Hydrolysis of soybean oil over solid acid catalysts

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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. The hydrolysis is conducted industrially in severe operational conditions: T≈ 300°C, pressure up to 7 MPa and with a high water/oil molar ratio, in the absence of catalyst [2]. The development of catalysts for this reaction may make the conditions mild and the process economical.

Experimental

Catalysts used: Amberlyst-15 (Aldrich); sulfated zirconia (produced from zirconium hydroxide and ammonium sulfate); sulfated titania (produced from titanium oxide and sulfuric acid); niobium oxide (CBMM).

Characterization techniques: N_2 adsoprtion; acid titration [3]; X-ray diffraction.

Reaction procedure: a 600 mL batch reactor was used. Refined soybean oil and distilled water were the reactants. Default operational conditions were used to compare the catalysts: T=230°C, water/oil molar ratio=50:1, 5% w/w catalysts. Conversion was monitored by the acidity of the sample withdrawn along the reaction.

Operational conditions optimization: for the best catalyst, a factorial design type 2^3 with 3 central points was chosen and the dependent variable was the conversion. The independent variables were the temperature (x_1,210-250°C), water/oil molar ratio (x_2, 10:1-50:1) and catalyst percentage (x_3, 1-5% w/w).

Results and Discussion

Characterization of the catalysts show that niobium oxide has presented the higher surface area (111,49 m^2/g), followed by sulfated titania (55,93 m^2/g). Sulfatation has not altered the cristalinity of zirconia and titania, while Amberlyst-15 has presented a much higher acidity (1896 μmol/g), followed by sulfated zirconia (295 μmol/g).

Figure 1 shows that most of the catalysts have promoted an increase in conversion compared to the non-catalytic reaction. Sulfated zirconia and niobium oxide were the most active catalysts, but Nb_2O_5 was more active at a lower catalyst concentration (3% w/w) – not shown. So this catalyst was chosen as the best one.

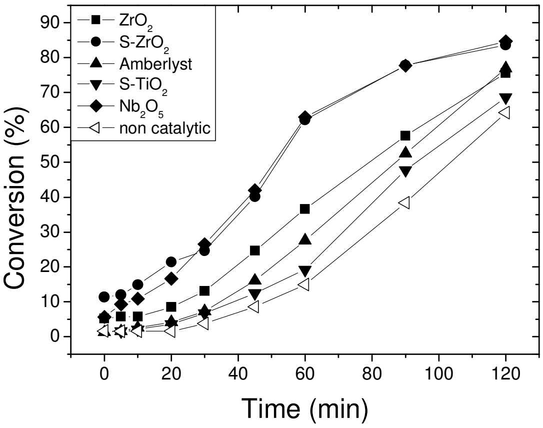

Figure 1 – Activity of catalysts in the hydrolysis of soybean oil. T=230℃, 5% w/w catalyst, water/oil = 50:1

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.

$$Conversion = a_0 + a_1 \cdot x_1 + a_2 \cdot x_2 + a_3 \cdot x_3 + a_4 \cdot x_1 \cdot x_2 + a_5 \cdot x_1 \cdot x_3 + a_6 \cdot x_2 \cdot x_3 \qquad (1)$$

The significant parameters with 95 % of confidence were the temperature (linear), catalyst percentage (linear) and an effects combination between the temperature and the molar ratio, as shown in the Equation 2.

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

It can be observed that the temperature is the most influential variable, being a linear and positive parameter. According to Table 1, it is possible to observe the F Test employed between the model and the experimental variances, resulting in the $F_{calculated}$, it is within the tabulated interval, meaning that the prediction errors of the model are similar to the experimental errors.

Table 1 – F Test between the central points and of the model variances (Equation 2).

Variance			**$F_{tabulated}$**		
Central point (σ^2_{model})	**Model ($\sigma^2_{experimental}$)**	**$F_{calculated}$**	**Inferior**	**Superior**	**Correlation coefficient**
24.02	12.95	1.85	0.02	6.54	0.995

Conclusions

Niobium oxide was the best catalyst for the hydrolysis of soybean oil. Temperature was the most significant operational variable.

References

[1] L. L. Rocha et al. *Lett. Org. Chem.* **2010**, 7, 571-578.

[2] K. Ngaosuwan et al. *Ind. Eng. Chem. Res.* **2009**, 48, 4757

[3] D. E. López et al. *J. Catal.*, **2007**, *245*, 381–391.