Fuel xxx (xxxx) xxx-xxx

Contents lists available at ScienceDirect

Fuel

journal homepage: http://ees.elsevier.com

Full Length Article

Biodiesel synthesis using a novel monolithic catalyst with magnetic properties (K_2CO_3/γ-Al_2O_3/Sepiolite/γ-Fe_2O_3) by ethanolic route

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ARTICLE INFO

Keywords
Magnetic monolithic catalyst
Unconventional reactor
Magnetic field
Biodiesel

ABSTRACT

A novel magnetic monolithic catalyst based on K_2CO_3/γ-Al_2O_3/Sepiolite/γ-Fe_2O_3 was developed seeking to convert efficiently soybean oil and bioethanol to ethanolic biodiesel and glycerol. The magnetic monolithic was attained by extrusion method and characterized by EPR, VSM, SEM, Dynamometry, XRD, BET, and CO_2-TPD, showing satisfactory magnetic, morphological, mechanical, structural and textural properties. The catalytic performance of this monolithic 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 5 wt% of catalyst with 1:12 oil/ethanol molar ratio at 70 °C after 1.5 h. The magnetic properties of this monolithic catalyst allowed the bed stabilization under magnetic field and the catalysts separation, enabling its reuse by four reaction cycles.

1. Introduction

The use of biofuels, particularly bioethanol [1] and biodiesel [2], has increased worldwide as an alternative to fossil fuels which have important environmental and health consequences. The largest producers of bioethanol and biodiesel are the United States and Brazil [3]. The bioethanol production technology is already well consolidated, but, comparatively, despite more than 25 years of research, development and commercial use of Biodiesel, its production still demands technological solutions to improve industrial processes, reduce production costs and environmental impact as well as diversify and increase its production mainly from non-edible feedstocks [4].

The conventional biodiesel production is carried out via chemical transesterification of vegetable oils or animal fats with methanol [5] using homogeneous catalysts, as has been extensively reviewed [6]. However, in Brazil the use of bioethanol in biodiesel production has been progressively increasing [4] and thus it is possible to reduce the negative environmental impact of methanol from fossil origin as it is mainly produced from natural gas. But the environmental and economic consequences of using homogeneous catalysts, such as wastewater generation and the impossibility of catalyst reuse, have not yet been resolved. Thus, nowadays trends point essentially to the use of non-edible oils; new design of heterogeneous catalysts; environmental impact and techno-economic analysis for unconventional processes [7].

In this context, the heterogeneous catalysts have received special attention for the biodiesel production but mainly powdery derivatives have been extensively evaluated [8–13] which despite their relevance to homogeneous ones also present problems that affect their performance and therefore need attention. Improvements in this regard can be observed using extruded catalytic derivatives with different geometries [11,14,15]. On the other hand, monolithic catalysts are very attractive, but studies are still relatively scarce in the literature and a few papers have been published [16–24] showing oil conversions in biodiesel between 50 and 99%, approximately.

In the present work, a monolithic catalyst with magnetic properties was employed for biodiesel synthesis in a monolithic reactor under magnetic field. In recent years, our research group (Biomagnetism Applied to Process Engineering) has been studying the biofuels production by unconventional routes, among which reactors / bioreactors assisted by magnetic field stand out [1,12,25]. Thus, this work evaluates the magnetic, morphological, mechanical, structural and textural properties, as well as the catalytic performance of a novel monolithic catalyst with magnetic properties (K_2CO_3/γ-Al_2O_3/Sepiolite/γ-Fe_2O_3) as alternative to the ethanolic biodiesel synthesis.

2. Materials and methods

2.1. Materials

Soybean oil was purchased from the local market. C4-C24 fatty acid ethyl esters (FAEEs) mixture was used as a standard for ethanolic biodiesel identification (SUPELCO). Boehmite (PURAL SB) and sepiolite (Pansil 100)

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were purchased from SASOL and TOLSA, S.A., respectively. Potassium carbonate, anhydrous ethanol and other chemicals were purchased from Sigma-Aldrich.

2.2. Experimental methods

2.2.1. Preparation of magnetic monolithic catalyst

Magnetic γ-Fe_2O_3 nanoparticles were prepared by co-precipitation method [25]. The monolithic catalyst containing K_2CO_3 (active phase), boehmite, sepiolite and maghemite was prepared according to four steps: a) homogenization of the mixture; b) extrusion (at 9 rpm using a Cone Drive Transverse) [7]; c) drying (105 °C during 16 h) and d) calcination (500 °C for 4 h). Briefly, the materials (175 g of K_2CO_3, 400.2 g of boehmite, 97.5 g of sepiolite, 150 g of maghemite) were mixed with water until total homogeneity and good plasticity. In addition, just for comparative purposes extruded catalysts extruded in solid cylinder shape with a diameter of 1.80 mm and 5 mm length were prepared using the same procedure and chemical composition.

2.2.2. Biodiesel synthesis using magnetic monolithic catalysts

The catalytic performance of the magnetic monoliths was evaluated thought biodiesel synthesis by ethanolic route. The transesterification reaction was performed at the following conditions: 1:12 oil: alcohol molar ratio, 5% catalyst (mass of the whole calcined monolith) at 70 °C in a glass column jacketed reactor (Height: 250 mm and internal diameter: 15 mm) under magnetic field (Fig. 1). 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) [26].

2.3. Analytical methods for monoliths characterization

The magnetic properties of the γ-Fe_2O_3 and magnetic monoliths were assessed by EPR spectra obtained from a Bruker EMX 300 spectrometer and by SQUID VSM (Quantum Design® models MPMS 57, MPMS 7 T) at 10,000 Oe. Scanning Electron Microscopy was performed in a HITACHI TM1000 Tabletop Microscope model using a magnification of 100×. The mechanical strength of the magnetic monolithic 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 under conditions defined previously by Silveira-Junior et al. [7]. For textural properties determination, the monoliths 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 [27]; while the accumulative superficial area, volume, medium diameter and distribution of pores, using the BJH method [28] based on the capillary condensation model. 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) [7].

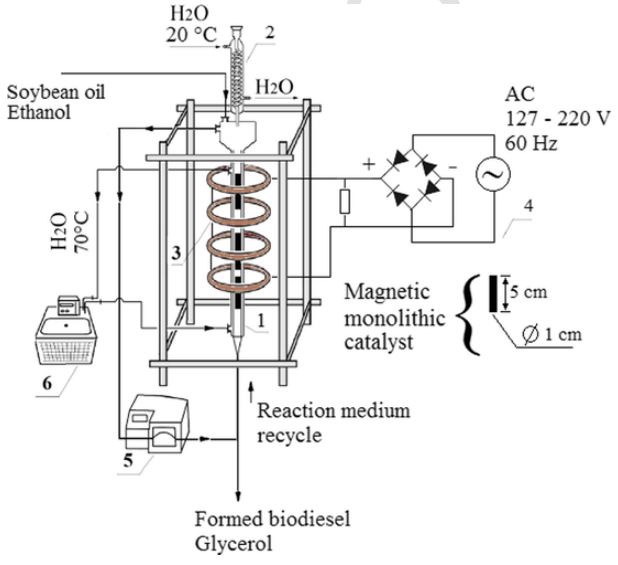

Fig. 1. Experimental setup for biodiesel synthesis in a reactor assisted by magnetic field. Symbols: (1) reactor, (2) condenser, (3) coils, (4) Tension source (5) peristaltic pump, and (6) thermostatic water bath.

3. Results and discussion

The monolithic catalyst developed in our study has a cylindrical geometry with an external diameter of 10 mm and internally composed by 7 parallel cylindrical channels with 2 mm of diameter and 5 cm of length (Fig. 2a). This monolithic catalyst containing magnetic particles (γ-Fe_2O_3) was prepared to carried out transesterification reactions in a reactor under magnetic field which allows the magnetic catalysts stabilization according to the used axial magnetic field lines. Also, solid cylinder catalysts (1.8 mm diameter × 5 mm length) prepared for comparative purpose are shown in the Fig. 2b.

The XRD patterns of maghemite particles and the magnetic monolithic catalysts are shown in Fig. 3. Diffractogram of maghemite has diffraction peaks corresponding to γ-Fe_2O_3 (JCPDS #39-1346). In the case of the magnetic monolithic catalyst, peaks related to γ-Fe_2O_3 (JCPDS #39-1346), Al_2O_3 (JCPDS #46-1212) and sepiolite (JCPDS #39-1425; 34-1216), that represent the support of monolithic catalyst were also found. The active phase ($KAlSiO_4$) has also been identified in the region 2θ: 28–30° and around 40° (JCPDS #31–0965).

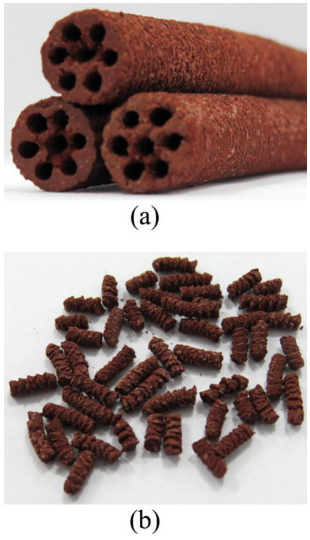

Fig. 2. Prepared catalysts with magnetic properties by extrusion containing K_2CO_3/γ-Al_2O_3/Sepiolite/γ-Fe_2O_3: a) monoliths and b) solid cylinders.

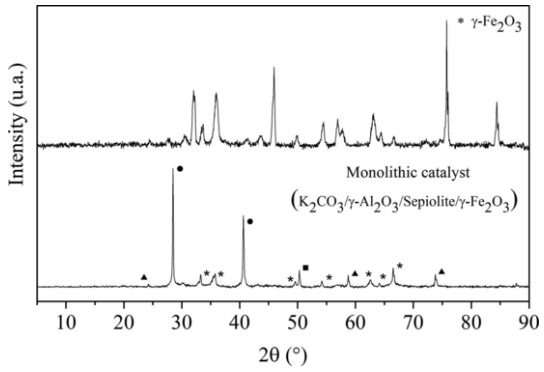

Fig. 3. X-ray diffraction patterns of the: a) maghemite (γ-Fe_2O_3) particles and b) magnetic monolithic catalyst. Symbols: •, Active phase ($KAlSiO_4$); ! Sepiolite; $7Al_2O_3$); □ γ-Fe_2O_3.

The N_2 adsorption-desorption results shown in the Fig. 4 presented a Type IV isotherm, typical of the mesoporous materials and the specific area, volume and mean pore size for the monolithic catalyst were 41 m^2/g, 0.14 cm^3/g and 13.1 nm, respectively.

Fig. 5a shows the biodiesel yield over reaction time and the fatty acid ethyl ester profiles, as well as, the catalysts performance in four reuse cycles (Fig. 5b-d). In all cases the reactions were carried out under the same conditions, based on previous studies (Silveira Junior et al., 2019) which showed good results using 5% of catalyst mass and 1:12 M ratio oil: bioethanol. In addition, the reactions were performed at 70° C and recycling the medium in a closed loop at 16.6 mL/min. Then, as can be observed in the Fig. 5a, high conversion was obtained at 1.5 h.

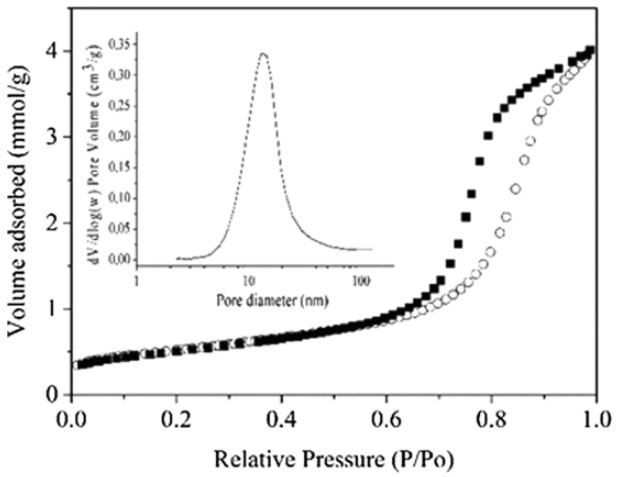

Fig. 4. Nitrogen adsorption–desorption isotherm of magnetic monolith catalyst upon calcination and prior to transesterification reaction.

This result can be considered satisfactory and can be associated with the basicity observed in the catalysts by the CO_2-TPD analysis, whose values of total desorbed CO_2 and total density of basic sites (0.50 mmol/g and 0.01 mmol/m^2 ,respectively) were attained at 245 °C desorption temperature, equivalent to medium strength basic sites [7]. In addition, the active phase appears to be well distributed in the monolith as can be observed in the SEM micrograph by the presence of white clusters on the surface (Fig. 6a) and whose composition was also validated by EDS around 49.8% (Fig. 6b). The monolithic catalysts presented a resistance of 2.00 kgf/cm whose value was satisfactory to preserve their structure after each reaction.

In addition, the catalytic performance of the developed monoliths can also be correlated with their physico-chemical properties such as textural and catalyst basicity. However, some published works using monoliths present divergent results, making it difficult to establish objective criteria for comparison between their physical properties or about the used reaction conditions. For example, Tonetto and Marchetti [23] prepare a Monolith K/Al_2O_3-Cordierite that had a BET area of 107.1 m^2/g, achieving a 59% biodiesel yield. A similar analysis can be made on the reaction conditions, considering that the used oil was soybean at higher reaction temperature (120 °C) and excess alcohol (1:32) has not resulted in better conversion rates comparatively with our work.

On the other hand, the progressive loss of activity from the third and four cycle of reuse (Fig. 5c and 5d) can be attributed to the leaching of the active phase of the catalyst. This fact was corroborated put into contact the monolith with ethanol for 2 h at the 70 °C reaction temperature and then, using this alcohol in a new reaction with soybean oil, but without monolith at same reaction conditions (1:12 oil: ethanol molar ratio and 70 °C). Thus, the observed results showed around 14% of biodiesel formation and consequently, the lack of adherence of the active phase in the catalysts, leads to a poor performance of

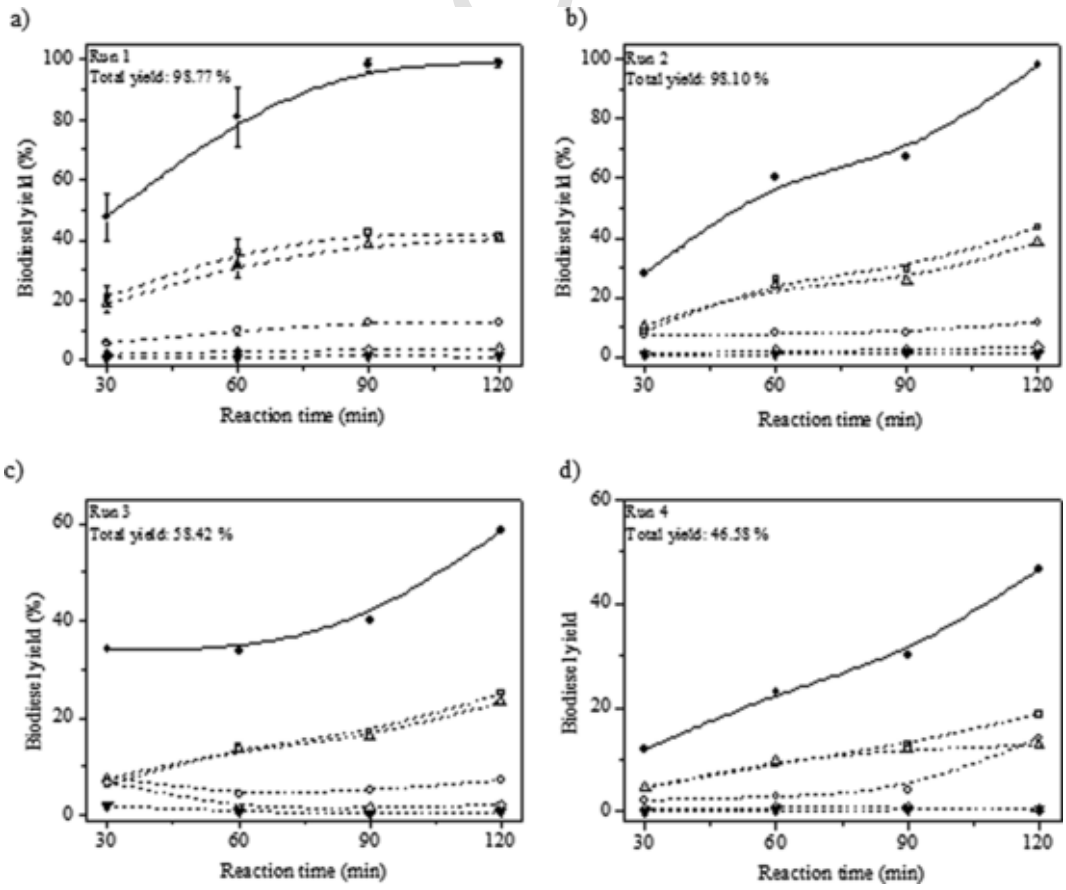

Fig. 5. Biodiesel synthesis and catalytic performance of the magnetic monolithic (K_2CO_3/γ-Al_2O_3/Sepiolite/γ-Fe_2O_3) in the four reuse cycles. The reaction conditions were: 1:12 oil: bioethanol molar ratio, 5 wt% catalyst at 70 °C and 2 h reaction time under 12.5 mT magnetic flux density. Symbols: ● Total biodiesel yield and fatty acid ethyl ester profiles (○ C16; □ C18:2; Δ C18:1; ◇ C18; ▾C18:3).

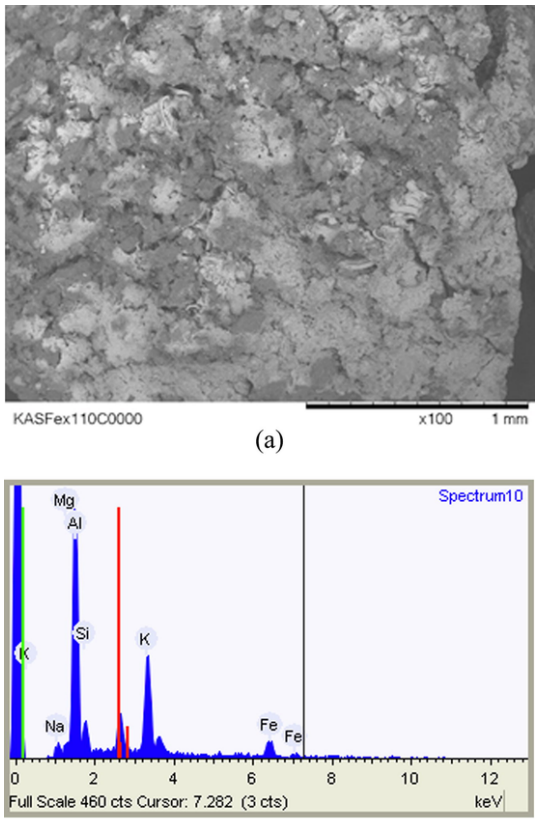

Fig. 6. Micrograph of $K_2CO_3/\gamma\text{-}Al_2O_3$/Sepiolite/$\gamma\text{-}Fe_2O_3$ monolithic surface obtained by SEM analysis. Summary of the attained composition by EDS: Na (4.2 wt%); Mg (2.5 wt%); Al (44.5 wt%); Si (6.7 wt%); K (27.6 wt%); Fe (14.4 wt%).

the reutilized monoliths. This reveals that the development of heterogeneous catalysts with adequate stability and activity for the synthesis of biodiesel demands still great challenges.

Respect to the magnetic properties evaluated by EPR analysis, both maghemite and the magnetic monolithic catalyst show broad anisotropic signals at low temperatures, which are characteristic of ferromagnetic particles of different sizes and/or shapes (Fig. 7). The magnetic moments of these particles tend to align with the application of a low temperature magnetic field. However, with increasing temperature thermal fluctuations of magnetic moments became dominant, increasing this alignment and giving rise to isotropic signals above the so-called blocking temperature. This effect is called superparamagnetic resonance. Therefore, the smaller the size of the magnetic particles dis-

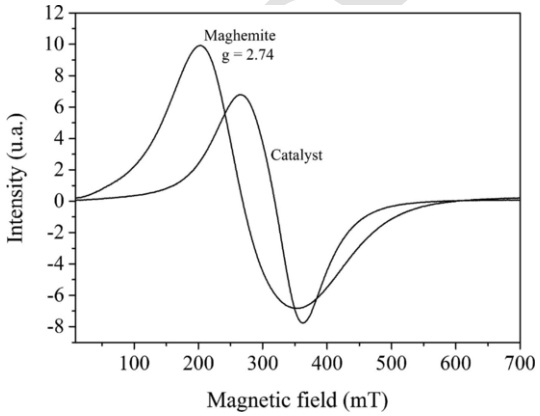

Fig. 7. EPR spectra of $\gamma\text{-}Fe_2O_3$ and magnetic monolithic catalyst measured as a function of temperature.

tributed in the catalyst, the lower the blocking temperature, and may be up to 300 K, since signal anisotropy is still persistent [29].

Anyway, it is not possible to identify only by EPR spectroscopy (Fig. 7) the superparamagnetic phase of maghemite and monolith particles with magnetic properties. Thus, Fig. 8 shows VSM analysis for both $\gamma\text{-}Fe_2O_3$ particles and formulated magnetic monolithic catalysts. The $\gamma\text{-}Fe_2O_3$ nanoparticles show superparamagnetic behavior, as it is indeed observed. The magnetization versus field curves show saturation at high fields and lack any hysteretic behavior at low fields, with absence of any detectable remanent magnetization. This superparamagnetic behavior in the range of temperatures of interest, was corroborated by Zero Field Cooled (ZFC) and Field Cooled (FC) magnetization measurements [30]. Attention should be paid to the observation that in the M vs H curves the magnetization decreases by 5.6 times, i.e., from 32.57 to 5.73 emu/g during catalyst preparation respect to the value for pure magnetic particles. This low magnetization of the catalyst is most likely related to the maghemite mass that was effectively incorporated in the composition of the monolith, in this case, around 0.3 g of maghemite/g of $K_2CO_3/\gamma\text{-}Al_2O_3$/Sepiolite. However, the superparamagnetic properties of the monoliths prepared were satisfactory to their magnetic stabilization during the reaction and reuse when the biodiesel production was completed in several cycles.

Table 1 shows some published studies with monolithic catalysts to produce biodiesel. It should be noted in these researches, that monolithic catalysts with magnetic properties and unconventional reactor assisted by magnetic field as presented in our work were not used. In general way, the works found in the literature are divergent because in some cases, it is possible to verify high conversions (around 73 to 98%), but at high temperature and long reaction times (around 5 to 100 h) [17,18,20,22] which is undesirable from an industrial point of view. Whereas, other more attractive works reported results with high conversions in short times (between 3 and 4 h) and moderate reaction conditions (between 60 and 80 °C) [19,21,24,31] revealing the potential of these catalytic systems even in relation to pelletized or powder catalysts which presents several drawbacks such as agglomerations and complicated recovery at the reaction end, despite of their good conversion for biodiesel production [7,32]. Besides, other studies have focused on cordierite monoliths (Table 1) using high reaction temperatures and pressures, but achieving oil conversions below 70% [16,18,23].

In our study, the prepared monolithic catalysts proved to be highly efficient, promoting the high conversion of soybean oil to fatty acid ethyl esters (biodiesel) in a short reaction time comparatively with other monolithic systems (Table 1). Thus, this magnetic monolithic was compared with a with a solid cylinder catalyst prepared with the same composition and at the same reaction conditions. According to the attained results (Fig. 9) the best performance was showed by the monolithic catalysts probably due to uniform reactants flow patterns observed, as opposed to channeling, by-passing, or the formation of stagnant/dead zone regions, in view of the length scales of catalysts, or by external diffusional limitation in the reactions when catalysts solid cylindrical were used.

Monoliths can be constructed of different geometric forms and their channels within of them can be square, hexagonal, triangular, oval or circular shape, among others. These geometrical parameters, as well as, the cells number per unit of cross-sectional area are important factors, which affect the mass and heat transport, as well the pressure drop during the reaction steps [33]. However, the properties of the monoliths should not be described solely by their geometry or shape of the channels, but also by the hydraulic diameter of the channels because it decreases as the cell density increases [33].

Finally, should be understand that, the incorporation of magnetic nanoparticles in the monolith does not affect its catalytic properties during the reaction. So the major contribution of the reactor operation with magnetic catalysts under the influence of magnetic fields is due to improvements in the fluid-dynamic conditions in the reactor because by controlling the strength of the field and recycle velocity of the reagents, the monoliths are magnetically stabilized and aligned in the interest catalytic region in the reactor axial direction, avoiding deviations of the fluid lines, catalysts rupture by friction/contact' with the reactor walls and allowing the use of high recy-

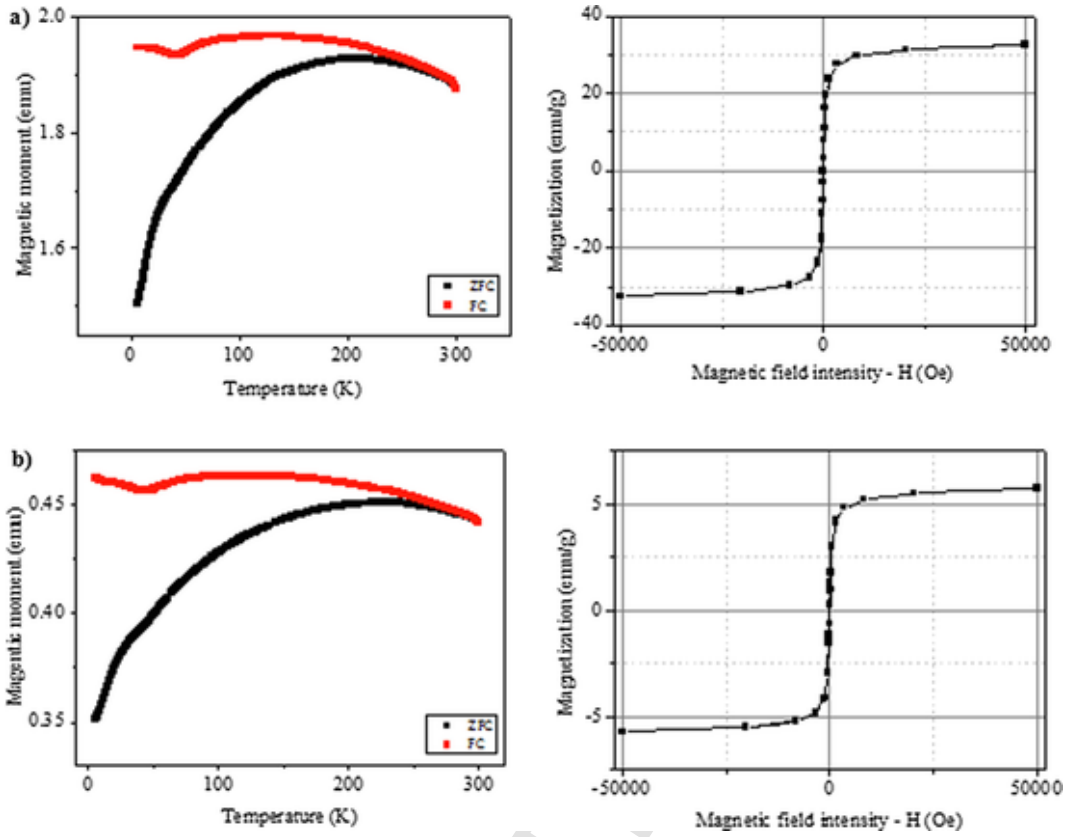

Fig. 8. Magnetic characterization by VSM analysis for: a) maghemite (γ-Fe_2O_3) particles and b) magnetic monolith catalysts. Analysis conditions: M vs T, give H = 10000 Oe as applied field and for the M vs H, give T = 300 K.

Table 1
Biodiesel production by transesterification reaction using monolithic catalysts.

Catalysts	Reactor characteristics	Reaction conditions			Yield (%)	Ref.
		Oil: alcohol (molar ratio) and catalyst mass (wt.%)	Temperature and reaction time	Stirring (rpm)		
Ca-Ce mixed oxides on Fecralloy® monoliths	0.25 L monolithic stirrer batch reactor	Sunflower oil: methanol (1: 12); 2 wt%	60 °C/4 h	200	99.0	[21]
Honeycomb monolith supported sugar catalyst	500 mL flask equipped with a reflux condenser	Fatty acid distillate, by-product from palm oil: methanol (1:15); 2.5 wt%	80 °C/4 h	–	95.5	[31]
KF/γ-Al_2O_3/honeycomb ceramic (HC) monolithic	Fixed-bed reactor	Palm oil: methanol (1:18); 5 wt%	140 °C/ 0.55 h	–	>96.0	[19]
KF/Ca-Mg-Al hydrotalcites on monoliths	Membrane reactor	Soybean oil: methanol (1:24); 1.5 g (5 wt%)	67 °C/3 h	–	91.7	[24]
Honeycomb γ-alumina-wash-coated monolithic with different active phases: B1-B4) Zn-Na-Mg-Zn; B2-B3) Zn-Mg-Na-Ca-Zn; B5) Mg-Na-Ca-Zn.	Honeycomb monolithic reactor	Canola oil: methanol (1:38 and 1:50)/catalyst mass was not specified. B1) Zn-Na-Mg-Zn	250 °C/ 6.5 h	–	98.0	[20]
SrO on cordierite monoliths	Single monolithic bed reactor (6.2 mm i.d. and 400 mm heated length)	Rapeseed oil: methanol (1:50)/the monoliths coated with SrO (19.6 wt% SrO)	195 °C/ 100 h	–	65.4	[18]
CaO deposited on cordierite monoliths	1000 mL monolithic reactor	Vegetable oil: methanol (1:20); 4 wt%	65 °C/5 h	900	73.1	[17]
Mg-Al hydrotalcites on Fecralloy® monoliths	Monolithic stirrer batch reactor	Sunflower oil: methanol (1:48); 2 wt%	60 °C/10 h	200	77.0	[22]
Monolith K/Al_2O_3-Cordierite	600 mL Parr reactor	Soybean oil: methanol (1:32); 0.5 wt%	120 °C/6 h	500	59.0	[23]
Zinc amino acid complex [ZnL_2] coated on cordierite monolith	120 mL autoclave (20 bar) reactor	Rapeseed oil: methanol (1:12); catalyst coated monolith (containing 0.3 g ZnL_2)	195 °C/2 h	1500	54.0	[16]
K_2CO_3/γ-Al_2O_3/Sepiolite/γ-Fe_2O_3 monolith	Magnetically stabilized reactor	Soybean oil: ethanol (1:12); 5 wt%	70 °C/1.5 h	–	98.07	This study

cling rates contribute to a better mixing and contact between ethanol and oil during the reaction. In addition, after reaction, this operating strategy facilitates both, the separation and purification steps of the catalysts for reuse purposes.

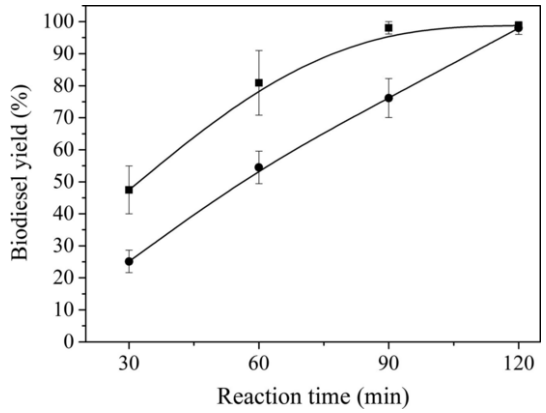

Fig. 9. Biodiesel synthesis and catalytic performance of the $K_2CO_3/\gamma\text{-}Al_2O_3$/Sepiolite/$\gamma\text{-}Fe_2O_3$ in different forms: • solid cylinder shape and □ monolithic shape. The reaction conditions were: 1:12 oil: bioethanol molar ratio, 5 wt% catalyst at 70 °C and 2 h reaction time under 12.5 mT magnetic flux density.

4. Conclusions

A new monolithic catalyst based on $K_2CO_3/\gamma\text{-}Al_2O_3$/Sepiolite/$\gamma\text{-}Fe_2O_3$ was developed with good morphological, mechanical, structural and textural properties and with an active phase well distributed on its surface. Thus, the high soybean oil conversion in ethanolic biodiesel after 1.5 h corroborated the potential of this monolithic reactor, comparatively to the homogeneous catalysts conventionally used for biodiesel production. Nevertheless, further experimental studies about the stability of these monoliths, as well as, techno-economic and environmental analysis of this technology must be carried out to verify its viability at industrial scale.

CRediT authorship contribution statement

Euripedes Garcia Silveira Junior: Conceptualization, Methodology, Formal analysis, Investigation, Writing - review & editing. **Oselys Rodriguez Justo:** Conceptualization, Formal analysis, Writing - original draft. **Victor Haber Perez:** Conceptualization, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Fabiana da Silva Melo:** Formal analysis. **Inés Reyero:** Methodology, Formal analysis, Writing - original draft. **Ana Serrano-Lotina:** Methodology, Formal analysis, Writing - original draft. **Federico J. Mompean:** Methodology, Formal analysis, Writing - original draft.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

We are grateful to the State University of Northern of Rio de Janeiro for the Postdoctoral Position Fellow (No. 001/2017), Institutional Program of the Estacio de Sá University for Research Productivity Fellow and the Brazilian agencies: FAPERJ (E-26/210.508/2014) and CAPES (Finance Code 001) for the financial support.

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