Biodiesel from Tall Oil Fatty Acids using Homogeneous and Heterogeneous Catalysts

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Introduction

The use of high acidity raw materials for biodiesel production is an interesting option, since these materials usually are of low commercial value. In our case, concentrated fatty acid was used obtained from crude tall oil, which is a by-product in the pulp manufacturing by craft or sulphate pulping process. The esterification reaction of tall oil fatty acids was tested with different acids catalysts, methanol/fatty acid molar ratios (MR), temperatures and pressures. Reactions were carried out in homogeneous and heterogeneous media using sulfuric acid and solid niobic acid ($Nb_2O_3.nH_2O$, commercially available as HY-340) as catalysts, respectively. Even though the niobic acid is less active than the sulfuric acid, it is important to follow the research in the field of solid catalysts since it makes possible to simplifies the purification process.

Materials and Methods

Experiments were carried out using tall oil fatty acids of *Pinus* sp. with an acidity of 96.5 (g of oleic acid/ 100 g of sample), provided by M.A. Liberman & CIA S.R.L. – Arizona Chemical, and methanol/fatty acid molar ratios (MR) of 2:1, 3:1, 8:1 and 40:1. Sulfuric acid was loaded at 0.18 and 0.5 %v/v, and Niobic acid (provided by CBMM) 12 %w/w. Samples from the reactor were washed and centrifugated prior to the acidity determination [1]. After the reaction was completed, phases were separated, and complete analyses were carried out, measuring the concentration of homogeneous catalyst, water, alcohol, fatty acid and methylester. Tests with sulfuric acid as catalyst were performed at atmospheric pressure in a glass balloon under reflux, with a magnetic stirring, in a water bath at 60ºC. The esterification studies using the solid catalyst was carried out in a pressurized stainless steel reactor, with a magnetic stirring, at 130 and 180ºC. After reaction the acidity determination was made to quantify the conversion obtained. The catalyst was characterized by TPD of pyridine before and after regeneration. The coke was characterized by TPO and FTIR.

Results and Discussion

Figure 1 shows results of experiments carried out at atmospheric pressure with methanol/fatty acid MR 3:1, 8:1 and 40:1, 0.18 and 0.5% H_2SO_4 and 60°C. By increasing the methanol/fatty acid ratio increases both the reaction rate and the final conversion, which is limited by equilibrium. On the other hand, for a given molar ratio, increasing catalyst concentration (sulphuric acid) from 0.18 to 0.5%v/v, leads to an improvement of the reaction rate. In the case of the reaction carried out with MR 40:1, it was observed that at just 3 minutes of reaction the conversion levels are very close to equilibrium, achieving a very low acidity of the sample from 96.5 to 1.55 (final acidity), which corresponds to a conversion of 98.4%. However when MR 8:1 and 0.5 %w of sulphuric acid are used the acidity only decreased to 7.0 after 1 h of reaction (92.7% conversion), and reached 2.5 after 4.5 hours (97.4% conversion). This is important because the use of large excesses of alcohol, e.g. molar ratio 41:1 [2], limits the use of industrial reactors. The solid catalyst at atmospheric pressure showed very low activity (Figure 1A).

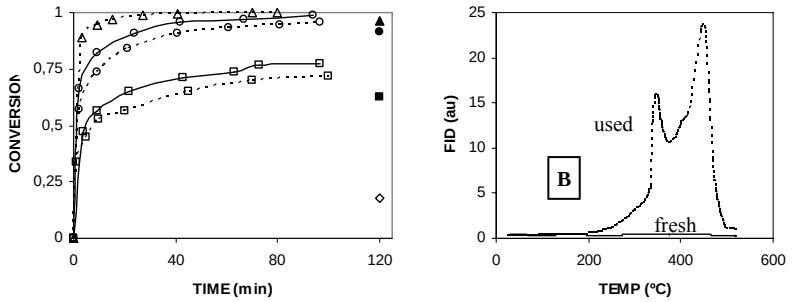

Figure 1. (**A**) Esterification reaction: atmospheric pressure, 60ºC: H_2SO_4 0.18%v (--),0.5%v (–), MR: 40:1 (Δ), 8:1 (○) and 3:1 (□); HY-340 12%w (◊); pressurized reactor: H_2SO_4 0,5%v, 140 ºC, MR 2:1 (▲); HY-340 12%w, MR 3:1: 130ºC (■) and 180ºC (●); (**B**) TPO profiles: solid niobic acid fresh (–) and after used (--) in reaction

When the esterification reaction was carried out in the pressurized reactor, the homogeneous catalysis (0.5 %v Sulphuric Acid) achieved a final acidity value of 3.44 (2 h reaction, 140 ºC), being almost an order of magnitude lower than the heterogeneous catalysis (Figure 1A). However the solid catalyst showed the best ester yield at 180 ºC with MR 3:1, 12 wt% catalyst and reaction time 2h, when the acidity dropped to 8.06 (91.6% conversion). Factorial planning (2^2) for the heterogeneous catalysis (HY-340) experiences was made and found that the effect of the temperature increase is 28.47%, while the effect due to the increase in molar ratio is only of 2.52%.

Figure 1B shows the TPO profile for the catalyst. It can be observed that temperatures up to 500°C are needed in order to fully remove the coke deposits (%C=16.5).

Significance

It is possible to obtain biodiesel from tall oil fatty acids and methanol with very high yield (>90%), at atmospheric pressure with sulfuric acid, and at higher pressures either with niobic acid or sulphuric acid. Even though the heterogeneous catalyst is less active than the homogeneous one, it is important to understand the deactivation mechanism and regenerability due to the advantages that it has related to post-purification processes.

References

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