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Deoxygenation of Soybean Free Fatty Acids on Pd/C Catalysts

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Abstract – *Pd/C catalysts were evaluated in deoxygenation reactions synthesized to obtain hydrocarbons in the diesel range from soybean free fatty acids in a solvent free system. Carbon support characteristics were also investigated and its influence in deoxygenating reaction., The conversions were about 88% with a selectivity of 90% to hydrocarbons under 573 K and 10 bar of H_2 pressure (1,44 H_2/fatty acids molar ratio).*

Keywords: *Deoxygenation, Palladium, Hydrocarbons, Carbon*

I. Introduction

The increase in consumption of fossil fuels in the past decades and growing on environmental awareness has become renewable fuels an interesting alternative and several methods for biofuels production are currently well established. However, new solutions are necessary to meet the demand for energy and environmental preservation [1]. The conversion of vegetable oils and animal fat in a diesel fuel of good quality has been extensively studied, being biodiesel the most known biofuel. Nowadays, biodiesel is associated to mono-alkyl esters of long chain of fatty acids, being the transesterification the most common process to obtain it [2]. However, some properties of fuels based on mono-alkyl esters of fatty acids, such as high cloud point, and high acidity limit its applicability. In addition, transesterification reactions require raw materials with low acidity and low moisture content, which implies in high costs. In order to overcome these issues, the research activities have been devoted to develop next generation biofuel, which is characterized by at least two criteria: (i) produces a diesel-like hydrocarbon product and (ii) uses non-food raw materials. A new method for the production of hydrocarbons in the range of diesel from free fatty acids has been studied [1]-[2]. It was shown by Snåre *et al* [1], that free fatty acids in liquid phase, under high pressure and temperature over heterogeneous catalysts, tend to the decarboxylation. The main products of this kind of reaction are a mixture of hydrocarbons in the diesel fuel range.

In the present work, catalytic tests were performed comparing a commercial Pd/C catalyst (5% of Pd, Aldrich) with three different Pd/C catalysts, previously synthesized, to evaluate their behavior on real mixtures of free fatty acids in a solvent free system. The soybean free fatty acids are the main by-product of soybean oil refining and they are formed during the neutralization step of crude soybean oil refining.

Free fatty acids in oils and fats are related to the phenomenon of rancidity, and this is detectable by changes in odor and flavor, so the free fatty acids are removed during the refining process. In the production of biodiesel, fatty acids are also removed, because, in transesterification reactions, oil acidity over 3% lead to soap formation decreasing the yield of biodiesel [3]. Thus, there is an excess of this feedstock in the market and it is used, in most of the cases, for soap production and in animal feed. The catalysts were characterized by additional characterization techniques. A kinetic test was carried out with the commercial catalyst.

II. Experimental

II.1. Catalysts Synthesis and Characterization

Four different palladium carbon system were tested in deoxygenation reactions: a commercial Pd/C (5 wt% Pd – Aldrich), catalyst I, and three different palladium catalysts impregnated on activated carbon (Carbomafra S. A.). Samples of Pd/C were synthesized by wet impregnation and palladium content were 5 and 1wt%, catalysts II and III respectively. It was also tested an oxidized support pre-treatedwith HNO_3 (5% wt), catalyst IV (1wt% Pd). The impregnation procedure was the same for all the catalysts. Palladium solution of H_2PdCl_4 was added on carbon solution followed by the addition of Na_2CO_3 solution with a molar ratio Pd/Na=21, after this step this mixture was kept under stirring at room temperature for 6 h. After this the samples were washed and dried in oven at 373 K for 12h.

Catalysts were characterized by complementary techniques. Chemical composition of the materials was determined by X-ray fluorescence (XRF) using a Bruker spectrometer (AXS S4 Explorer) equipped with an X-ray tube of rhodium (Rh), XRF analyses were performed in fused samples: a known amount of catalyst was burned

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