ZEOLITE-CATALYZED RESIDUAL OIL TRANSESTERIFICATION: A REVIEW

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ABSTRACT

The fuels obtained by renewable sources aim to reduce the dependence from countries on fossil fuels, in addition to contributing to the reduction of greenhouse gas emissions. Biodiesel, produced from oils and fats, is an alternative to petroleum diesel, already consolidated in Brazil with more than 60 plants distributed throughout the country. This biofuel is conventionally obtained by a catalytic process of homogeneous transesterification. Despite good yields and simple operational conditions, the product purification stages are costly and generates residues. To solve these problems, researchers are testing different solid catalysts for the heterogeneous transesterification process that offers good yield and require low reagent consumption and relatively mild operational conditions (alcohol: oil ratio, reaction time). The use of zeolites as heterogeneous catalysts for the biodiesel production has stood out for its versatility, high activity, and low production cost, making the process efficient and sustainable. The objective of this article was to review the findings of the scientific literature on the use of zeolites, natural or synthetic, in the production of residual oil biodiesel between the years 2019 and 2023.

Keywords: Biodiesel. Zeolite. Transesterification. Heterogeneous Catalysis.

1 INTRODUCTION

The discovery and exploitation of fossil fuels has driven substantial advances in human civilization and socioeconomic growth. However, the increasing reliance of fossil fuels has resulted in political and economic issues, as well as serious environmental concerns. Therefore, biofuel is a sustainable alternative compared to fuel, as it is renewable and generates fewer polluting gases, leading it to be considered as a solution to mitigate greenhouse gas emissions.[1]

Ethanol and biodiesel are the most common biofuels produced today. In 2023, Brazil had 167 plants in operation, producing more than 500 million liters of ethanol. Brazil is also the second largest producer of biodiesel in the world, only behind the United States.[2,3] The use of biodiesel mixed with petroleum diesel has been mandatory since January 2008, with an addition of 2%. This was only possible when biodiesel was included in the Brazilian energy matrix by the National Program for the Production and Use of Biodiesel (PNPB) as a stimulus for its production and support for the participation of family farming in the production chain. The following year, with the approval of Law 11.097/2005, the optional use of 2% biodiesel mixed with mineral diesel (B2 blend) was established. The National Energy Policy Council (CNPE) is increasingly increasing this percentage, so that in March 2024 the amount of biodiesel mixed with diesel went from 12% to 14%, with the possibility of an increase to 15% in 2025.[3,4]

Ethanol is obtained from the hydrolysis of biomass derivatives (sugar cane, sugar beet, corn), followed by the fermentation of sugars. Meanwhile, biodiesel is produced through the conventional process of homogeneous transesterification of fatty acids, oils and fats, in the presence of short-chain alcohol (methanol or ethanol) and KOH or NaOH (catalyst) to obtain fatty acid methyl esters and glycerin (glycerol) (Figure 1). Despite the good yield and simplicity, this process is invalidated by the separation of the product in the reaction medium, requiring excessive use of washing water, generating contaminants and soaps. The process of producing biodiesel via heterogeneous catalysis allows the catalysts to be easily separated from the reaction mixture at the end of the reaction; in this process, the catalyst can be reused, and the esters formed are more pure.[1,5]

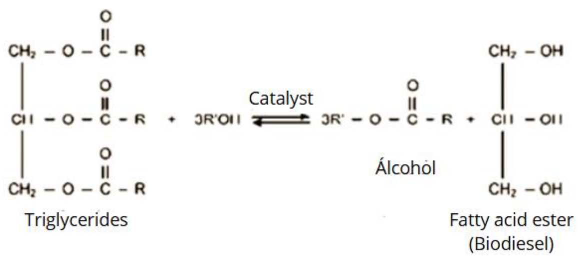

Figure 1 -Trasesterification reaction process for biodiesel production. Source: Adaptado de Widayat, 2013.

For this reason, researchers have sought to develop new heterogeneous catalysts for biodiesel production, and among the different materials researched for this purpose are zeolites. Zeolites are highly porous and versatile aluminosilicates which also function as molecular sieves, enabling smaller molecules to pass through selectively, while larger molecules or molecules with different physicochemical properties are retained. These materials are widely used in various industrial applications due to their high surface area, high molecular selectivity and acid-base properties. Their structure is made up of a network of aluminum, silica and oxygen tetrahedrons (Figure 2), which bond to each other, creating a crystalline network with channels and cavities of uniform size. [5]

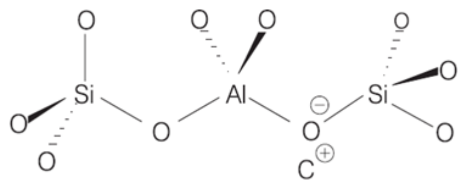

Figure 2 – Molecular structure of zeolites. Source: Mascarenhas, 2001.

Some zeolites occur naturally because of hydrothermal or volcanic phenomena [4], however, there are research that have-focused on synthetic strategies, modifications, and analysis of the properties of new zeolitic materials for application in biodiesel production. Therefore, the aim of this work is to review the results published on the use of heterogeneous zeolitic catalysts that have potential for application in the production of biodiesel from waste oil.

2 MATERIAL & METHODS

The proposed study is based on a systematic review of the literature on the use of zeolitic catalysts in biodiesel production, with a focus on answering the questions: what are the technologies and perspectives developed between 2019 and 2023 on the use of zeolitic catalysts in biodiesel production? what are the advantages and disadvantages observed in the use of these catalysts to produce biodiesel from waste cooking oil? The keywords used in the search were zeolite, biodiesel, transesterification, and waste oil.

In addition to the research questions and definition of the keywords, inclusion and exclusion criteria were established. The inclusion criteria considered were: articles published between 2019 and 2023; presence of the keywords in the title, abstract or keywords and research articles. The exclusion criteria were: course completion papers, dissertations or theses and review articles from the Science Direct database, the following filters were used for the search: publications between 2019 and 2023, document type: research articles and the keywords defined: transesterification, zeolite, biodiesel, residual cooking oil. The search returned 298 articles. After applying the selection criteria, 6 articles were chosen, and after thorough reading, only 3 were selected.

3 RESULTS & DISCUSSION

The three articles selected in the research were: Efficient and economical transesterification of residual cooking soybean oil into biodiesel catalyzed by the external surface of ZSM-22 supported by different Mo catalysts [9]; Transesterification of commercial residual cooking oil into biodiesel on innovative zeolite nanocomposites trapped in alcaqui as green environmental catalysts [8]; and Ni/Zeolite catalyst derived from solid geothermal waste for processing residual cooking oil.[10]

In the work by Zhang et al. (2022) [9], the authors tested a molybdenum (Mo) catalyst supported on a ZSM-22 type zeolite for the synthesis of biodiesel from residual soybean oil. The ZSM-22 zeolite has an orthorhombic structure with a high silica content and one-dimensional linear channels, making it suitable as a support in transesterification reactions due to its own weak catalytic activity, while molybdenum (IV) oxides (Mo 6+) have excellent catalytic activity in these reactions. The authors synthesized the xMo/ZSM-22 catalyst (with x ranging from 1 to 10%) by the wet impregnation method. X-ray diffraction (XRD) of the samples showed good dispersion of Mo on the zeolite surface without damaging the zeolite structure. Comparing the textural properties of unmodified ZSM-22 with xMo/ZSM-22, it was found that increasing the Mo species leads to a decrease in the specific surface area and pore volume of the supported catalysts. The 5Mo/ZSM-22 catalyst (5% Mo) showed the best results, with well-dispersed Mo (VI) oxide and greater acidity, generating greater conversion of waste oil and greater selectivity in biodiesel. Increasing the Mo content did not improve the activity, due to the formation of Mo aggregates which reduced the catalytic efficiency. In addition, the XRD and FTIR spectra confirmed that the crystalline structure of the 5Mo/ZSM-22 catalyst remained intact after recycling/calcination, maintaining good catalytic performance. The biodiesel produced with the Mo/ZSM-22 catalyst met the established international standards (ASTM D66751).

Abukhadra et al. (2020) [8] developed and tested green clinoptilolite catalysts for the production of biodiesel from waste oil. Clinoptilolite is a natural zeolite with a large surface area and thermal stability, in the study they modified clinoptilolite with alkali metals (potassium, sodium, magnesium and calcium) to increase the basicity of the zeolite and improve catalytic activity for the transesterification of waste cooking oil into biodiesel. XRD analysis confirmed the presence of clinoptilolite in the modified samples. Scanning electron microscopy (SEM) showed that clinoptilolite modified with magnesium (Mg) resulted in a more porous surface and texture and a nanoporous matrix, increasing the surface area and pore volume. Meanwhile, infrared (FTIR) and Raman spectroscopy indicated changes in the material's chemical structure. In the transesterification tests, the sample modified with MgO showed greater catalytic activity and biodiesel yield (95%), due to its high surface area (greater availability of active sites) and greater pore volume, resulting in greater conversion. The reuse of the catalysts maintained a good yield in the first cycles of use, but this decreased over time due to the reduction in surface area caused by the coating of the active sites by the transesterification by-products.

Satriadi and colleagues (2022) described the synthesis of a sustainable nickel catalyst supported on zeolite (Ni/Zeolite) obtained as of residues from an Indonesian geothermal energy generation company for biodiesel production. The catalyst was prepared through wet impregnation. Characterization of the residues materials using Energy Dispersive X-ray Spectroscopy (EDS) coupled with Scanning Electron Microscopy (SEM) indicated the predominant presence of SiO3 (75%) and traces of Al2O3. These oxides form the architecture of zeolites and contributes to the reduction of acidity, resulting in increased basicity, which is favorable for biodiesel production, enhancing the catalytic activity and selectivity of the process [10]. The authors evaluated the effects of catalyst concentration and operating temperature on biodiesel production from residual cooking oil. The study demonstrated an increase in biodiesel yield from 82% to 89.4% with the addition of 1% to 3% w/w Ni/Zeolite at an operating temperature of 60°C. Furthermore, larger quantities of the catalyst led to reduced biodiesel yield due to interactions between the reactants and active sites of the catalyst, thereby compromising its activity by decreasing the available reaction sites [10].

4 CONCLUSION

The studies presented have shown that both synthetic and natural zeolites are promising alternatives for the transesterification of residual oils into biodiesel. Zeolites possess microporous structures, high surface area, high stability, high cation exchange capacity, and high mechanical strength, making them ideal for catalyzing transesterification reactions. Additionally, controlled functionalization of zeolite surfaces with acidic or basic groups can further enhance their catalytic activity.

Modifying zeolites with other species can increase surface area, improve acid-base properties, and increased amount active catalytic sites.

Ultimately, the research results indicate that using zeolites as catalysts for converting residual oil into biodiesel could be a promising alternative to homogeneous catalysis in the transesterification process.

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