

# Glycerol conversion in the experimental study of catalytic hydrolysis of triglycerides for fatty acids production using Ni or Pd on Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>



Gisel Chenard Díaz<sup>a</sup>, Neyda de la C. Om Tapanes<sup>a</sup>, Leôncio Diógenes T. Câmara<sup>b,\*</sup>, Donato A.G. Aranda<sup>a</sup>

<sup>a</sup> GreenTech Laboratory, Escola de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro-RJ, Brazil

<sup>b</sup> Instituto Politécnico da Universidade do Estado do Rio de Janeiro, Nova Friburgo, RJ, Brazil

## ARTICLE INFO

### Article history:

Received 12 September 2012

Accepted 1 November 2013

Available online 25 November 2013

### Keywords:

Glycerol conversion

Hydrogen

Biodiesel

Hydrolysis

Soybean

Tallow

## ABSTRACT

In many reactions to produce biodiesel the glycerol represents 10 wt% of the total products therefore it is important to find an adequate destination of such byproduct. The catalytic hydrolysis of triglycerides is another way to produce biodiesel from fatty raw materials. This work shows the catalytic hydrolysis of triglycerides (soybean oil and tallow) with nickel (NiO) or palladium (PdO) catalysts supported on Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>. The results showed the direct conversion of in situ generated glycerol into hydrogen (H<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>). The glycerol conversion was evaluated through the capacity to hydrogenate the unsaturated fatty acids leading to the formation of stearic acid (saturated compound). The catalyst, temperature and time were varied and evaluated in the experiments utilizing the two different kinds of raw materials (beef tallow and soybean oil). Selectivity and statistical planning studies were performed to optimize the formation of stearic acid as it is linked to the hydrogenation of unsaturated compounds by hydrogen generated from the glycerol liquid reforming.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Free fatty acids (FFAs) are compounds that can be used to produce a great variety of products such as pharmaceuticals, cosmetics, food etc. [1]. The catalytic hydrolysis of triglycerides (TGs) and fats is an important reaction route to produce FFAs that can be used to produce biodiesel from esterification reactions with methanol and ethanol [2]. The hydrolysis reactions of TGs also generate glycerol as observed in the schematic representation presented in Fig. 1. The usual procedure is the separation of glycerol from the medium to produce a pure stream of FFAs to be used latter.

The novelty of this work is the use of the same hydrolysis process (see Fig. 2) also to convert the glycerol of the medium into carbon dioxide and hydrogen which hydrogenates the unsaturated free fat acids (FFAs<sub>unsat</sub>) leading to the formation of stearic fatty acid (saturated). This is desirable in such process as it eliminates the further separation procedures of glycerol as well as producing valuable saturated fatty acids for food and oleochemical industries.

The conventional hydrolysis process to produce FFAs (fat splitting processes) is carried out reacting vegetable oils and/or fats with superheated water (100–260 °C and 100–7000 kPa using 0.4–1.5 wt% of water–oil ratio) [3]. The Twitchell process is one of the earliest industrial processes utilized to produce FFAs from catalyzed hydrolysis of TGs [4]. In such process the hydrolysis reaction of TGs is catalyzed by strong homogeneous acids at the boiling point of the water. This process is not interesting due to the great reaction time as well as high consumption of water. The continuous countercurrent Colgate–Emery process is a non-catalytic and effective technology which the high pressure and temperature lead to short reaction times [5]. The negative aspect of this process is the high capital investment and high operational cost from the great amount of steam utilized. There are other technologies for the production of FFAs from TGs hydrolysis as the subcritical water medium [6,7], the supercritical CO<sub>2</sub> [8], the processes catalyzed by enzymes [9,10] and those which utilizes heterogeneous solid catalyst [11,12]. In the work of Sutton and Moore [11] an acid regenerated cation exchange resin (Dowex-50 catalyst) was used for tallow splitting. A two-stage operation (12 h at 100 °C) leads to fatty acid yields which ranged from 96% to 100%. Ngao-suwan et al. [12] utilized strong solid acid catalysts (tungstated zirconia, WZ, and nafion/silica composite, SAC-13) for continuous

\* Corresponding author. Tel.: +55 22 2519 2166.

E-mail addresses: [diogenescamara@gmail.com](mailto:diogenescamara@gmail.com), [dcamara@iprj.uerj.br](mailto:dcamara@iprj.uerj.br) (L.D. T. Câmara).

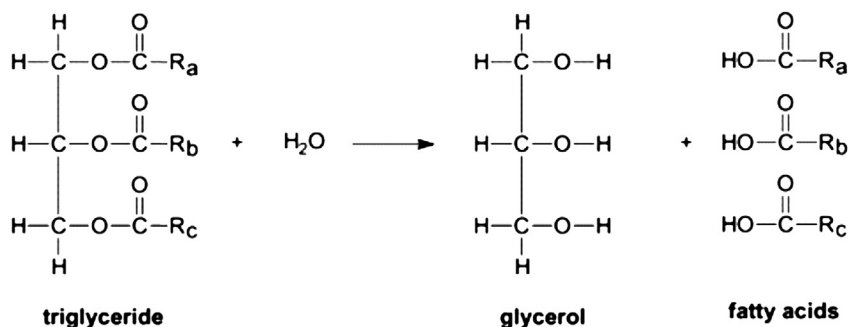


Fig. 1. Hydrolysis of triglyceride generating glycerol and FFAs.

hydrolysis of Tricaprylin (model compound representing TGs) to produce FFAs in a well-stirred semi-batch reactor at atmospheric pressure and temperature in the range between 110 and 150 °C. The authors observed that both catalysts have the capacity to convert 100% of the TG into FFA (caprylic acid).

The glycerol from the hydrolysis reactions of triglycerides can be transformed into valuable products through different steam reforming technologies [13–19]. In general these catalytic processes convert the glycerol into gaseous products such as hydrogen and syngas which can be used further for other purposes. In the work of Kim and Woo [13] the production of syngas was investigated by steam reforming of glycerol using Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/CeO<sub>2</sub>, and Ni/SiC at temperatures below 773 K. The authors observed the following glycerol conversions for the above catalyst, respectively, 77.1%, 49.8% and 90%. The Ni/SiC catalyst generated syngas ratio (H<sub>2</sub>/CO) within 1.0–1.9 which is the molar relation required for the Fischer–Tropsch synthesis. Manfro et al. [14] utilized nickel catalysts supported on Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub> to evaluate the steam reforming of glycerol (10% v/v) to produce hydrogen in a continuous flow reactor. All catalysts showed conversions close to 100% performed at 500 °C with the following hydrogen selectivity: ZrO<sub>2</sub> > Al<sub>2</sub>O<sub>3</sub> ≈ CeO<sub>2</sub>. Dave and Pant [15] also studied steam reforming of glycerol over nickel based catalyst promoted by zirconia and supported over ceria. The Ni–ZrO<sub>2</sub>/CeO<sub>2</sub> catalyst showed complete conversion of glycerol and high hydrogen yield at 700 °C in a tubular fixed bed reactor. Hakim et al. [16] utilized hydroxyapatite-supported Ni–Ce–Cu catalysts to study the steam reforming of glycerol to produce hydrogen. The authors achieved 57.5% hydrogen yield for high glycerol conversion (97.3%) with 240 min reaction time in a fixed-bed reactor at 600 °C.

In this work the hydrolysis potential of the catalysts (NiO or PdO supported on Al<sub>2</sub>O<sub>3</sub> or SiO<sub>2</sub>) was evaluated through the conversion of soybean oil and tallow into FFAs. Also was verified the potential to convert the in-situ generated glycerol into hydrogen (H<sub>2</sub>) and carbon dioxide (CO<sub>2</sub>). The glycerol conversion was measured through the ability of the hydrogen to hydrogenate the unsaturated fatty acids leading to the formation of stearic acid (saturated compound).

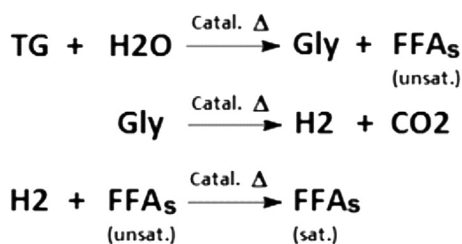


Fig. 2. Steps in the hydrolysis reaction of triglyceride (TG).

## 2. Experimental section

### 2.1. Reactants and catalyst preparation

The raw materials utilized were soybean oil and beef tallow which are different source of triglycerides. The catalysts utilized in the heterogeneous reactions were nickel or palladium supported either on gamma alumina (Al<sub>2</sub>O<sub>3</sub>) or silica (SiO<sub>2</sub>). The following metallic precursors were used as a source of Ni and Pd, respectively, the nickel nitrate salt (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O) and palladium chloride (PdCl<sub>2</sub>). The metallic precursor was loaded into the support, through the wet impregnation method, to incorporate the metals as nickel oxide (NiO) or palladium oxide (PdO). The pretreated  $\gamma$ -alumina is added to the solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in demineralized water and then dried in oven for 12 h. The mixture is calcined at 500 °C for 3 h through a programmed temperature increase. Similar procedure was made to obtain palladium catalyst, using a solution of palladium chloride as precursor.

The following analyses were utilized in the catalysts characterization: X-ray fluorescence spectrometry (model Bruker S4 explorer); nitrogen physisorption (Tristar 3000; Micromeritics); BET method for determination of specific area and BJH method for calculations of the specific volume and the pore diameter; X-ray diffraction (Rigaku model miniflex, 30 kV, 15 mA); X-ray photoelectron spectroscopy–XPS (Physical electronic 5701); Thermogravimetric analysis (Pyris TGA, Perkin Elmer); Temperature programmed reduction (Micromeritics autochem TPR 2920 cryocooler II); Scanning emission microscopy–SEM (Jeol 840); Transmission electron microscopy–TEM (Philips CM 200).

### 2.2. Sample analysis

The free fatty acids were determined through the methodology of Yoo et al. [20]. The samples were previously treated with 2 mL of methanol (5% HCl) to generate fatty acid methyl esters which were analyzed by gas chromatography (EN 14103). An important analysis was the enzymatic glycerol content which follows the technique described by Sampaio and Camacho [21]. Another analyses carried out were the acidity, the iodine number and also the elemental (Elemental analyzer Perkin–Elmer 2400 CHN). The gaseous products, carbon dioxide and hydrogen, were determined, respectively, via the gas analyzers NOVA (model 5005) and PGA (E-One).

### 2.3. General reaction procedure

Reactions were performed in 300 mL stainless steel batch reactor (Parr instruments 4842) with maximum pressure of 3000 psia being equipped with a sample withdrawal valve, stirring and heating systems. In the experimental runs were utilized 30 g of soybean oil or

Download English Version:

<https://daneshyari.com/en/article/300081>

Download Persian Version:

<https://daneshyari.com/article/300081>

[Daneshyari.com](https://daneshyari.com)