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Research Article

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Sunflower Oil Ethyl Esters (Biodiesel) Production Using Extruded Catalyst Based on Potassium Carbonate, Sepiolite Clay and Magnetite

Euripedes Garcia Silveira Junior

Center of Science and Agropecuary Technologies, State University of Northern of Rio de Janeiro, Brazil

***Corresponding author**
Euripedes Garcia Silveira Junior, Center of Science and Agropecuary Technologies, State University of Northern of Rio de Janeiro, Brazil.

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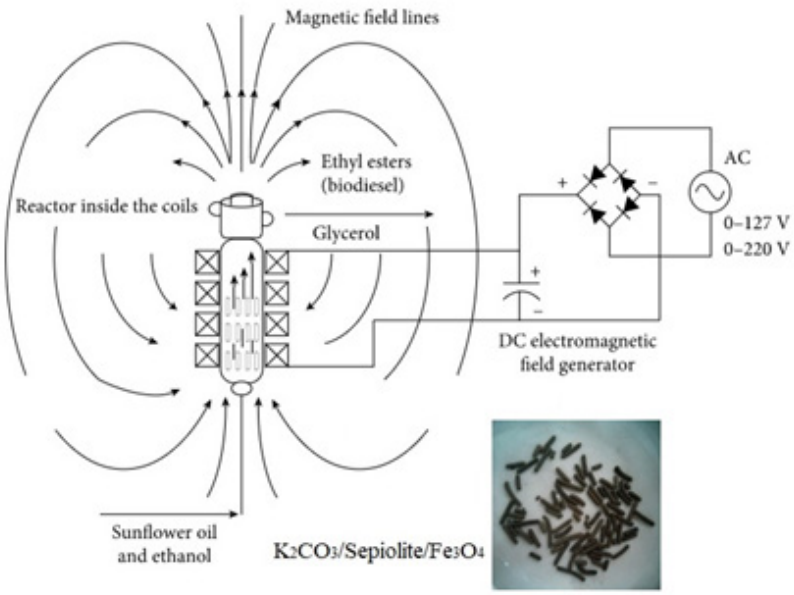


Graphical Abstract

Abstract

In this study, a magnetic catalyst based on potassium carbonate, sepiolite and magnetite was prepared seeking to convert efficiently sunflower oil into ethanolic biodiesel. The magnetic catalyst was attained by extrusion method and characterized by magnetic, mechanical, structural and textural properties. The catalytic performance of this catalyst was also evaluated in a reactor assisted by magnetic field. The reactor was operated in a closed loop, recycling the reaction mixture. High oil conversion to biodiesel was obtained using 2 wt% of catalyst with 1:12 oil/ethanol molar ratio at 70 °C after 2 h. The magnetic properties of this catalyst allowed the bed stabilization under magnetic field and the catalysts separation, enabling its reuse in other reaction cycles.

Keywords: Sunflower Oil, Heterogeneous Catalyst, Magnetic Particles, Reactor Assisted by Electromagnetic Field

Introduction

The use of biofuels has increased worldwide as an alternative to fossil fuels which have important environmental and health consequences. Particularly, the biodiesel, a biofuel produced from vegetable oils and/or animal fatty, achieved a world production around 47 billion litters in 2019 [1].

The conventional biodiesel production is carried out via chemical transesterification of vegetable oils or animal fats with methanol using homogeneous catalysts, as has been extensively reviewed [2]. This process presents some problems such as the use of methanol as reactant alcohol, because is produced from fossil origin as it is mainly produced from natural gas and the use of homogeneous catalysts that makes the process more expensive due to the purification of biodiesel and also treatment of waste water before returning it to the environment. The environmental and economic consequences of using homogeneous catalysts, such as wastewater generation and the impossibility of catalyst reuse have not yet been resolved.

The heterogeneous catalysts have received special attention for the biodiesel production, however, the majority studies present powder catalysts which despite their relevance to homogeneous ones also present problems that affect their performance and therefore need attention [3, 4]. Improvements in this regard can be observed using extruded/ structured catalytic derivatives with different geometries [5-7].

Natural clays such as bentonite, sepiolite, and palygorskite are abundant in nature and have been widely used as support for heterogeneous catalysts, due to their low acquisition cost and their ease of handling, all of which makes studies into the application of these minerals very relevant and advantageous [8-18].

Thus, in this work, a catalyst with magnetic properties based on potassium carbonate, sepiolite and magnetite in pellets shape was employed for sunflower biodiesel synthesis in reactor assisted by magnetic field. In addition, this catalyst was characterized by magnetic, mechanical, structural and textural properties.

The reactor assisted by electromagnetic field is an alternative process that can be used in catalysis/biocatalysis to avoid mass and heat transfer limitations, to improve the reaction times and mixing and the easy bio/catalysts separation from reaction medium by applied magnetic field, thus allowing their reuse in other reaction cycles. This technology has already been used successfully in the biodiesel and bioethanol production [19-23].

Materials and Methods

Preparation of Magnetic Particles and Catalysts

Magnetic Fe_3O_4 nanoparticles were prepared by co-precipitation method [24]. Regarding to the catalysts, firstly, was prepared the K_2CO_3/Sepiolite catalyst. In this case, 35 g of potassium carbonate and 65 g of sepiolite was mixed until total homogeneity and water was adding until a mass forming which that was extruded forming the pellets. For comparative, two catalysts with magnetic properties also were prepared. Thus, 35 g of potassium carbonate and 65 g of sepiolite were mixed until total homogeneity and magnetite (0.2 and 0.4 g to each K_2CO_3/sepiolite gram) was added in the mixture and finally water was added until a mass forming which that was extruded forming the pellets. The catalyst pellets were extruded in solid cylinder shape with a diameter of 1.80 mm and 5 mm length.

Catalyst Characterization

The magnetic properties of the Fe_3O_4 and magnetic catalyst were assessed by SQUID VSM (Quantum Design® models MPMS 57, MPMS 7 T) at 10,000 Oe. Simultaneous thermogravimetric and differential thermal analyses (TGA-DTA) of catalysts were carried out in a flowing air atmosphere using an analyzer (STA 6000) equipped with a gas cell (PerkinElmer). The mechanical strength of the magnetic catalysts was determined using a dynamometer (Chatillon, LTMC model) according to ASTM D4179-82. Qualitative structural analysis was carried out by X-ray diffractometry (XRD, X'Pert PRO Theta/2theta, PANalytical and the patterns were recorded over the angular range of 5–80° (2θ) with a step size of 0.0334° and a time per step of 100 seconds, using Cu Kα radiation (λ = 0.154056 nm) with a working voltage and current of 40 kV and 100 mA, respectively. For textural properties determination, the catalysts were calcined, crushed and subjected to N_2 adsorption at −196 °C in the ASAP 2420 apparatus (Micromeritics Instrument Corp., USA). The specific superficial area, volume and medium diameter of mesopore were obtained by using the BET method; while the accumulative superficial area, volume, medium diameter and distribution of pores, using the BJH method based on the capillary condensation model [25, 26]. The temperature programmed desorption (CO_2-TPD) analysis was carry out using apparatus with thermal conductivity detector (AutoChem II 2920V4.01 model, Micromeritics Instrument Corp., USA). Before the CO_2-TPD experiment, samples (0.2000 g) were treated in situ in a helium flow, heated to 200 °C at 10 °C/min and maintained for 30 min. The samples were then exposed to CO_2 at an initial temperature of 40 °C and with a ramp of 10 °C/min for 60 min and then heated to 500 °C at 10 °C/min under a Helium flow while it was monitoring the desorption of CO_2.

Biodiesel Synthesis

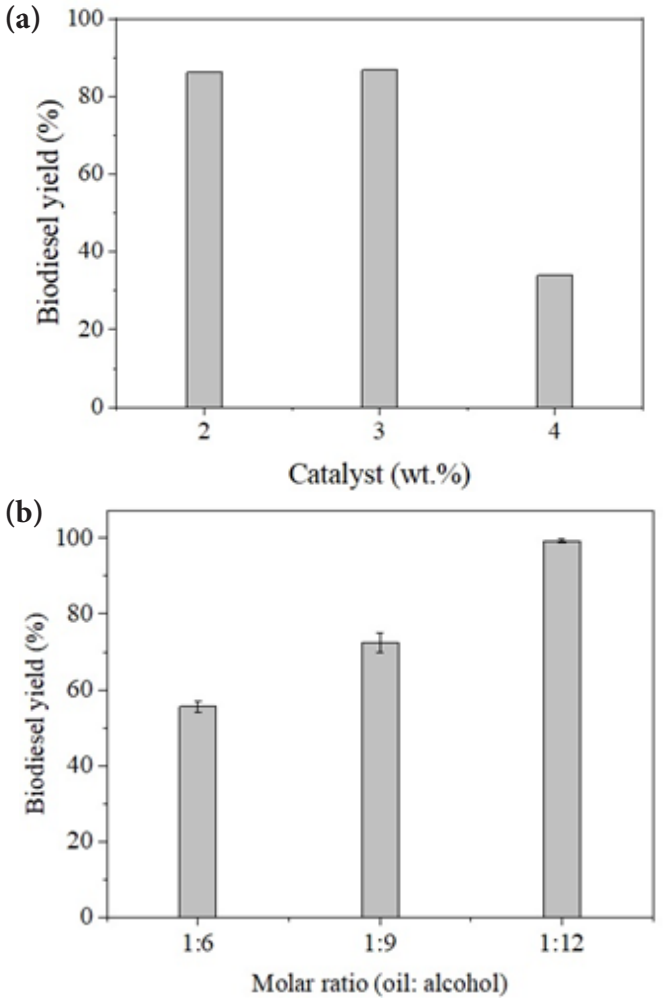
The catalytic performance of the magnetic catalysts was evaluated thought biodiesel synthesis by ethanolic route. The transesterification reaction studies were performed varying the reaction parameters at the following conditions: sunflower oil: ethanol molar ratio (1:6; 1:9 and 1:12 oil), catalyst mass (2, 3 and 5%) and reaction temperature at 70 °C in a glass column jacketed reactor (Height: 250 mm and internal diameter: 15 mm) under magnetic field. The magnetic flux density (12.5 mT) was monitored by a GM08 Gaussmeter (Hirst Magnetic Instruments Ltd., UK). The reactor was operated in a closed loop recycling the reaction mixture at 16.6 mL/min. The formed biodiesel was analyzed and quantified by GC (Shimadzu, GC 2014 model).

Results and Discussion

Firstly, was evaluated performance catalytic of K_2CO_3/Sepiolite on the transesterification reaction of the sunflower oil and ethanol in function of oil: ethanol molar ratio and catalyst mass in the reaction medium (Fig. 1). Fig. 1a shows the effect of K_2CO_3/Sepiolite loading on the transesterification reaction. As can be observed, when the catalyst mass was between 2 and 3wt. % the

conversion achieved was 86%. However, when the mass was doubled to 4 wt. %, the conversion fell by half, suggesting the existence of diffusion limitations in the system and consequently, subsequent syntheses of biodiesel in this work were carried out in a kinetic regime using just 2 wt% of catalyst. Several studies have shown positive effects of increasing the amount of catalyst in the performance of biodiesel formation, up to certain limits [27-30]. However, excessive amounts of catalyst can generate regions of high alkalinity which in turn can trigger, among other problems, in saponification reactions, as occurs, in similar way, when homogeneous catalysts are used in the transesterification, where, excessive amounts of these catalysts can result in negative effects on the biodiesel yield, due to the formation of soap in the reaction and thus, hindering the separation of the glycerin from the esters formed [30, 31]. As can be observed in Fig. 1b, the experimental results showed that the biodiesel yield increased with increasing molar oil/ethanol ratio (1:6, 1:9 and 1:12). At 2 h, the best yield (99.2%) was obtained using a molar ratio of 1:12.

Seeking to evaluate the K_2CO_3/Sepiolite catalytic performance over reaction time, a kinetic study was carried out with 2 wt. % catalyst mass, sunflower oil: ethanol molar ratio of 1:12, 70°C and 200 rpm. Thus, in Fig. 1c, it can be seen that in 60 min of reaction, the biodiesel yield was 90% and since then the reaction rate was slower, reaching 96% biodiesel yield in 2h. In this case, the transesterification reaction can be ended at 2 hours of reaction.



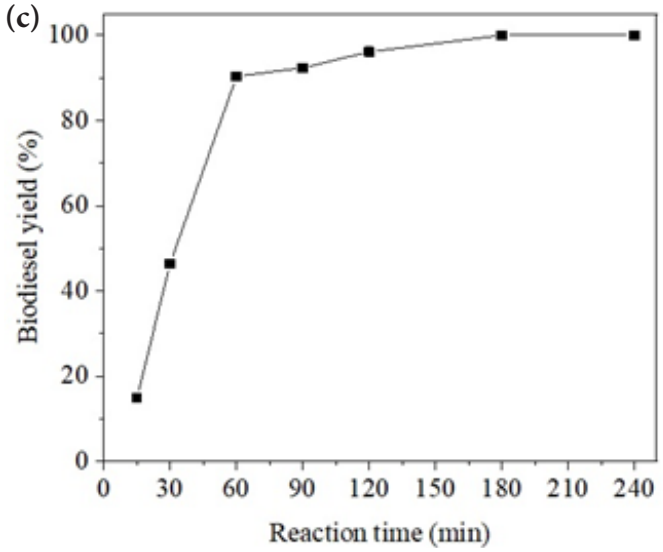
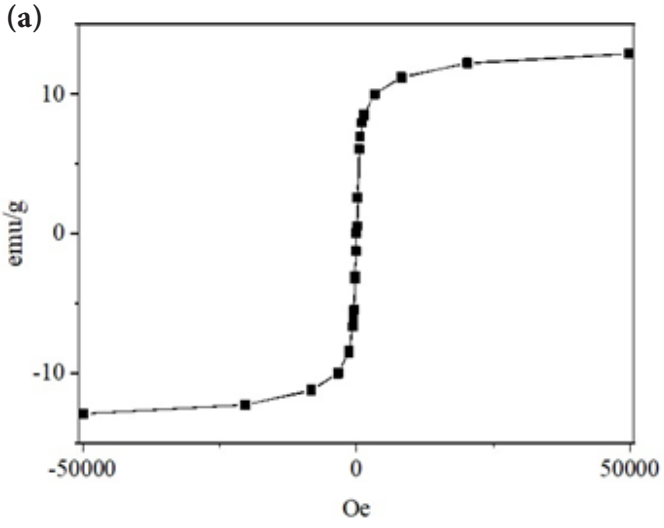


Figure 1: Biodiesel production from sunflower oil, ethanol and K_2CO_3/Sepiolite catalyst with the following reaction parameters: a) 2 h reaction, 200 rpm, 70°C and catalyst mass (2, 3 and 4%); b) 2 h reaction, 200 rpm, 70°C, 2 wt. % catalyst and oil: ethanol molar ratio (1:6, 1:9 and 1:12); c) 4 h reaction, 200 rpm, 70°C, 2wt. % and 1:12 molar ratio.

Seeking the application of this catalyst in a reactor assisted by electromagnetic field, magnetite was used as an additive to the support to impart magnetic properties to the catalyst. Thus, for comparative purposes, 0.2 and 0.4 g of magnetite were added to the catalyst (K_2CO_3/Sepiolite/0.2 Fe_3O_4 and K_2CO_3/Sepiolite/0.4Fe_3O_4, respectively). To characterize magnetic properties of catalysts, VSM magnetization measurements were performed for each catalytic system prepared (Fig. 3). As it can be observed, there were increase in the magnetization value when the magnetite content added to the prepared derivatives increased from 0.2 to 0.4 g/g of K_2CO_3/sepiolite, i.e. 12.93 to 17.13 emu/g. However, a fluid dynamics analysis of these catalysts with magnetic properties performed in the magnetic field reactor (Fig 4), showed that the magnetic properties of these catalysts were suitable for magnetically stabilizing the particle bed with a applied magnetic field between 10 to 12.5 mT, thus enabling the separation of the catalyst in the reaction end.



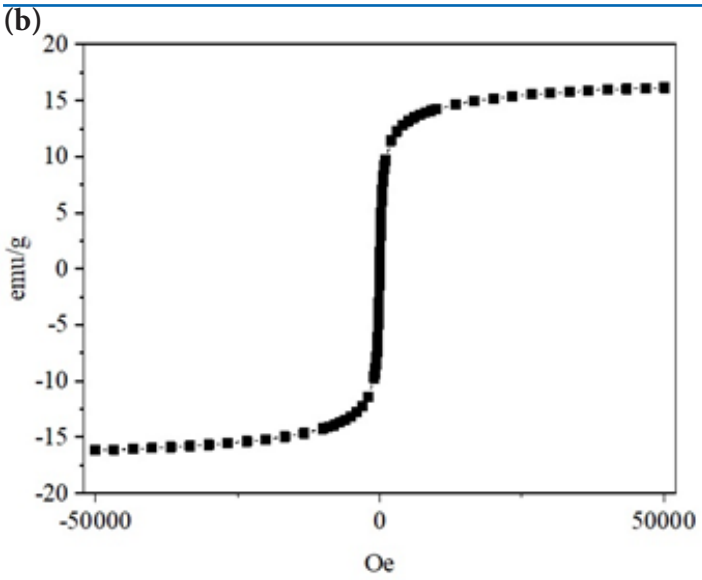


Figure 2: Magnetic characterization by VSM analysis for: a) K_2CO_3/Sepiolite/0.2Fe_3O_4 and b) K_2CO_3/Sepiolite/0.4Fe_3O_4. Analysis conditions: M vs T, give H = 10000 Oe as applied field and for the M vs H, give T = 300 K.

In addition, the catalytic activity of the developed catalysts was measured by the transesterification reactions for biodiesel formation (Figure 5), carried out according to the conditions previously described, i.e., 2wt.% catalyst, 1:12 molar ratio, 70°C and the reactor was operated in a closed loop recycling the reaction mixture at 16.6 mL/min. In this context, the kinetic results of the transesterification reaction (Figure 5) revealed that in all cases biodiesel formation occurred independently of the Fe_3O_4 content in the catalyst, showing the best results, i.e., 98.15% in 3h, when K_2CO_3/Sepiolite/0.2Fe_3O_4 was used.

As can be seen, the catalyst K_2CO_3/Sepiolite/0.2Fe_3O_4 has presented a better performance and this can be explained by the fact that the electromagnetic field has a smaller effect on the catalyst stabilization inside the reactor, since the concentration of magnetite in the catalyst is smaller. In this way, the pellets flow freely in the reactor column, which provides a better yield in the synthesis of biodiesel. With a higher content of magnetite in the catalyst (K_2CO_3/Sepiolite/0.4Fe_3O_4), when an electromagnetic field is applied, the pellets tend to align better in the direction of the electromagnetic field lines, however, forming particle agglomerates that formed due the presence of strong interparticle attraction forces and this agglomeration can reduce the contact area between the reactants and the catalyst, thus resulting in a lower biodiesel yield.

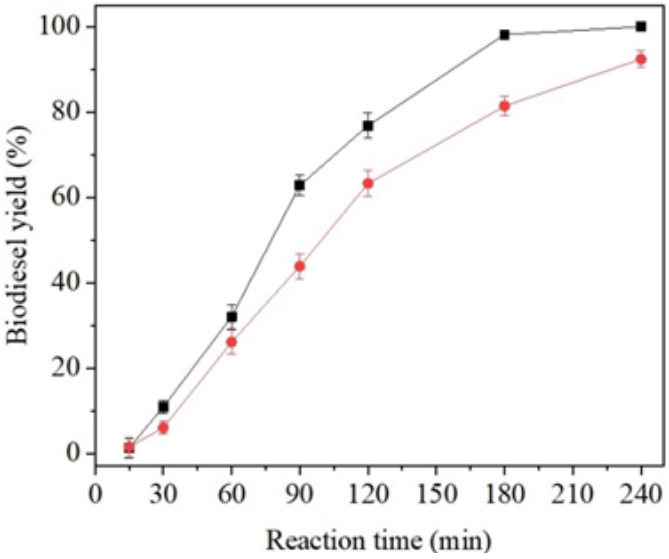


Figure 3: Biodiesel synthesis by magnetic catalyst in reactor assisted by electromagnetic field. Symbols: ■ K_2CO_3/Sepiolite/0.2Fe_3O_4; ● K_2CO_3/ Sepiolite/0.4Fe_3O_4.

After the reaction, it was possible to observe that the catalysts were all in their entirety, i.e., without breaks or ruptures. As can be seen in Table 1, the magnetic catalyst mechanical strength obtained after dynamometry analysis was adequate to avoid breaking the catalysts during the transesterification reactions, which can occur due to collisions with the blade's stirrer or the reactor walls. Regarding transesterification reactions, the results can be considered satisfactory and can be associated with the catalyst basicity that presents basic sites with moderate strengths and your textural properties (specific area, volume and size pores) which contributed to a great performance of catalyst.

Table 1: Physico-Chemical Properties of Magnetic Catalysts

Physico-chemical properties	K_2CO_3/Sepiolite/0.2F_3O_4	K_2CO_3/Sepiolite/0.2F_3O_4
Mechanical strength (kgf/cm)	1.81± 0.47	2.00 ± 0.03
Specific area (m^2/g)	8.3	12.4
Pore volume (cm^3/g)	0.04	0.06
Pore size (nm)	23.8	23.2
Basicity (mmol/g of CO_2)	0.52	0.75
Density of basic sites (mmol of CO_2/m^2)	0.06	0.06

In addition, thermogravimetric analysis (Fig. 4) was carried out to determine the best calcination temperature, in the case, the K_2CO_3/Sepiolite/0.2Fe_3O_4 catalyst. Thus, according to the obtained results (TGA/DTG) it is possible to calcinate the catalyst at 500 °C, since at this temperature no degradation stage was observed in the catalyst.

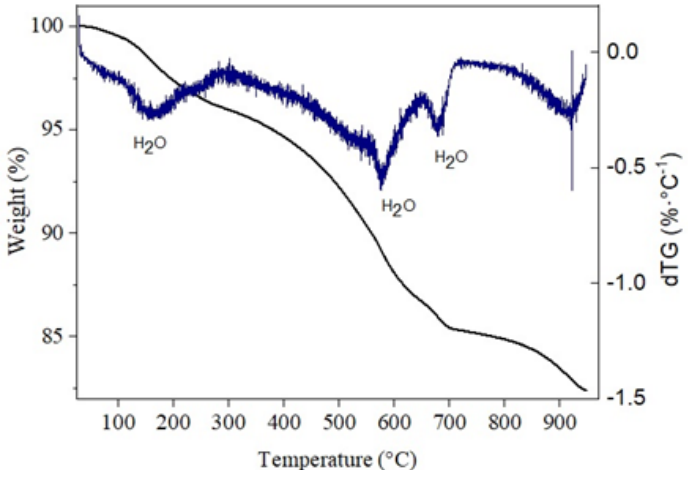


Figure 4: Thermogravimetric analysis (TGA/ DTG) for the catalyst K_2CO_3/Sepiolite/ $0.2Fe_3O_4$.

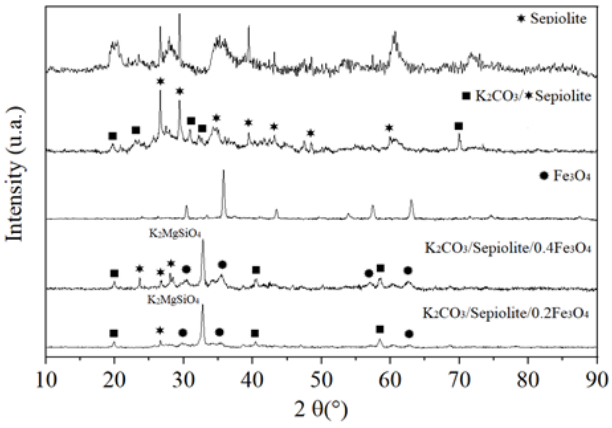


Figure 5: X-ray diffraction patterns of the: sepiolite, K_2CO_3/ Sepiolite, magnetite, a) maghemite, K_2CO_3/Sepiolite/$0.2Fe_3O_4$ and K_2CO_3/Sepiolite/$0.4Fe_3O_4$.

The XRD patterns of sepiolite, K_2CO_3/Sepiolite, magnetite and magnetic catalysts are shown in Fig. 3. The sepiolite has a characteristic diffraction peaks (JCPDS #26-1226), showing to be amorphous material. In the K_2CO_3/Sepiolite catalyst case, can be observed that potassium carbonate is well distributed in the sepiolite, and the diffraction peaks are between 20-40° (JCPDS #45-1499). The magnetite has diffraction peaks corresponding to $FeFe_2O_4$ (JCPDS #019-0629). Finally, in the case of magnetic catalysts, peaks related to magnetite (JCPDS #19-0629) and active phase (K_2MgSiO_4) has been identified (JCPDS #39-1426).

The Table 2 show some studies reported in the literature with catalysts prepared using sepiolite clay as catalytic support in heterogeneous catalysts. Comparatively, the presented catalyst in this work shows a satisfactory performance, catalyzing the sunflower oil into biodiesel with high conversion rate under moderate reaction conditions when applied in a reactor assisted by electromagnetic field. As it has already been reported in the literature, the powder catalysts present great difficult to be separated from a viscous reaction media, due the particles sizes of the powder catalysts to be very fine and consequently forming agglomeration in the reactional medium, thus affecting their catalytic performance [11].

Regarding the extruded catalysts, these presents a great potential in biodiesel synthesis and are very attractive due to their conformed structure which present good mechanical properties and allow for easier recovery from reactional medium for regeneration resulting in excellent catalysts for several applications. In addition, the reactor assisted by electromagnetic field showed suitable for magnetically stabilizing the particle bed and it is possible to guarantee the separation of the catalyst from the reaction medium when the biodiesel formation is completed.

Table 2: Studies Showing Heterogeneous Catalysts using Sepiolite as a Catalytic Support

Catalyst type	geometry	Reaction parameters			Biodiesel Yield (%)	Ref.
		Oil: alcohol (molar ratio) and catalyst mass	Reaction temperature (°C) and reaction time (min)	Reaction stirring or other parameters		
K_2CO_3/Sepiolite/$0.2Fe_3O_4$	pellets	Sunflower oil: ethanol (1:12) and 2% catalyst	70°C and 180 min	reactor operated in a closed loop recycling (16.6 mL/ min) and 12.5 mT	98.15	In this study
K_2CO_3/Sepiolite	pellets	Sunflower oil: ethanol (1:12) and 2% catalyst	70°C and 120 min	200 rpm	96	In this study
KOH/Sepiolite	powder	Canola oil: methanol (1:9) and 9% catalyst	79.8°C and 20 min	Microwave Irradiation	57.14	Karaoğlu et al., 2021 [10]
K_2CO_3/Sepiolite	pellets	Forage turnip oil: ethanol (1:12) and 2% catalyst	70°C and 240 min	Magnetic stirrer	99	Silveira Junior et al., 2019 [19]

NaOH/Sepiolite	powder	Canola oil: methanol (1:9) and 6% catalyst	60°C and 180 min	Magnetic stirrer	80.93	Aslan et al., 2019 [12]
K-Sepiolite	powder	Grapeseed oil (10 mL): methanol and 3% catalyst	160°C (~15 bar) and 15 min	Biotage microwave system	100	Al-Ani et al., 2018 [13]
K_2CO_3/Sepiolite	powder	Canola oil: methanol (1:6) and 3% catalyst	65°C and 480 min	temperature controlled magnetic stirrer	98.5	Degirmenbasi et al., 2014 [14]

Conclusion

In this work, the catalysts based on potassium carbonate, sepiolite clay and magnetite where was prepared with good magnetic, mechanical, structural and textural properties. The best results were obtained when K_2CO_3/Sepiolite/(0.2)Fe_3O_4 was used as a catalyst in the transesterification reaction in reactor assisted by electromagnetic field, reaching a yield in ethanolic biodiesel around 98.15% at the reaction end. Thus, the high sunflower oil conversion in ethanolic biodiesel corroborated the potential of this magnetic catalyst in reactor assisted by electromagnetic field, comparatively to the homogeneous catalysts conventionally used for biodiesel production. Also, magnetic separation can be a good alternative to separate a magnetic catalyst after each reaction step, guaranteeing a high recovery for its further reuse in several cycles. In this context, this heterogeneous catalyst can be considered as an attractive alternative for biodiesel production.

Acknowledgement

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