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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 C₁, C₂, C₄, H₂ and CO_x. The solid fraction showed the presence of Na₂CO₃, Na₂O and particles of amorphous and graphene like carbon. Upon treatment at 800 °C the carbonate decomposes to CO₂, oxidizes the carbon and regenerated the Na₂O 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.

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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).

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)).

Hereon, a detailed investigation of the processes described in Eqs. (1) and (2) using oleic acid ($\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$) 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 synthesized 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($\text{K}\alpha$) 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 synthesized 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.

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.

Fig. 3. Product distribution (wt%) for the thermal decomposition of oleic acid and the different precursors at 550 °C.

Three fractions were obtained: solid, liquid and gas. It can be observed that the pure oleic acid almost completely evaporates (about 90%) with the formation of very small amount of gas, probably due to some decomposition process. For all the precursors investigated, the gas fraction was the main product, *ca.* 52–70 wt%. The liquid fraction was generally small except for the sample 0.7Na or any lower sodium content, which is probably due to the evaporation of oleic acid. Previous literature works on the pyrolysis of different Na and Ca soaps in the presence of catalysts or under extreme conditions (heating rate of 1000 °C s⁻¹) showed mainly the formation of liquid products [17–20].

3.3. Characterization of the solid fraction

The composition of the solid fraction was investigated by different techniques such as XRD, Raman spectroscopy, TG, SEM and TEM.

Fig. 4. Raman spectra for the solid obtained by thermal decomposition at 550 °C of the precursors and selected TEM showing carbon and Na₂CO₃ structures.

The XRD patterns obtained for the grey-black solid indicated the presence of sodium carbonate (Na₂CO₃ JCDPS 37-451, see Supplementary material).

The Raman spectra (Fig. 4) of the solids precursors showed three bands at 1068, 1350 and 1588 cm⁻¹. The band at 1068 cm⁻¹ is related to the symmetric stretching of CO band from Na₂CO₃ [23]. TEM images (see detail in Fig. 4) showed many sharp edged dense structures likely related to crystalline Na₂CO₃. The bands at 1350 and 1588 cm⁻¹ are referred as D and G bands, respectively, typical for carbonaceous materials [24]. The D band is related to the presence of defective carbon structures whereas the G band is related to sp² more organized graphene carbon structures [25]. In fact, TEM

Fig. 5. SEM images for the crude solid obtained by thermal decomposition of all precursors at 550 °C.

Fig. 6. TG analyses for the solid fraction obtained by thermal decomposition of the precursors at 550 °C.

images (see detail in Fig. 4) clearly showed amorphous structures and graphene like particles related to carbon.

After washing the solid with diluted acid, the carbonate band in 1068 cm⁻¹ was removed and only the D and G bands are observed (see Supplementary material). TEM analyses of this washed sample showed the different carbon amorphous and graphene like structures (see Supplementary material).

SEM images (Fig. 5) showed needle-shaped agglomerates structures which are in agreement with Na₂CO₃ crystals [26–28].

The amount of carbon present in the solid fraction was determined by the weight loss in the TG (Fig. 6) due to oxidation as shown in Eq. (4).

The carbon oxidation was observed at relatively low temperatures, i.e. 300–500 °C (Fig. 6) compared to other carbon based materials [29], which suggests a very reactive defective carbon. According to the observed weight losses, the carbon contents were 17, 25, 9 and 5% for the precursors 0.7Na, 1.0Na, 1.5Na, 2.0Na, respectively.

It can also be observed a weight loss at temperatures higher than 750 °C related to carbonate decomposition [22]. The carbonate content was analyzed by TC after dissolution of the Na₂CO₃ in water. Fig. 7 shows the composition of the solid fraction estimated by TG and TC. In all cases, the Na₂CO₃ is the main product and the carbon content decreased as excess of sodium is used in the reaction. It is interesting to observe that the Na₂O does not seem to increase for higher Na content in the precursor. This is likely related to the catalytic effect of excess sodium on the formation of more solid carbon and also more carbonate.

3.4. Characterization of the liquid product

The liquid products were analyzed by CHN which showed similar results for all samples, i.e. 65–76% C and 6–7% H. This general composition clearly suggests a very high C/H ratio which indicates the presence of aromatic compounds. In fact IR spectra (Fig. 8) showed bands in the range of 3040–3290 cm⁻¹ related to =C–H stretching, 1400 and 1650 cm⁻¹ possibly due to the C=C stretching of aromatic compounds. Some of the spectra showed a small band at 1718 cm⁻¹ indicating the presence of low amounts of carboxylic acids [30]. Moreover, UV–vis spectra (see Supplementary Material) showed bands at 340 nm related to aromatics.

Fig. 7. Composition of the solid fraction.

Fig. 8. FT-IR spectra for the liquid fractions obtained by the thermal decomposition of the different precursors.

Preliminary GC–MS showed, besides the presence of oleic acid, the formation of a complex mixture of different hydrocarbons which needs a more detailed characterization.

3.5. Characterization of the gas fraction

TG–MS analyses were carried out in order to detect the molecules formed in the gas product during the thermal decomposition. Also, at the end of the experiments, the gases were collected and analyzed by GC. The TGMS obtained results are shown in Fig. 9.

The obtained spectra showed the formation of H₂, CO, CO₂ and hydrocarbons C₁–C₄ for all precursors (see the other TGMS profiles in Supplementary material).

The GC analysis showed that, at 550 °C, the gases formed were essentially hydrocarbons (60–70 mol%), H₂ (20–32 mol%) and carbon oxides (Fig. 10). Moreover, the selectivity for C₃ was higher than 90 mol% among the hydrocarbons.

It is interesting to observe that the gas composition were very similar for all the precursors with a slight increase in H₂ for higher Na content.

After decomposition at 550 °C the gas from the reactor was removed and the sample was further heated up to 900 °C. A very

Fig. 9. TG-MS spectrum of the precursor 1.0Na.

Fig. 10. Gas fraction composition (mol%) at 550°C.

small amount of gas was produced between 550 and 900°C which is in agreement with the TG weight loss observed at higher temperatures. GC analysis of this gas showed the presence of hydrogen, hydrocarbons and carbon oxides.

3.6. General considerations

Considering the information gathered from the mass balance, GC and TG analyses of the different fractions a general idea of product distribution for the precursor 2.0Na is presented in Fig. 11.

It can be observed that the solid product *ca.* 31 wt% is composed mainly of sodium carbonate, sodium oxide and carbon. TG results showed that at temperatures near 800°C the sodium carbonate decomposes and oxidizes the carbon to produce CO and CO₂ and a white powder composed of Na₂O. The most important aspect of this decomposition/carbon oxidation is the regeneration of Na₂O which can be reused for a new reaction with more fatty acid.

The liquid products are formed in relatively small amounts and initial IR, UV and CG-MS analyses suggest the significant presence of aromatic compounds (see Supplementary material). A more detailed characterization of this liquid fraction is necessary to envisage potential applications, *e.g.* fuel, solvent, etc.

The major gas fraction, 58 wt%, was composed of propane and small amounts of H₂, C₁, C₂ and C₄. The carbon distribution in the different reaction products is shown in Fig. 12.

It can be clearly observed that almost 70% of the carbon atoms from the oleate ended up as propane and a significant fraction of the C is present in the liquid products.

Fig. 11. Product distribution for the 2.0Na precursor.

Fig. 12. Carbon atoms distribution (mol%) in the different products of 2.0Na decomposition at 550 °C.

Although the reaction mechanism is not clear, apparently a complex reaction involving different processes is taking place during the decomposition of the sodium oleate precursor. Fig. 13 shows some possible reactions.

The hydrocarbon chain is fragmenting to produce propane as the main product. A simple calculation shows that from the 18C atoms, 12C will result in 4 propane molecules. The formation of high amounts of propane from C₁₇H₃₃ chain involves a significant hydrogen transfer among the carbons. As a result of this process, part of the carbons will be converted to aromatic compounds (as observed in the liquid fraction with a C/H ratio near 1/1) and a significant amount of solid carbon (char). Therefore, these data suggests that the sodium oleate precursor decomposes/cracks, produces/transfers hydrogen and aromatize to small molecules and solid carbon

It is interesting to observe that sodium has a fundamental role in these reactions, since pure oleic acid does not decomposes and only evaporates. The strong basic character of Na₂O formed in the reaction likely promotes catalytic cracking reactions and also the H transfer processes [31].

The reason for the remarkable selectivity observed for propane is not clear and further investigation is necessary in order to

Fig. 14. Formation and decomposition cycle of sodium oleate.

understand the possible reaction steps, the interaction of the alkyl chain with the Na⁺ ion, the dehydrogenation and H-transfer processes.

The obtained results also point to a possible cyclic process where the sodium hydroxide or oxide can be regenerated and reused for a new reaction (Fig. 14).

4. Conclusions

This work shows that free fatty acid, a common and undesirable contamination present in vegetable oils, can be converted to hydrocarbons by a simple process of reaction with NaOH followed by a controlled thermal decomposition. In this decomposition process the sodium oleate is converted with a remarkable selectivity to propane and in small amounts C₁, C₂, C₄ and H₂, which is similar in several aspects to liquefied petroleum gas. This process also results in a liquid mixture with aromatic compounds with potential for use as fuels. The sodium oxide can be regenerated at temperatures higher than 800 °C and reused for a new reaction cycle.

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Fig. 13. Scheme of the products formed (wt%) during the thermal decomposition of the precursor 2.0Na and the selectivity achieved (mol%).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.cattod.2016.04.035>.

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