

Heterogeneous Catalyst applied in esterification reactions

J. A. Gonçalves⁽¹⁾, D. A. G. Aranda^{(1)*}, N. Furtado⁽²⁾ and C. Taft⁽²⁾

(1) Greentec, Escola de Química. Universidade Federal do Rio de Janeiro. *donato@eq.ufrj.br

(2) Centro Brasileiro de Pesquisas Físicas.

Abstract – Biodiesel was obtained from free fatty acids (linoleic, oleic, lauric, palmitic and stearic) by esterification with heterogeneous catalyst (niobic acid powder). Through 2³ experimental design for each one were obtained empirical and global models. They show that the temperature, reaction time and the amount of catalyst were the most important variables. Reaction rates represented by two types of homogeneous models had good adjustments. The increase in reactivity was directly related to the increase of unsaturation and reduction of the length of carbonic chain.

Unlike the traditional transesterification process, esterification uses raw materials that allow an economy. Beside this, the use of heterogeneous catalysts such as niobic acid (Nb₂O₅.nH₂O) has demonstrated higher conversions as well as the simplification of the process. Its removal is easily carried out by simply filtration. It also allows its regeneration and reutilization, and there are reduction of corrosion problems, formation of salts and effluents [1]. We studied some features of esterification reaction with aims to understand its kinetic, empiric and molecular characteristics.

FAME (fatty acid methyl esters) were obtained using niobic acid in powder form as a catalyst (CBMM's HY-340) under a 2³ experimental design and 3 center points for linoleic, oleic, palmitic, stearic, and lauric acids. Samples were collected in different times to measure the conversion (dependent variable) through the acid value according to the AOCS Ca-5a-40 method. All reactions were carried in a batch reactor (Parr Instruments 4842). Analysis of the results and its analogies made possible to obtain the mathematical and kinetic modeling of the reactions by using Statistica 6.0 software. It was verified the influence of the independent variables and was calculated the parameters of the models based on the principles of Langmuir-Hinshelwood and Eley-Rideal [2]. Reactivity was established experimentally by the comparison of measured and theoretical conversions for the calculations of the energy of the reactants border orbitals for molecular modeling with semi-empiric AM1 method by using TITAN software.

The obtained correlations were very satisfactory (R²>0.99) and the temperature was the most important process variable and reaction time and catalyst amount were the most significant variables for the global model.

Kinetic study of heterogeneous catalysis using Langmuir-Hinshelwood and Eley-Rideal models did not produce good correlations. However, a homogeneous second order for the fatty acid model ($-r_A = k.C_A^2$) can also be used as a simplified way. The reactivity data obtained experimentally was confirmed by theoretical calculations based in the quantum physics. The reactivity was influenced by difference in the molecular structure of the fatty acids. Reaction rates were faster for fatty acids with more unsaturation and smaller carbon chains. The reactivity order decreased in the following sequence: linoleic>oleic>lauric>palmitic>stearic. It was also found that the orbital in which the reaction occurred was through LUMO orbital of the fatty acid with HOMO of the methanol because of greater symmetry and smaller difference of energy (Figure 1). Thus, no steric impediment by acids in relation to pore the catalyst was observed.

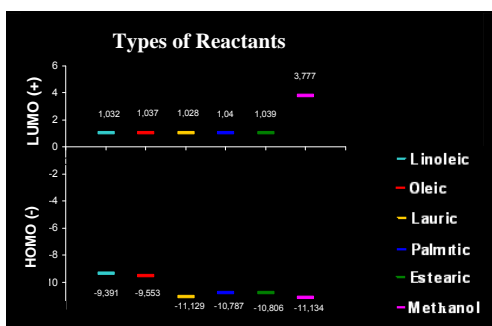


Figure 1: HOMO and LUMO energies for the reactants.

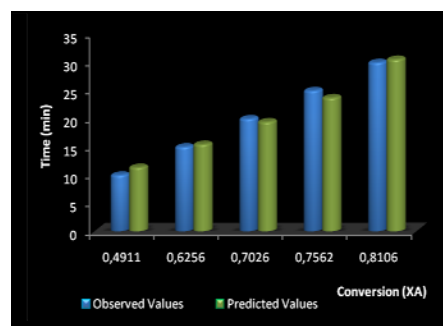


Figure 2: Predicted and observed conversion values for the esterification.

References

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