



Thermal and catalytic pyrolysis of sunflower oil using AIMCM-41



Aruzza Mabel de Moraes Araújo^{a,*}, Regineide de Oliveira Lima^a,
Amanda Duarte Gondim^b, Juraci Diniz^b, Luiz Di Souza^c, Antonio Souza de Araujo^b

^a Federal University of Rio Grande do Norte, Sciences and Petroleum Engineering Graduate Program, Natal, RN, 59078-970, Brazil

^b Federal University of Rio Grande do Norte, Institute of Chemistry, Natal, RN, 59078-970, Brazil

^c State University of Rio Grande do Norte, Department of Chemistry, Mossoró, RN, 59610-210, Brazil

ARTICLE INFO

Article history:

Received 2 November 2015

Received in revised form

20 September 2016

Accepted 24 September 2016

Keywords:

AIMCM-41

Thermal pyrolysis

Thermal-catalytic pyrolysis

Green diesel

Biofuel

Sunflower oil

ABSTRACT

This study was conducted on thermal pyrolysis and thermal-catalytic pyrolysis using the AIMCM-41 catalyst with a Si/Al ratio of 50, as an alternative process for turning sunflower oil into biofuel. The catalyst was characterized by X ray diffraction (XRD), N₂ adsorption/desorption and total acidity by adsorption of *n*-butylamine, in which it was confirmed an obtainment of AIMCM-41 with an excellent surface area of 857.7 m² g⁻¹ and good total acidity. TG curves were used to determine the calcination temperature (450 °C) and the infrared spectroscopy (FTIR) confirmed a complete removal of the CTMA⁺. Two liquid fractions were obtained from the thermal and thermal-catalytic pyrolysis of sunflower oil: the first, named bio-oil, is a mixture of hydrocarbons similar to mineral diesel; the second, which was named acid fraction, is composed mainly of high acidity components. It was found by gas chromatography (GC/MS) and infrared spectroscopy (FTIR) that the proportion of acid present in the fraction of bio-oil without catalyst is higher than the proportion of acids in the fraction of bio-oil with catalyst, which indicates that the deoxygenation of the products occurred. Thus, it can be noted that the thermal catalytic sample of the bio-oil features more appropriate results to the diesel range, indicating that the acid sites found in AIMCM-41 catalysts were effective for the oil pyrolysis.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

The world energy matrix is still based on non-renewable and highly polluting fossil fuels, which makes energy generation a critical issue worldwide [1]. The study of alternative energy generation sources was intensified after the second half of the 20th century, due to its renewable nature, wide availability, biodegradability and low cost. In addition, this was also encouraged by the oil crisis, the rise of the fuel demand and the constant growing in environmental consciousness.

Currently, the main processes for the obtainment of biofuels from vegetable oils are transesterification and thermal cracking (pyrolysis) or thermal-catalytic cracking (catalytic pyrolysis). Therefore, pyrolysis becomes an attractive alternative for generating green fuel in an inert atmosphere, which contributes to minimizing the environmental impacts. Thermal pyrolysis operates at high temperatures (700–1000 °C) and yields mostly gaseous products containing straight-chain hydrocarbon fuels. Thermal-

catalytic pyrolysis, on the other hand, occurs at a lower temperature (450 °C) when compared to thermal pyrolysis [2].

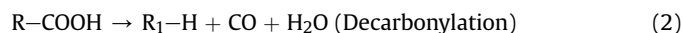
The products, which are a result of the triglycerides breakdown, consist mostly of a mixture of linear hydrocarbons [3,4] and present similar properties to petroleum products such as gasoline or diesel oil, allowing them to be directly used in conventional engines [5]. The presence of the catalyst not only reduces the reaction temperatures but also allows for the obtainment of specific fractions (gas, gasoline or diesel oil) due to its selective property. The acidity level, the porosity of the material and other factors contribute to the selectivity of the catalysts, which is verified by chemical analysis of the cracking products [6]. Ramya et al. [7] studied the production of biofuels, through catalytic cracking of jatropha oil with AIMCM-41, and obtained products composed of hydrocarbons lower than C18. AIMCM-41 (Si/Al = 18) was found to be the most active catalyst as it converted 65% of the jatropha oil, yielding 39% of bio-liquid fuel, with 47% and 36% selectivity towards green diesel and green gasoline, respectively.

Primary cracking corresponds, mainly, to the breaking of C–O bonds of the triacylglyceride and the carboxylic acids resulting in the formation of carbonic-chains, oil residues, and fatty acids. In the second step, known as secondary cracking, there is a deoxygenation

* Corresponding author.

E-mail address: aruzzamabel@gmail.com (A.M.M. Araújo).

of the product formed during the primary cracking [8]. The main reactions proposed for the transformation of carboxylic acids into hydrocarbons are decarboxylation and decarbonylation, which occur during the secondary cracking. Alkanes and carbon dioxides are formed during decarboxylation. Formation of alkenes, water and carbon monoxides are present during decarbonylation [4,9] as shown by the following equations:



R = saturated alkyl group, R₁ = unsaturated alkyl group.

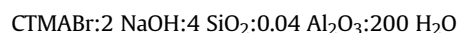
This process has a disadvantage, which is the formation of oxygenated compounds that make the product acid, which can, as a consequence, damage the engine. When the pyrolysis is performed in the presence of heterogeneous catalysts the deoxygenating process is further accentuated [10].

The obtention of biofuel from the pyrolysis of a vegetable oil, such as sunflower, has recently become of great importance due to its renewable nature, wide availability, biodegradability and the possibility of including a new source of energy, one that does not depend on fossil fuels, into the matrix. The study of catalyst application for the pyrolysis of oil is very important for the future of biorefinery. In this sense, new research in the area is necessary and welcome. This project has the aim of performing the synthesis, characterization and the efficiency test of the AIMCM-41 catalyst during the pyrolysis of sunflower oil - using thermal-catalytic pyrolysis as a base for comparison - and of characterizing the liquid products obtained by FTIR and gas chromatography.

2. Materials and methods

2.1. Catalyst synthesis and characterization

The synthesis of the AIMCM-41 mesoporous sieve was performed by the hydrothermal method using a Si/Al ratio of 50, based on experimental procedures from a previous study [11] and on the following molecular composition:



The AIMCM-41 catalyst obtained was characterized by X-ray diffraction (XRD), infrared spectroscopy (FTIR), N₂ adsorption/desorption (BET) and thermogravimetric analysis (TG/DTG) according to methodologies found in the literature [12].

The structural properties of the samples were analyzed by a SHIMADZU XRD 6000, using a CuK radiation source and a nickel filter with a 30 kV tube voltage and 30 Ma, respectively. Data were collected using the powder method in the range of 1–10°, at a scan speed of 2 °C min⁻¹ and a diffraction angle of 2θ.

Infrared analyses were carried out on a BOMEM FTIR spectrophotometer (MB102) in KBr pastille. The FTIR spectra correspond to the sum of 64 scans at a spectral resolution of 4 cm⁻¹.

The surface area of the sample was determined by BET method and nitrogen adsorption/desorption isotherms. Results were obtained using a NOVA 1200e equipment, from Quantachrome. Prior to these measurements, the sample was degassed overnight under vacuum at 573 K, and then subjected to the adsorption of nitrogen at 77 K.

The thermogravimetric (TG/DTG) experiments were carried out using simultaneous Q 600 TA instruments. Approximately 5 mg of the materials were used for the thermogravimetric analyses. The samples were subjected to heat ranging from 30 to 900 °C in a heating rate of 10 °C min⁻¹ with a nitrogen flow of 25 mL min⁻¹ and

using an alumina crucible of 90 μL.

The surface acidity measurement was determined by the method based on adsorption followed by temperature programmed desorption [11]. The base used as a probe molecule is *n*-butylamine and determining the amount of base retained at each temperature range was performed in a METTLER TOLEDO TGA/SDTA 851 thermogravimetric analyzer. The catalyst was subjected to heat ranging from 30 to 900 °C with a heating rate of 10 °C min⁻¹ in nitrogen atmosphere.

2.2. Cracking reaction

The sunflower oil was purchased without any prior treatment from the company Campestre Ind. & Com. of vegetable oil LTDA. The FT-1200 fixed bed reactor from Flyover was used for the cracking reaction, see Fig. 1. The heating was supplied by an electric resistance placed in the inner wall of the oven. The whole process was conducted in the laboratory, at an experimental scale and in batches.

The sunflower oil was placed in a glass boat (d = 15.0 mm, W = 250.0 mm), which was inserted into a borosilicate glass reactor (d = 30.0 mm, W = 50.0 mm). This assembly was placed inside a tubular furnace, equipped with a Type S thermocouple, digital control unit and temperature programming. A condenser was attached to the reactor outlet to cool and condense the products formed, which were then collected with the aid of a round flask.

For the thermal pyrolysis and thermal-catalytic pyrolysis reactions, which occurred under an inert nitrogen atmosphere flow rate of 100 mL min⁻¹, approximately 20 g of sunflower oil were used.

The process of thermal pyrolysis began at room temperature (28 °C). Then, the sunflower oil was heated at a heating rate of 8 °C min⁻¹, remaining 10 min at 425 °C. After removal of the first phase, the remnant oil was heated to 470 °C with a heating rate of 8 °C min⁻¹.

For the thermal-catalytic reaction, the AIMCM-41 was added to the sunflower oil at room temperature (-28 °C). 1% wt of the catalyst in relation to the mass of the oil, was used. Next, the oil was heated to 300 °C with a heating rate of 11 °C min⁻¹ (first phase). The remnant oil was heated to 425 °C with a heating rate of 11 °C min⁻¹ and remaining 7 min at this temperature. The results obtained for the pyrolysis were two fractions: the first one called bio-oil (F1) and the second called the acid fraction (F2). Two other phases were also reported: the gaseous phase (F3) and the solid phase (F4).

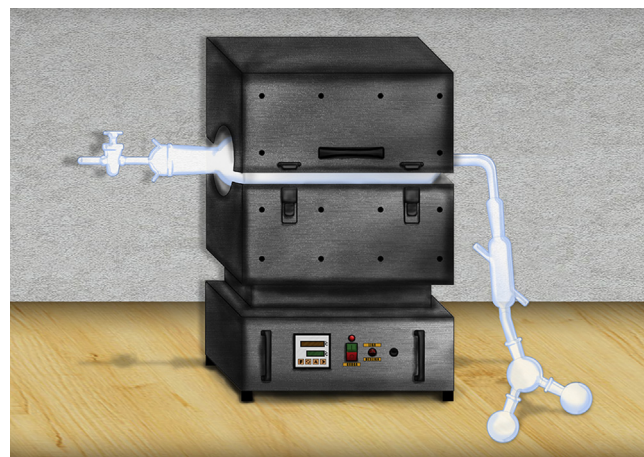


Fig. 1. FT-1200 fixed bed reactor was used for the cracking reaction.

Download English Version:

<https://daneshyari.com/en/article/4926937>

Download Persian Version:

<https://daneshyari.com/article/4926937>

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