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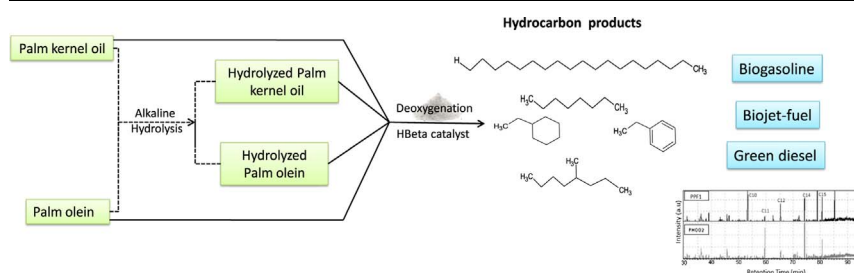
Simultaneous deoxygenation, cracking and isomerization of palm kernel oil and palm olein over beta zeolite to produce biogasoline, green diesel and biojet-fuel



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GRAPHICAL ABSTRACT



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ABSTRACT

Drop-in fuels have aroused great interest for automotive and aeronautical use, constituting the newest area of biofuel research. These fuels do not contain oxygen, like fossil fuels, and require no modifications to engines and distribution infrastructure. In this work, biohydrocarbons were obtained in the distillation ranges of gasoline, diesel and aviation kerosene from palm kernel oil and palm olein in the form of triglycerides or their hydrolysates. A 15% ratio of the thermally activated HBeta zeolite catalyst to the mass of the fatty material was used. Deoxygenation reactions (5 h, 800 rpm, batch reactor) occurred at 350 °C under 10 bar H₂ atmosphere to furnish as much as 96% conversion to liquid hydrocarbons. The products were analyzed by FTIR for a rapid quantification of the deoxygenation efficiency using a method developed for this purpose. These products were also characterized by thermal analysis and GC–MS. The freezing temperatures of the biohydrocarbons and their mixtures with fossil aviation kerosene were determined by DSC. The results obtained were very promising, especially considering the relatively mild process conditions as low H₂ pressure and catalyst without noble metal and with high reusability.

1. Introduction

The limited reserves of fossil fuels and global warming, caused by large CO₂ emissions, have sparked a worldwide search for alternative and sustainable sources of energy for the transport sector. Biodiesel (FAME, methyl esters of fatty acids) is one of the most widely used

biofuels in the world. However, there is a need for engine modifications when it is used in mixtures with fossil diesel at levels above 20%. In addition, it is common to experience a series of problems, such as filter clogging, as a result of the high hygroscopicity of the biodiesel-diesel mixture, which is directly related to the presence of oxygenated molecules that facilitate the proliferation of microorganisms during

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storage and the formation of undesirable solids [1].

An alternative is the use of drop-in biofuels (bio-hydrocarbons) because these can be used in current vehicles in any proportion without the need for modifications in the engines and other mechanical components and without changes in the existing infrastructures for storage and transportation of the fuels. These biofuels can be synthesized by the reduction of fatty materials at high temperatures (300–450 °C) under H₂ pressure (40–150 bar) using special catalysts [2–7]. Hydrocarbons in the boiling point range of gasoline, aviation kerosene and diesel can be synthesized by this route. However, the cost and technological complexity are much greater than those involved in transesterification for the production of biodiesel. Thus, further studies in this area are justified.

The aeronautical sector has demanded technologies that permit the use of these biofuels, which must be oxygen free. Quality requirements are rigid, and the required physicochemical characteristics, such as freezing points below –40 °C [8], excellent oxidative stability, and heat of combustion greater than 42.8 MJ/kg, are difficult to achieve. Saturated linear molecules do not have suitable cold properties for use as aviation kerosene. An alternative is the use of short and unsaturated chain compounds, but this option results in a lower calorific value and oxidative stability [9]. Therefore, a subsequent isomerization step, which results in the branching and cyclization of the hydrocarbons, is required.

Heterogeneous acid catalysts are promising for isomerization and cracking reactions [6,10,11]. Zeolites are prominent because they exhibit great catalytic activity, but in most studies in the literature [7,12], zeolites are used as support for noble metals, such as Pt, Pd, Ni, etc., in bifunctional catalysts with high costs. Sankaranarayanan et al. [2] have investigated the hydroprocess of mixtures of sunflower oil and a straight run gas oil in the diesel fuel ranger over sulfided NiO(3%)–MoO₃(12%)– γ -Al₂O₃ incorporating 0, 15 or 30 wt% zeolite beta (HBeta). Catalyst containing 30% HBeta achieved nearly 100% conversion of the vegetable oil into hydrocarbons at 330 °C, 60 bar H₂ and a WHSV of 2 h⁻¹.

Peng et al. [13] have studied the conversion of microalgae oil over Ni supported on HBeta zeolite in diesel-ranger alkanes. Their best conversion of stearic acid in hydrocarbons was 96% of liquid alkanes obtained under 260 °C, 40 bar, 10 wt% Ni/HBeta, using a continuous reactor. Shafaghat et al. [14] investigated the hydrodeoxygenation of a phenolic mixture catalyzed by Ni/HBeta, Fe/HBeta and NiFe/HBeta. They observed that hydrogenation was the dominant pathway in catalysts producing cycloalkanes over Ni/HBeta, while aromatic hydrocarbons were mostly produced through hydrogenolysis over Fe/HBeta. The best conversion in hydrocarbons was approximately 60% under 300 °C, 16 bar H₂, 4 h and 800 rpm;

Twaiq et al. [15] studied hydrocarbon extraction from palm oil using ZSM-5, beta, USY zeolites and hybrids obtained from physical mixtures without metal supported. The reactions occurred in a continuous flow reactor at atmospheric pressure and at temperatures of 350–450 °C. The maximum conversion to hydrocarbons was 53.7% at 400 °C when the beta type zeolite was used. This degree of conversion is considered low for industrial applications.

Aiming to reduce the costs of biohydrocarbons, which must be competitive with fossil fuels, there is a demand for studies of the deoxygenation of fatty compounds using non-doped zeolites, and the dearth of studies in the literature justifies new research. In the present paper, deoxygenation reactions of palm kernel oil (palmist) and olein oil (palm olein) were investigated. Their respective free fatty acids obtained via previous alkaline hydrolysis, were also tested using the non-doped beta zeolite as catalyst. The hydrolysis was done to evaluate the shape-selectivity of HBeta catalyst and to simulate the use of highly degraded, low-priced fatty materials. Zeolites are known as catalysts in isomerization processes because of their acidic character [16]. Their performance was evaluated for producing linear and cyclic or branched biohydrocarbons in a single step. Simultaneous deoxygenation,

cracking and isomerization are of great industrial interest because this route would contribute to reduce costs, which would make the use of biogasoline, green diesel and aviation biokerosene feasible and meet the new demands of the highway and aeronautical sectors with great environmental benefits.

2. Experimental

In this work, two fatty materials from palm were used: the palm kernel oil (Palmist) and the oil extracted from palm pulp (Palm olein). Both raw materials were tested in deoxygenation reactions. They were used in the natural form (triglycerides) and hydrolyzed form (free fatty acids), in a total of four raw materials. The use of hydrolysates simulates the use of waste oils, with high acidity.

2.1. Hydrolysis of oils

The palm kernel oil (50 g) was saponified by heating 23.5 g (0.42 mol) of KOH in 250 mL of 80% ethanol under reflux with stirring at 600 rpm for 1 h. After separation, the product was washed once with a 2 M solution of HCl and with distilled water to pH 6. The olein was hydrolyzed using an analogous procedure. The efficiency of hydrolysis was evaluated using FTIR analysis. It was monitored the disappearing of the band in 1742 cm⁻¹ (C=O of esters), which was present in the triglycerides molecules and the appearing of the band in 1712 cm⁻¹ (C=O carboxylic acid), due to the free fatty acids (FFA) obtained in the alkaline hydrolysis.

2.2. Preparation and characterization of the H-Beta catalyst

For the production of highly acidic beta zeolite (Hbeta) the CP814E* material (Zeolyst International) with Si/Al molar ratio of 25 was heated at 550 °C for periods of 3 h and 15 h in a muffle furnace [12], aiming to change the NH₄⁺ form to H⁺. Structural analysis of the catalyst was performed by X-ray diffraction (XRD). The diffractograms were obtained on a model 6000 Shimadzu diffractometer, with a Cu tube, 30KV voltage, 30 mA current and a scanning speed of 1°/min in a 2 θ range of 5° to 80°. The adsorption and desorption of N₂ were performed on a Quantachrome ASi Qwin 2.0 equipment, with the collection of 50 points. About 200 mg of the calcined HBeta sample was degassed at 200 °C for 12 h prior to analysis. The surface areas were calculated by the BET method (at relative pressures below 0.3), and the pore distribution was calculated by the DFT method at relative pressures higher than 0.35. The evaluation of the catalytic acid sites via TPD (Thermal-Programmed Desorption) was accomplished on a Quantachrome ChemBET-3000 equipment with a TCD (Thermal Conductivity Detector); the current was 150 mA, and the attenuation was 32. A 0.2 g aliquot of each sample was maintained at 200 °C for 1 h in a helium flow (80 mL/min). The adsorption of NH₃ was achieved at 50 °C, followed by desorption at increasing temperatures. To calculate the number of acid sites of the calcined HBeta catalyst at different temperatures (3 h and 15 h), a standard beta zeolite was used for comparison.

2.3. Deoxygenation reactions of palm oils

Simultaneous deoxygenation, cracking and isomerization reactions were performed in a Parr 4348 reactor with 10 g of fatty material (palm kernel oil, hydrolyzed palm kernel oil, palm olein and hydrolyzed palm olein) and 1.5 g of the Hbeta catalyst. Reaction times ranged from 5 h to 10 h, the temperature was 300–350 °C, the initial H₂ pressure was 10 bar and stirring was at 800 rpm.

2.4. Characterization of the deoxygenation products

Fourier transform medium-range infrared spectroscopy (FTIR) was

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