Selection of heterogeneous acid catalyst and operational conditions for the esterification of oleic acid and production of biodiesel

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1 Introduction

The combination of the hydrolysis of vegetal oil, followed by the esterification of the fatty acids produced, may be considered an alternative route to produce biodiesel [1] and both steps are catalyzed by acid catalysts. This route has several advantages in relation to the traditional route (homogeneous transesterification of oils and fats), like the possibility of using oils with high acidity and water content without producing soap and the production of glycerol with high purity [2]. The development of catalysts for these reactions may make the conditions mild and the process economical.

The objective of this work is to test several solid acid catalysts in the esterification of oleic acid (model fatty acid) and evaluate the effect of the operational variables for the best catalyst by a factorial design.

2 Experimental/methodology

The catalysts used were Amberlyst-15 – A-15 (Aldrich); zirconia (ZrO_2); sulfated zirconia – S-ZrO_2 (produced from zirconium hydroxide and ammonium sulfate); titania (TiO_2); sulfated titania – S-TiO_2 (produced from titanium oxide and sulfuric acid); niobium oxide – Nb_2O_5 (CBMM).

Catalysts were characterized by N_2 adsorption at 77 K (Micromeritics ASAP 2000), acid titration [3] and X-Ray Diffraction (Rigaku Miniflex II).

Reactions were conducted in a 600 mL batch reactor. Oleic acid (Aldrich) and methanol (Merck) were the reactants. Default operational conditions were used to compare the catalysts were: T=100°C, methanol/oleic acid molar ratio=5:1, 5% w/w catalysts. Conversion was monitored by the acidity of the sample withdrawn along the reaction. A factorial design type 2^3 with 3 central points was applied for the best catalyst and the dependent variable was the conversion. The independent variables were the temperature (x_1,60-80°C), methanol/oleic acid molar ratio (x_2, 5:1-1:1) and catalyst percentage (x_3, 1-5% w/w).

3 Results and discussion

3.1. Characterization

Table 1 shows the results of acidity and surface area. Comparing the acidity values, it can be observed that sulfatation was very efficient, especially for zirconia, with a high increase in acidity. Amberlyst-15 was the most acid catalyst. Nb_2O_5 was the catalysts which presented the higher surface area. X-Ray Diffraction (not shown) has indicated that Nb_2O_5 and Amberlyst-15 were amorphous, since no pattern was obtained. Comparing the profiles of ZrO_2 and sulphated zirconia, a small loss of cristalinity was observed, which explains the loss of surface area. This loss of cristalinity was not observed for TiO_2.

Table 1. Catalysts characterization

Catalyst	Acidity (µmol/g)	S_{BET} (m^2/g)
Nb_2O_5	49 ± 7	111.5
ZrO_2	7 ± 0,3	31.4
S-ZrO_2	295 ± 6	12.5
TiO_2	17 ± 1	58.0
S-TiO_2	68 ± 4	55.9
A15	1896 ± 50	91.0

3.2. Selection of catalyst

Figure 1 presents the conversion of the reaction for all the catalysts used. Comparing with the non catalytic reaction, it can be observed that, except non sulphated zirconia, all the catalyst were active. Amberlyst-15 has had a much better performance, reaching a final conversion of 95% with 2 hours of reaction. This result can be attributed to the higher acidity of this catalyst. The second best catalyst was sulfated titania.

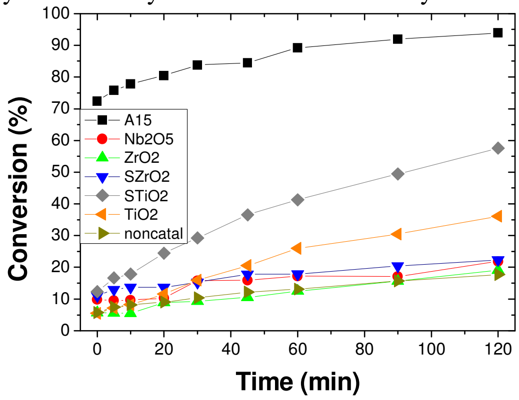

Fig. 1. Esterification of oleic acid – comparison of catalysts. T=100°C, methanol/oleic acid molar ratio=5:1, 5% w/w catalysts

3.3. Effect of operational variables

Table 2 shows the results of the experimental planning. The higher conversion was 64.3%, using the higher values of the variables.

Table 2. Conversions obtained using Amberlyst 15

Catalyst	T (°C)	MR	%Cat	T^{norm}	MR^{norm}	C^{norm}	Conversion (%)
1	60	1:1	1	-1	-1	-1	21.7
2	60	1:1	5	-1	-1	+1	24.4
3	60	1:5	1	-1	+1	-1	38.0
4	60	1:5	5	-1	+1	+1	36.1
5	80	1:1	1	+1	-1	-1	23.4
6	80	1:1	5	+1	-1	+1	42.1
7	80	1:5	1	+1	+1	-1	52.1
8	80	1:5	5	+1	+1	+1	64.3
9	70	1:3	3	0	0	0	44.0
10	70	1:3	3	0	0	0	41.3
11	70	1:3	3	0	0	0	42.6

Eq. 1 means that the effects of the variables in the conversion can be represented by a sum of linear contributions. Model parameters and parameter variances can be obtained with the aid of maximum likelihood estimation procedures. $Conversion = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + a_3 \cdot x_3 + a_4 \cdot x_1 \cdot x_2 + a_5 \cdot x_1 \cdot x_3 + a_6 \cdot x_2 \cdot x_3$ (1)

All the variables were significative 95 % of confidence, as well as effects combination between the temperature and the molar ratio, as shown in the Equation 2:

$$Conversion = (43.82 \pm 1.08) + (32.90 \pm 1.27) \cdot x_1 + (3.13 \pm 1.27) \cdot x_3 + (5.79 \pm 1.27) \cdot x_1 \cdot x_2 \quad (2)$$

The proposed model was satisfactory to predict the experimental data considering the test F of Fisher.

Conclusions

Amberlyst-15 was the best catalyst for the esterification of oleic acid, probably due to its higher acidity. Conversions up to 95% were reached with 2 h of reaction, at 100°C and 5% w/w catalyst. Reactants molar ratio was the most influential variable.

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