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Conversion of fatty acids into hydrocarbon fuels based on a sodium carboxylate intermediate

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ABSTRACT

In this work, it was investigated the conversion of fatty acids into hydrocarbon based on the reaction with NaOH followed by a controlled thermal decomposition. FTIR, Raman, UV–vis, XRD, TG-MS, SEM/TEM, CHN, GC–MS showed that precursors based on NaOH/oleic acid (molar ratios 0.7, 1.0, 1.5 and 2.0) decomposed at 550 °C to produce three fractions, *i.e.* liquid (5–37 wt%), gas (52–70 wt%) and solid (10–31 wt%). The liquid fraction was composed of a complex mixture containing mainly aromatic compounds. On the other hand, the major gas fraction showed a remarkable selectivity for propane (56–61 wt%) with some C_1, C_2, C_4, H_2 and CO_x. The solid fraction showed the presence of Na_2CO_3, Na_2O and particles of amorphous and graphene like carbon. Upon treatment at 800 °C the carbonate decomposes to CO_2, oxidizes the carbon and regenerated the Na_2O which can potentially be used for a new reaction cycle. These results are preliminary discussed in terms of a catalytic effect of the basic sodium oxide to promote cracking, dehydrogenation and H-transfer reactions.

1. Introduction

The production of fuels from renewable substrates has been intensively investigated in the last decades [1]. The use of vegetable oils to produce biodiesel is currently the most important route [2–4]. The biodiesel production is usually performed using homogeneous (Na and K hydroxide or alkoxide) or heterogeneous basic catalysts for the transesterification [5–7].

A very important common contamination in vegetable oils is free fatty acids (FFA), for instance, palm (*Elaeis guineensis*), macauba (*Acrocomia aculeata*), pinhão manso (*Jatropha curcas*), usually have high FFA contents, *e.g.* 20–70% [8]. Soybean used oil which is a very important waste can also have fairly high concentrations of FFA, *e.g.* 2–10% [9]. The presence of these FFA in concentrations higher than 2% completely hinders the basic catalysed biodiesel production due to the alkaline catalysts deactivation, with the formation of soap (fatty acid salts), stable emulsions and complications in the purification step [6,10,11]. An alternative route to deal with acidic oils consists in esterification in the presence of homogeneous [12] and heterogeneous acidic catalyst [5–7]. In some cases, the vegetable oil is further hydrolyzed to produce FFA and then esterified using acid catalysis [13].

Different approaches to produce fuels from FFA have been described in the literature such as reform to hydrogen [14], catalytic hydrodeoxygenation [15], hydrotreating [16] and catalytic pyrolysis of soaps [17–20].

In this work, it is investigated the conversion of free fatty acids contaminants directly into hydrocarbon fuels. In this process, the fatty acid reacts with NaOH to form a sodium carboxylate intermediate as shown in Eq. (1).

$$C_nH_mCOOH + NaOH \rightarrow C_nH_mCOO^-Na^+ + H_2O \quad (1)$$

The sodium carboxylate can then be thermally treated to decompose due to the strong R-COO-Na + ionic interaction the sodium cation can retain the oxide anion, and a deoxygenation might take place. The deoxygenation process of the carboxylate can lead to the

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fragmentation of the FFA molecule producing hydrocarbon derivatives and likely carbon oxides and sodium oxide (Eq. (2)).

$$C_nH_mCOO^-Na^+ \rightarrow \text{ hydrocarbons} + CO_x + Na_2O \quad (2)$$

Hereon, a detailed investigation of the processes described in Eqs. (1) and (2) using oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$) and NaOH with different molar ratios followed by thermal decomposition is described with the characterization of the different solid, liquid and gas products.

2. Experimental

The precursors were synthetized from the reaction of NaOH and oleic acid (OA) in different molar ratios (0.7, 1.0, 1.5 and 2.0). The resultant mixture was treated at 80 °C for 24 h and then cooled in a desiccator. The carboxylate salts were characterized by Infrared Spectroscopy (IR, Perkin-Elmer Spectrum GX FT-IR System, 4000–400 cm^{-1}, 4 cm^{-1} of resolution, 64 scans, KBr pellets) and Thermogravimetric Analysis coupled to Mass Espectrometry in an argon flux of 20 mL min^{-1}, temperature range of 40–900 °C and heating rate of 5 °C min^{-1} (TG-MS, NETZSCH thermobalance model STA 449 F3 coupled with mass spectrometer NETZSCH Aëolos model QMS 403C with EI and quadrupole analyzer).

For the thermal decomposition experiments, 60–100 mg of the carboxylate salts were placed in a closed tubular quartz reactor (batch mode) connected with a condenser to collect the liquid products and a volumetric system to measure and collect the gas products for GC analysis. The reactor was heated in a ceramic furnace from room temperature to 550 and to 900 °C, both with a heating rate of 10 °C min^{-1}. The materials were kept at those temperatures for 20 min. From this experiment, three fractions were obtained: solid, liquid and gaseous.

The solid products of the thermal decomposition experiments were collected and characterized by Raman spectroscopy (Bruker Senterra, CCD detector, 633 nm and 2 mW LASER), X-Ray Diffraction (XRD, Shimadzu XRD-7000, Cu(Kα) radiation, scanning range 10–80°, 4° min^{-1}), Thermogravimetric Analysis (TG, Shimadzu, model DTG-60H, air or nitrogen flow of 50 mL min^{-1}, temperature range of 25–900 °C and heating rate of 10 °C min^{-1}), Scanning Electron Microscopy (SEM, Quanta 200 FEI) and Transmission Electron Microscopy (TEM, Tecnai G2-20 – SuperTwin FEI – 200 kV). Moreover, the solution obtained after washing the solid with water was analyzed by Total Organic Carbon Analysis (TOC, Shimadzu model TOC-V CPH, 1000 times dilution factor).

The liquid products condensed in a trap during the thermal decomposition experiment were collected and characterized by Elemental Analysis (CHN, Perkin Elmer), Infrared spectroscopy and Gas Chromatography coupled with mass spectroscopy (GC–MS, Agilent model GC 7890, HP-5 column) coupled with a mass spectrometer model 5975C with EI and a quadrupole analyzer).

The gas products formed during the thermal decomposition experiment were characterized by Gas Chromatography (GC, Shimadzu GC-2014 ATF equipped with methanator, TCD and FID).

3. Results and discussion

3.1. Synthesis and characterization of the precursors

The precursors were synthetized from the reaction of NaOH and oleic acid (OA) in different molar ratios (0.7, 1.0, 1.5 and 2.0) named hereon as 0.7Na, 1.0Na, 1.5Na and 2.0Na, respectively.

IR spectra of the Na oleate precursors showed that the carbonyl band of the oleic acid at 1710 cm^{-1} strongly decreased with the appearance of a new band at 1560 cm^{-1} related to the Na^+ carboxylate which suggests that most of the oleic acid has been reacted (Fig. 1) [21].

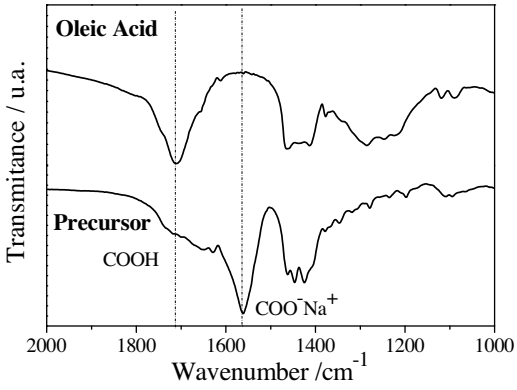

Fig. 1. FT-IR spectra obtained for precursors and oleic acid.

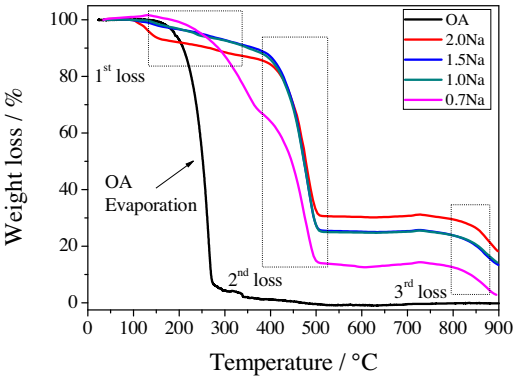

Fig. 2. TG analyses obtained for the precursors and pure oleic acid.

The temperature in which the carboxylates would decompose to produce hydrocarbons was determined by a TG study under argon atmosphere (Fig. 2).

The pure oleic acid presented a single weight loss in the temperature range of *ca.* 200–300 °C due to evaporation. On the other hand, the precursors showed three main weight losses in temperature ranges of 100–400 °C, 400–500 °C and 700–900 °C. The precursor 0.7Na showed a significant gradual weight loss between 100 and 350 °C, likely related to partial oleic acid evaporation due to its high concentration and low Na^+ content. On the other hand, for the 2.0Na precursor a weight loss of *ca.* 10% (100–150 °C) was observed, which is probably related to water molecules due to high Na^+ content on the sample. This event was followed by a small and gradual weight decrease of *ca.* 10%, up to 400 °C. For the precursors 1.0Na, 1.5Na and 2.0Na, a significant weight loss of *ca.* 60% was observed between 400 and 500 °C. These exothermic weight losses (see DTA in Supplementary material) are likely related to the decomposition of the precursors.

A third weight loss can be observed at temperatures higher than 700 °C which can be related to the carbonate decomposition to CO_2 and also to a reported [22] reaction of sodium carbonate with carbon (Eq. (3)) [22]. As expected, this weight loss increases with the increase of Na^+ content in the sample *e.g.* 3% for 0.7Na and 12% for 2.0Na.

$$Na_2CO_{3(s)} + 2C_{(s)} \rightarrow 3CO_{(g)} + 2Na_{(s)} \quad (3)$$

3.2. Investigation of the thermal decomposition of the precursors

Based on the TG results, the thermal decomposition of the precursors was studied in a tubular reactor in temperatures of 550 and 900 °C. The experiments were carried out under static argon atmosphere and the obtained results at 550 °C are shown in Fig. 3.

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