



Oxides derived from hydrotalcite for the production of biodiesel from raw material of high acidity

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Abstract – In this work, an environmental friendly process for the methanolysis of soybean oil of high acidity to methyl esters, using calcined Mg-Al hydrotalcites as heterogeneous catalysts, was developed. The catalysts derived from calcination at 400°C of hydrotalcites with Mg/Al ratio of 3.0. The catalysts were characterized by XRD, XRF, BET and TGA. The conversion was analyzed using gas chromatography method. When the reaction was carried out at 230°C with a molar ratio of soybean oil to methanol of 13:1, a reaction time of 1 h and a catalyst loading of 5%, the oil conversion was 85,3% for oil with 9.5% acidity and 90,4% for refined oil.

Hydrotalcite-like compounds (HTLCs) are anionic clays, with general formula $[M^{2+}(1-x)M^{3+}_x(OH)_2]^{x+}(A_x/n)^{n-} \cdot yH_2O$, where $M^{2+} = Mg^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}$; $M^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}$; $A = OH^-, Cl^-, NO_3^-, CO_3^{2-}$ and the ratio $Al/(Al+Mg)$ can vary between 0.20 e 0.33 [1]. The interest in catalytic applications of these materials is the ability to produce, by heat treatment, basic non-stoichiometric mixed oxides of high surface area [2]. Furthermore these materials have bifunctional properties acid-base.

It is known that there is a trend in the biodiesel production of using raw materials increasingly crude, therefore, it is valid and necessary to test soybean oil with high acidity. In this work, the oil used in the transesterification reaction presented an initial acidity of 9.5%, which was donated by A. Azevedo Industries and Trade of Oil Ltda. The catalyst was obtained by calcination of hydrotalcite at 400°C, whose $Al/(Al + Mg)$ molar ratio is 0.33. The catalysts were characterized with XRD, XRF, BET and TGA. The conversion was analyzed using gas chromatography method. The reaction was carried out at 230°C with a molar ratio of soybean oil to methanol of 13:1, a reaction time of 1 h and a catalyst loading of 5% in the Parr reactor (Figure 1).

The results of XRF analysis showed a real ratio $Al / Al + Mg$ equal to 0.31. In XDR analysis there was only formation of HTLC phase. The surface area (BET) of catalyst was 202 m²/g and pore volume of 0.51 cm³/g. The thermogravimetric analysis of Mg-Al hydrotalcite presents two stages of mass loss. The first stage, at temperatures up to around 200°C, suggests release of interlayer water. The second stage of decomposition occurs in the range of 200-450°C, suggesting the decomposition of hydrotalcite by the release of carbonates and hydroxyl ions. The result of the conversion of methanolysis (85.3%) although lower than that of refined oil (90.4%) showed a decrease of acidity of 9.5% to 1%. This is a result of extreme importance because this proves the bifunctional properties of hydrotalcite, suggesting that the acid sites generated in the calcination of hydrotalcite act both in the transesterification of oil and on the esterification of free fatty acids. The ethanolysis was also tested, using the same conditions of methanolysis. In this case the conversion obtained was 81%. Figure 2 shows the kinetic curves of the reactions performed.



Figure 1: Parr reactor.

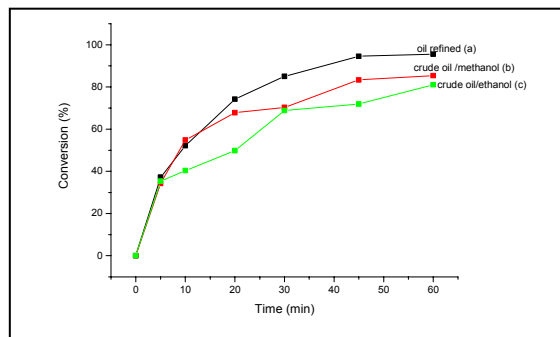


Figure 2: Kinetic curve of methanolysis using refined oil (a) and crude oil (b) and ethanolysis using crude oil (c)

References

- [1] Crepaldi, E. L.; Valim, J. B. *Química nova* 21(1998), 3, 300-311.
- [2] Cavani, F., Trifiro, F., Vaccari, A. *Catalysis Today* 11(1991), 2, 173
- [3] Quagliano J.V., Vallarino, L. M. *Química*, Rio de Janeiro. Guanabara Dois, p. 1979