Na-La}_2\text{O}_3$ calcined, respectively) and FAME yields above 90%. In addition, from these results we can conclude that calcination stage is not necessary, because using the calcined catalyst the biodiesel product viscosity increased slightly. Some authors have obtained similar results studying NaOH exchanged alumina as catalyst for transesterification reaction (calcined and uncalcined)^[16].

TABLE 3 summarizes the textural properties of the best materials found as catalysts for the transesterification reaction. The textural parameters included in this table are: values for the macropore and micropore surface area, pore size (D) and porosity. These data show that

the impregnation of lanthanum oxide with NaOH causes a decrease of BET specific surface area; however, it is observed a slight increase of macro and mesopore area and porosity. From a qualitative point of view, the decrease of S_{BET} are not surprising since in heterogeneous catalysis the reduction of specific surface area of the support is a well documented consequence of the promotion of a catalyst with alkali metals^[16-18]. The textural properties for $\text{Na-La}_2\text{O}_3$ used are very similar to those to the $\text{Na-La}_2\text{O}_3$, so it could carry out the reuse of the catalytic material after the transesterification reaction.

TABLE 3 : Textural properties of samples

Sample	N_2 adsorption		Mercury porosimetry		
	S_{BET} (m^2g^{-1})	D (nm)	Surface Area (m^2g^{-1})	Porosity (%)	D (nm)
La_2O_3	0.687	7.163	13.715	55.19	3755.4
$\text{Na-La}_2\text{O}_3$	0.304	3.732	16.447	55.51	11358.2
$\text{Na-La}_2\text{O}_3$ used	0.311	4.389	16.122	44.12	10992.2

Figure 4 presents the XRD patterns of these samples. It can be noticed that XRD patterns of Na-

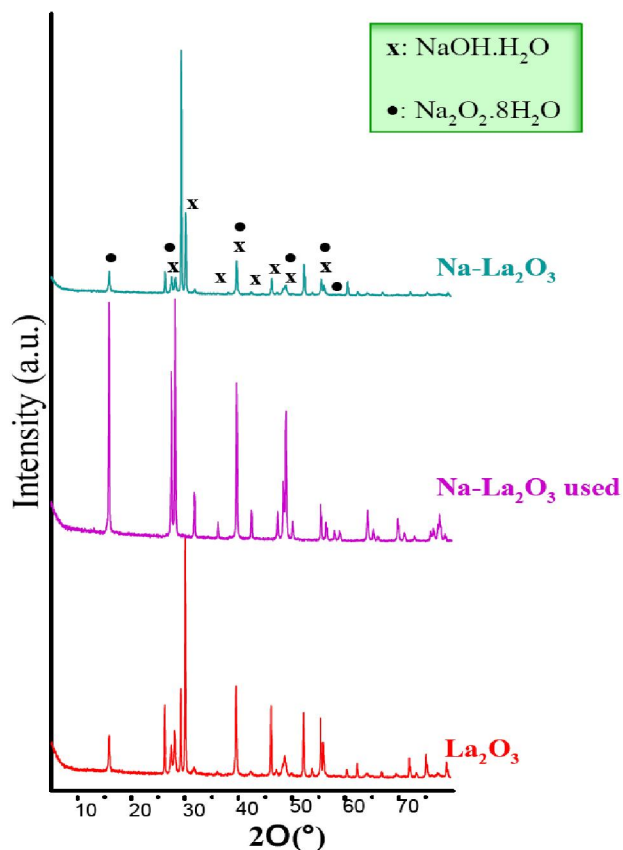


Figure 4 : XRD patterns of La_2O_3 , $\text{Na-La}_2\text{O}_3$ and $\text{Na-La}_2\text{O}_3$ used.

La₂O₃ is almost the same as the typical pattern of La₂O₃, this can be attributed to good dispersion of NaOH on the La₂O₃ support in the form of a monolayer at a low loading of NaOH. This justification has been provided by other authors^[19] when impregnated KOH on Al₂O₃. After the transesterification reaction occur slight modifications of the crystalline structure of the catalyst; this could be attributed to the presence of triglycerides and esters tracks on the catalyst surface.

CONCLUSIONS

In the present study the transesterification reaction of sunflower oil with different heterogeneous catalysts at low temperature was investigated. Zeolitic materials practically don't show an acceptable activity for reaction studied. Good conversions were obtained for lanthanum oxides and volcanic ashes. Both modified materials can be used as heterogeneous catalyst for transesterification reaction of vegetable oils at low temperature.

Na interchanged La₂O₃ was the solid that showed higher catalytic activity. Biodiesel product obtained is within the limits established by ASTM D6751 and EN 14214 standards. Using this catalyst (powder form), biodiesel can be obtained in a slurry discontinuous reactor at a relatively low temperature (60°C) when compared with conventionally used in the transesterification reaction by heterogeneous catalysis.

The use of titanated volcanic ashes as heterogeneous catalyst in the transesterification reaction could present great advantages, because it is a natural and inexpensive material. Moreover, this particulated catalyst could be used with the possibility of a continuous catalytic process for biodiesel production developing using catalytic fixed bed reactors. Therefore, fixed bed reactor operating conditions study could be performed in order to improve the transesterification reaction conversion obtaining better FAME yields.

ACKNOWLEDGEMENTS

The authors acknowledge a research grant support by Dirección General de Universidades, Gobierno de Canarias, Spain.

REFERENCES

- [1] C.Chiu, M.J.Goff, G.J.Supes; Bioengineering, Food and Natural Products, **51(4)**, 1274-1278 (2005).
- [2] F.Ma, M.A.Hanna; Bioresource Technology, **70**, 1-15 (1999).
- [3] A.Banerjee, R.Chakraborty; Resources, Conservation and Recycling, **53**, 490-497 (2009).
- [4] A.P.Vyas, N.Subrahmanyam, A.P.Patel; Fuel, **88**, 625-628 (2009).
- [5] S.Yan, C.DiMaggio, S.Mohan, M.Kim, S.O.Salley, K.Y.Simon Ng; Topics in Catalysis, **53**, 721-736 (2010).
- [6] G.Wen, Z.Yan, M.Smith, P.Zhang, B.Wen; Fuel, **89**, 2163-2165 (2010).
- [7] S.Semwal, A.K.Arora, R.P.Badoni, D.K.Tuli; Bioresource Technology, **102**, 2151-2161 (2011).
- [8] Y.C.Sharma, B.Singh, J.Korstad; Fuel, **90**, 1309-1324 (2011).
- [9] W.Xie, X.Huang, H.Li; Bioresource Technology, **98**, 936-939 (2007).
- [10] M.Escudey, S.A.Moya; Colloids and Surfaces, **37**, 141-148 (1989).
- [11] E.López-Salinas, P.Salas, I.Schifter, M.Morán, S.Castillo, E.Mogica; Studies in Surface Science and Catalysis, **105**, 1565-1570 (1997).
- [12] E.Borges, M.C.Alvarez-Galván, P.Esparza, E.Medina, P.Martín-Zarza, J.L.G.Fierro; Ene. Environ.Sci., **1**, 364-369 (2008).
- [13] P.Esparza, M.E.Borges, L.Díaz, M.C.Álvarez-Galván, J.L.G.Fierro; AIChE Journal, (2010).
- [14] W.Xie, Z.Yang; Catalysis Letters, **117**, 159-165 (2007).
- [15] G.Gelbard, O.Brès, R.M.Vargas, F.Vielfaure, U.F.Schuchardt; Journal of the American Oil Chemist's Society, **72(10)**, 1239-1241 (1995).
- [16] G.Arzamendi, I.Campo, E.Arguiñarena, M.Sánchez, M.Montes, L.M.Gandía; Chemical Engineering Journal, **134**, 123-130 (2007).
- [17] S.Szczepanska, S.Malinowski; Journal of Catalysis, **15(1)**, 68-82 (1969).
- [18] V.Perrichon, M.C.Durupty; Applied Catalysis, **42(2)**, 217-227 (1988).
- [19] K.Noiroj, P.Intarapong, A.Luengnaruemitchai, S.Jai-In; Renewable Energy, **34**, 1145-1150 (2009).