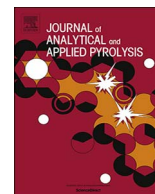




Contents lists available at ScienceDirect

## Journal of Analytical and Applied Pyrolysis

journal homepage: [www.elsevier.com/locate/jaap](http://www.elsevier.com/locate/jaap)

## Thermal and catalytic micropyrolysis for conversion of cottonseed oil dregs to produce biokerosene

Tarciane Greyci dos Santos Souza<sup>a</sup>, Brenda Lohanny Passos Santos<sup>a</sup>, Ayrila Murielly Alves Santos<sup>a</sup>, Anne Michelle Garrido Pedrosa de Souza<sup>a</sup>, James Correia de Melo<sup>b</sup>, Alberto Wisniewski Jr.<sup>a,\*</sup><sup>a</sup> Department of Chemistry, Petroleum and Energy from Biomass Research Group – PEB, Federal University of Sergipe – UFS, 49100-000, São Cristóvão, SE, Brazil<sup>b</sup> Northeast Strategic Technologies Center – CETENE, Experimental Biodiesel Plant, Caetés, PE, Brazil

## ARTICLE INFO

## Keywords:

Cottonseed oil dregs  
Bio-oil  
Biokerosene  
Micropyrolysis  
Catalytic thermal conversion

## ABSTRACT

A sample of cottonseed oil dregs was obtained by the alkali pretreatment of the oil to remove free fatty acids and other impurities before an industrial biodiesel production process. The alkali dregs was characterized and submitted to non-catalytic, catalytic, and reactive hydrogen atmosphere micropyrolysis experiments to assess the capacities for type SPK–HEFA biokerosene production. Non-catalytic and catalytic micropyrolyses were performed at 500 and 550 °C. In the catalytic experiments, catalysts based on Mo or W oxides supported on Zr or Ti oxides were tested for the first time for this purpose. The moisture content of the cottonseed oil dregs was 23.4% (wt%) and the other major components were triacylglycerols + free fatty acids (65.0%) and inorganic material (9.8%). The products of the micropyrolysis experiments were characterized by GC–MS and quantified by GC–FID. The presence of moisture in the initial feedstock provided better results in the thermal conversion to liquid biofuel (16%), compared to dry biomass (6%), considering the *n*-alkanes and *n*-alkenes produced in the range C<sub>9</sub>–C<sub>16</sub>. The mass conversion performed in the presence of catalysts at 550 °C resulted in an average yield of around 32%, compared to a value of 19% for a non-catalytic process under a nitrogen atmosphere, with the same values for the yields under a reactive hydrogen atmosphere. The reactive atmosphere and the catalysts did not have any substantial influence on the ratio between *n*-alkanes and *n*-alkenes.

### 1. Introduction

Biofuels have emerged as an alternative to replace fossil fuels used for energy, heat, and transport, which account for 80% of total global energy use [1]. The growth in energy demand has intensified the search for alternative sources to replace oil, minimizing the emission of pollutants [2].

To this end, the development of alternative aviation fuels has been gaining attention as this sector represents about 2% of global CO<sub>2</sub> emissions into the atmosphere. Some quantification methods have estimated values as high as 3.5% [3,4]. Although the aviation sector is 70% more efficient today than 40 years ago, due to the use of lighter aircraft and new engine designs, it is growing at a fast pace, with estimated growth of 5% per year up to 2030. This growth is higher than the expected increase in fuel efficiency over the same period (3% per year), leading to an increase in fuel consumption and concomitant increases in emissions [5]. Hence, there is an urgent need to find sustainable sources of raw materials to supply the demands of the aviation industry, which according to the International Air Transport

Association (IATA) is still a major challenge [6].

In this situation, waste materials rich in triacylglycerols (TAG) and Free Fatty Acids (FFA) are attracting increased attention in the context of green chemistry, because they are inexpensive and assist in waste management and the avoidance of environmental impacts. One such material, cottonseed oil sludge, is a promising alternative source for the production of biokerosene. Among other advantages, this material is rich in oil (TAG + FFA) (approximately 65%, by mass).

The use of non-edible oils as raw materials for the production of substitutes to fossil fuels, frequently find a high acid value oils which prevents their use to biodiesel production, however, they can be converted by pyrolysis in bio-oils as showed to a waste cottonseed oil [7]. The crude oil obtained from cottonseed is dark in color due to the presence of pigments including gossypol, a yellowish polyphenolic compound with well-defined physical and chemical characteristics. For biodiesel production, a refining process is employed to eliminate these thermolabile pigments using heat and caustic treatment to remove FFA for acidity decrease. This generates a sludge that is rich in FFA in the form of soap and TAG that are dispersed in the soap, together with

\* Corresponding author at: Universidade Federal de Sergipe, Departamento de Química, Rodovia Marechal Rondon, s/n, Jardim Rosa Elze, São Cristóvão, Sergipe 49100-000, Brazil.  
E-mail address: [albertowj@ufs.br](mailto:albertowj@ufs.br) (A. Wisniewski).

<https://doi.org/10.1016/j.jaap.2017.12.010>

Received 7 April 2017; Received in revised form 15 December 2017; Accepted 22 December 2017  
0165-2370/ © 2017 Elsevier B.V. All rights reserved.

phosphatides and other impurities [8]. The FFA and TAG constitute a mixture which can return for the production of biodiesel producing mono-alkyl esters, generally, methyl or ethyl esters, obtained by esterification or transesterifications of FFA or TAG, respectively. Waste biomasses rich in FFA + TAG in a soap form or mixed with inorganic elements do not have an attractive cost advantage to produce biodiesel [9].

Pyrolysis has been widely studied for obtaining fuels from biomass, with the aim of producing smaller molecules from the cracking of larger molecules by the application of thermal energy. Studies concerning the pyrolysis and catalytic cracking of residual fats, oils, and greases to produce kerosene-like hydrocarbons have been carried out at micro, laboratory, bench, and semi-pilot scales [10]. Allied to pyrolysis, diesel has been successfully obtained by the catalytic deoxygenation of fatty acids at high temperature under an inert gas or hydrogen [11,12]. Biokerosene and green diesel have been obtained by catalytic deoxygenation cracking of macauba oil over a palladium on carbon catalyst [2], and non-edible oil has been converted into a high-quality jet fuel product [13]. Catalysts based on zirconium oxide-modified tungsten or molybdenum oxides are widely used in the petrochemical industry and have been employed in important industrial reactions, such as isomerization and the alkylation of *n*-alkanes [14].

The pyrolysis of cottonseed has been described with a maximum bio-oil (liquid phase obtained by the biomass pyrolysis) yield of 49.50% (w/v) was obtained from cottonseed by thermal cracking at 500 °C, and chemical characterization of the bio-oil indicated that it consisted mainly of *n*-alkanes and alkenes [15]. A catalytic and non-catalytic pyrolysis on fixed-fluidized bed reactor was studied to produce hydrocarbons in a range from dry gas to light distillate, such as dry gas, liquefied petroleum gas and gasoline [16].

This work describes the production of SPK-HEFA biokerosene (Synthesized Paraffinic Kerosene – Hydroprocessed Esters and Fatty Acids) [17], as defined by the Brazilian National Agency for Petroleum, Natural Gas, and Biofuels [18], using catalytic heat treatment applied to cottonseed oil dregs. There have been few studies concerning the use of this type of feedstock for conversion into biofuels by these processes and we present an option for the industry to manage this sludge waste producing an add-value product.

## 2. Experimental

### 2.1. Characterization of cottonseed oil dregs

Analyses of namely moisture and ash contents were analyzed according to ASTM D3172-13, oil content were carried out following the methodology ISO 659:1998. A sample of cottonseed oil dregs was provided by the experimental biodiesel plant of the Northeast Strategic Technologies Center (CETENE, Caetes, Pernambuco, Brazil).

The moisture content was calculated from the mass loss after heating at 105 °C for 12 h. The ash content was determined by difference, using heating at 525 °C for 4 h. The oil content was determined by conventional liquid–liquid extraction, using 15 mL of dichloromethane (DCM) to 50 mg of dry biomass. The extracted organic layer was evaporated using a rotary evaporator at 40 °C and 60 rpm, followed by measurement of the final mass. The total acid value of the oil extracted from the cottonseed oil dregs was determined according to ASTM method D974, employing a mass of 0.5 g of oil. A sample of 50 mg of extracted oil was esterified using 1 mL of methanol and one drop of concentrated sulfuric acid, placing the mixture in an oven at 60 °C for 30 min. After cooling to room temperature, addition was made of 5 mL of distilled water and 2 mL of dichloromethane. The organic phase was collected and analyzed by gas chromatography.

The thermal behaviors of the wet and dry cottonseed oil dregs were evaluated by thermogravimetric analysis (TG) and differential thermal gravimetric analysis (DTG), employing a Shimadzu TGA-50 instrument. A 6 mg mass of sample was heated at a rate of 8 °C min<sup>-1</sup> in the range

26–600 °C, under an atmosphere of nitrogen at a flow rate of 40 mL min<sup>-1</sup>. FTIR spectra of the dried sludge sample and the oil sludge extracted with dichloromethane were obtained using KBr pellets and a Varian 640-IR spectrometer. The spectrum was scanned in the range 4000–400 cm<sup>-1</sup>, using a resolution of 4 cm<sup>-1</sup>, acquisition of 32 scans, and employing the air spectrum as the background. Samples of the dried biomass and the ash were characterized by energy dispersive X-ray fluorescence spectrometry, using a Shimadzu Model EDX-720/800HS instrument equipped with a rhodium tube X-ray generator, a silicon detector, a 10 mm collimator, and a liquid nitrogen cooling system. The working range covered atoms with atomic numbers 11–92, with a total analysis time of 50 s for each sample, operating in quantitative mode. Elemental composition (C, H, N, and O) was determined using a CHN analyzer (Model 628, LECO).

### 2.2. Off-line micropyrolysis

The micropyrolysis system was constructed in-house using a borosilicate glass test tube (100 mm × 4 mm), which was wrapped with nickel-chromium wire. A line of nitrogen at a constant flow rate of 2 mL min<sup>-1</sup> was attached to one end of the tube, and a cartridge containing an adsorbent material (activated charcoal) and silanized glass wool, which functioned as a trap for the bio-oil, was attached to the other side [19].

Approximately 50 mg of cottonseed oil dregs was placed inside the borosilicate tube, supported on the glass wool at the beginning of the resistance section. A purge of nitrogen gas (2 mL min<sup>-1</sup>) was maintained throughout the micropyrolysis process. The heating process was started, with an estimated time of 3 min to reach 500 °C monitoring with a thermocouple sensor. The system was maintained at the final temperature for a period of 0.5 min and then allowed to cool. After reaching room temperature, the trapped bio-oil was eluted with previously distilled tetrahydrofuran (THF) and collected in a 1 mL volumetric flask for subsequent analysis.

### 2.3. Bio-oil characterization

#### 2.3.1. Gas chromatography with flame ionization detector

Analysis and quantification of the biokerosene obtained from the catalyzed and non-catalyzed pyrolysis procedures employed gas chromatography using a LECO/Agilent Model 7890A GC × GC-FID operated in one-dimensional mode. The columns used were HP-5 ms (30 m × 0.25 mm ID, 0.25 μm) and DB-17 (1.5 m × 0.1 mm ID, 0.1 μm). The detector temperature was 320 °C, the carrier gas was hydrogen at a constant flow rate of 1 mL min<sup>-1</sup>, the injection volume was 1.0 μL, and the injector was operated at 280 °C with a 1:50 split ratio. The primary oven was operated at 40 °C for 5 min, followed by a ramp at 5 °C min<sup>-1</sup>–280 °C (held for 7 min). The temperature of the secondary oven was kept at 20 °C above the primary oven temperature.

The quantification was performed employing a commercial petrodiesel sample as external standard. Five solutions were prepared at concentrations range from 0.003–0.03 g mL<sup>-1</sup> in THF. An analytical curve was constructed by the total areas of all chromatographic peaks detected for the petro-diesel versus the concentration of each solution. For the determination of the bio-oil mass for each obtained solution were considered only the areas related to the alkenes and alkanes produced. The areas corresponding to the fatty acids that were not effectively pyrolyzed were not considered in the calculation. This methodology was used for all the percentage yield determinations in this work, and their values were taken as the average of at least three experiments with an experimental error of ± 5%.

#### 2.3.2. Gas chromatography-mass spectrometry (GC-MS)

The bio-oil solution and the esterified oil (methyl esters) were analyzed using a Shimadzu QP5050A GC-MS system fitted with a DB-5MS column (5% diphenyl, 95% dimethyl polysiloxane; 30 m, 0.25 mm

Download English Version:

<https://daneshyari.com/en/article/7606378>

Download Persian Version:

<https://daneshyari.com/article/7606378>

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