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Alternatives to rethink tomorrow: Biodiesel production from residual and non-edible oils using biocatalyst technology

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ABSTRACT

Esterification and/or transesterification of a residue from soybean oil obtaining process, *Jatropha hieronymi* oil (non-edible), waste frying oil (sunflower) and commercial sunflower oil were studied for biodiesel production. Enzyme lipase of *Pseudomonas fluorescens* immobilized on sodium-modified-SBA-15 was employed as biocatalyst. The experiments were carried out in a batch reactor taking samples at different times and determining the biodiesel production by HPLC. The biocatalyst was able to produce biodiesel from residual or undervalued oils (without any previous refinement) and commercial ethanol as co-substrate. The advantage of the latter is the possibility of obtaining ethanol from a fermentative process, which favors a sustainable development. Biodiesel yields between 70 and 95% were achieved depending on the employed oil.

1. Introduction

Currently, energy policy is based on two fundamental pillars: economic rationality and sustainability. The main objectives of this policy are: to significantly reduce greenhouse gas emissions in a sustainable manner; to strengthen the diversification of primary sources of energy; and to increase the energy efficiency of the economy and the efficient use of resources. All this without compromising the competitiveness of companies or the quality of citizens life [1]. In this context and satisfying the majority of the mentioned requirements, biodiesel emerges as a promising alternative fuel. It has been identified as one of the most successful options to replace, or at least complement, conventional fuels, using natural sources and renewable biological products for its production. It presents the following advantages respect to petrodiesel: it is renewable, non-toxic, biodegradable, does not contain sulfur and is a better lubricant [2,3]. The conventional process currently used to produce biodiesel employs sodium hydroxide as a homogeneous catalyst. This process presents environmental drawbacks such as the elimination of soaps and the resulting amounts of glycerol contaminated with the catalyst during the purification stage. Since the reaction must be carried out in batch, the catalyst must be neutralized and cannot be recycled, which is not economically viable and must be subsidized [4]. In addition, oily raw materials must have low free fatty acids and water contents to be used. These requirements increase the cost of production, since economic raw materials (fats, used or non-edibles oils) must be treated to meet these parameters before entering the biodiesel producing process [5].

The application of heterogeneous catalysts can provide great advantages to overcome such technological challenges: the purification steps decrease (the catalyst can be separated by filtration), the catalysts can be used in batch or continuous systems, they generally do not lead to the production of soaps, they allow the use of raw materials with high free fatty acid contents, they allow the improvement of product quality, corrosion and toxicity problems are mitigated comparing to homogeneous process [6–8]. Solid catalysts such as zeolites, mixed oxides, sulfated zirconia and exchange resins have already been studied for biodiesel production, using raw materials with high free fatty acids content [8–10]; however, they still have a low activity, which is why higher concentrations of catalyst are required respect to homogeneous processes. Within the nanostructured solids, SBA-15 type mesoporous

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molecular sieve has certain specific properties such as large areas (~1000 m^2/g) and pore volume (~1 cm^3/g), the possibility of electrostatic interactions and to modify its surface with metals, mechanical and chemical resistance. It also offers pores in the order of 2–10 nm that make it possible to discriminate molecules according to their size and allow the diffusion of substrates and products [11,12]. This nanostructured material can also be used as support to immobilize enzymes as active species, obtaining a solid biocatalyst. As result, the enzyme useful life and the stability against various agents (pH, oxidants, temperature) is increased and the separation of the reaction medium is facilitated. As it has been demonstrated by other authors, the fixation of biologically active species on inorganic materials combines the selectivity of enzymatic reactions with the chemical and mechanical properties of the support [13–17].

For the above reasons and aiming to produce biodiesel, a heterogeneous biocatalyst based on *Pseudomonas Fluorescens* lipase immobilized on sodium-modified-SBA-15 (L_{PF}/Na/SBA-15) has been designed and reported elsewhere [18]. In this work, the biocatalyst was tested with different raw materials: commercial sunflower oil, *J. hieronymi* oil, used frying oil and a residual soybean oil. *J. hieronymi* is an endemic specie from semiarid and arid northwest of Argentina and its oil is not edible. It is a non-conventional oilseed specie that does not represent competition with food crops and, for this reason, it presents an economic potential as alternative oil [19–22]. On the other hand, the used frying oil (a domestic and gastronomic industry waste) can also be reused for the production of biodiesel, avoiding contamination when it is discarded in drains [15,23,24]. Finally, the residual soybean oil used in this work is a byproduct of the refining process of crude oil which consists of the following stages: degumming, removal of phospholipids and other amphipathic lipids, neutralization to remove free fatty acids, bleaching and deodorization [39]. If the soapstock resulting in the neutralization step is acidulated, a mixture mainly composed by FFA and phospholipids, tri, di and mono acylglycerides, tocopherols, sterols, degraded oxidized components, pigments, salts, and color bodies in a small amount is obtained [40].

The above mentioned three raw materials contain high FFA, which does not allow using them directly in the homogenous process. Thus, a pretreatment with sulfuric acid as catalyst must be done to esterify the free fatty acids. Subsequently, the acid must be neutralized, and the product should be washed and dried before to use the obtained mixture of esters of free fatty acids and triglycerides as reagent for the transesterification reaction with the basic homogeneous catalyst. Once this reaction has been carried out, the catalyst must be neutralized, the obtained biodiesel must be washed and dried again to be commercialized as fuel [25,26]. In addition, the use of acids and bases to take advantage of these substrates may cause the oxidation and corrosion of the reactor, decreasing its useful life, increasing the cost of the process and being aggressive with the environment. These mentioned steps can be avoided if a biocatalyst is used. Thus, the developed L_{PF}/Na/SBA-15 catalyst has been tested in a batch system for the mentioned oils without any previous treatment.

2. Material and methods

2.1. Materials

Pseudomonas Fluorescens lipase (PFL, ≥20,000 IU/g at 55 °C, pH 8.0) was purchased from Sigma-Aldrich Co. (St. Louis, USA) [27]. Commercial sunflower oil (''Vicentin'' brand) was purchased at a local store. Waste frying oil was collected from different domestic sources and it was filtered before being used. Residual soybean oil was generously provided by Louis Dreyfus Company (Bahía Blanca, Argentina).

Other employed reagents were: KH_2PO_4, K_2HPO_4 and KOH (Anedra); commercial bioethanol 96% v/v (Porta Hnos.), hydrochloric acid-HCl and sodium carbonate-Na_2CO_3 (analytical grade, Cicarelli), n-hexane and acetonitrile (analytical grade, Merck), isopropyl alcohol (Fluka), triblock copolymer Pluronic P123 and tetraethyl orthosilicate-TEOS (Aldrich), and milliQ water. Syringe filters (polypropylene, 25 mm diameter and 0.2 μm pore size) were supplied by VWR.

2.2. Lipid extraction

J. hieronymi seeds were collected from wild populations located at Santa María valley, Catamarca, province of northwest Argentina (27° 00′ S, 66° 14' W, 2200 m a.s.l.) To obtain the oil, 50 seeds collected from several individual plants (approx. 20) were oven dried at 70 °C until constant weight, weighed and ground with a mortar. Then, 10 g of seed samples were extracted with 170 mL hexane for 6 h and at room temperature, using a Soxhlet apparatus. The hexane was separated and collected under reduced pressure in a vacuum concentrator. The residue (¼ lipophilic fraction) was dried for 12 h at 80 °C and then, it was weighed.

2.3. Acid value determination

The feedstocks acid value were determines by volumetric titration according to the standard EN ISO 14104 (2003). The required oil mass was mixed with 2-propanol in a conical flask (0.25 g sample/mL solvent) and titrated using an aqueous KOH 0.1 M solution. Phenolphtleine was used as the final point indicator. Results are expressed in mg KOH/g sample.

2.4. Na/SBA-15 synthesis

The SBA-15 support was synthesized dissolving 4.0 g of Pluronic P123 in 30 g of water and 120 g of 2 M HCl with magnetic stirring at 40 °C. Then, 8.50 g of TEOS were added, and the mixture was stirred at 40 °C for 20 h. The suspension was aged at 100 °C overnight without agitation. The solid product was filtered, washed and dried at 60 °C. Then, it was calcined at 500 °C for 6 h, with a heating ramp of 1 °C/min.

The support modified with sodium was prepared by wet impregnation method: 0.75 g of SBA-15 were mixed with an aqueous solution of metal salt (Na_2CO_3), to obtain a material with a theoretical sodium concentration of 2.5% by weight. Then, water was removed by rotary evaporation. The resulting powder was dried at 60 °C overnight, and calcined for 8 h at 500 °C. The sample was named as Na/SBA-15 (2.5).

2.5. Mesoporous Na/SBA-15 characterization

Small angle X-ray scattering analysis (SAXS) were carried out in the National Light Synchrotron Laboratory (LNLS) of Campinas, Brazil. The detector was a Pilatus 300k from Dectris. The empty Kapton cell was measured and subtracted from the signals after normalization. Data was radially integrated by using FIT2D V 12.077 from Andy Hammersley at ESRF. High angle X-ray diffraction analysis (XRD) were performed in a PANalytical X-Pert Pro X-ray powder diffractometer, with a Bragg-Brentano geometry. A CuKα lamp was used (40 kV, 40 mA), in a 2θ range between 20 and 80°. Transmission Electron Microscopy images (TEM) were obtained using a JEOL model JEM-1200 EXII. Specific surface was determined using a Micromeritics Pulse ChemiSorb 2700 by the Brunauer-Emmett-Teller method (BET). The basicity of the synthetized catalysts was studied by carbon dioxide temperature programed

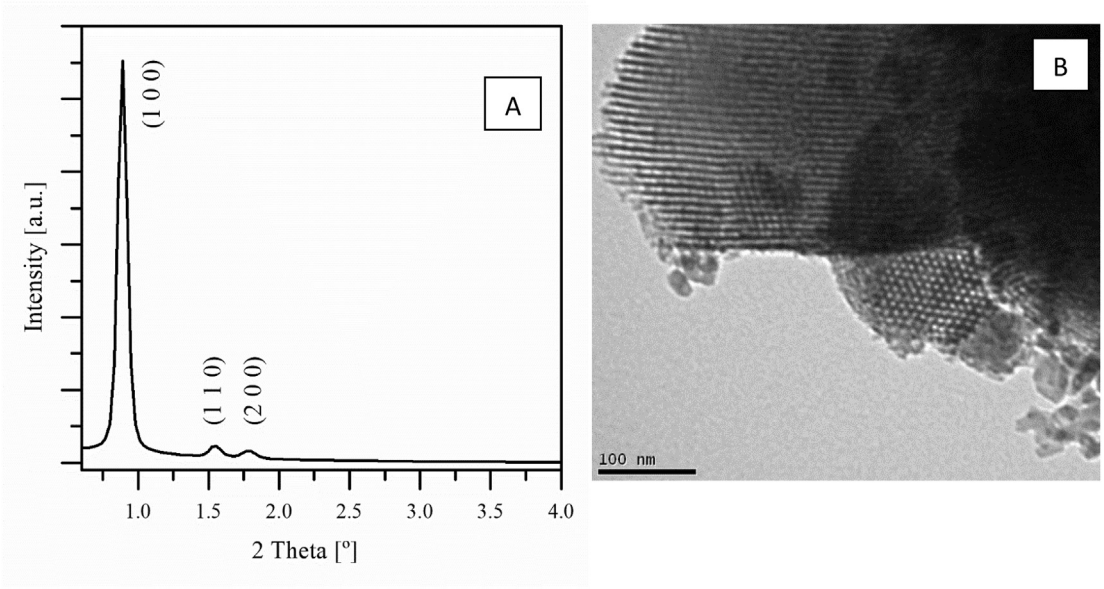

Fig. 1. Structural characterization of Na/SBA-15 (2.5) mesoporous support: A) SAXS pattern, B) TEM image.

desorption (CO_2 TPD) between 80 and 950 °C, with a 10 °C/min heating rate and a 50 mL/min gas flow in a ChemiSorb 2720 equipment. XPS analysis was performed on a SPECS Multi-technique equipment, equipped with a dual X-ray source (Mg/Al) and a hemi-spherical analyzer PHOIBOS 150 in fixed analyzer transmission mode (FAT). The sodium content in the samples was determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP) using a spectrophotometer VISTA-MPX CCD Simultaneous ICP-OES-VARIAN.

2.6. Pseudomonas fluorescens lipase immobilization

A lipase solution (5 mg/mL) was prepared with 25 mM phosphate buffer (pH = 8). Then, 0.125 g of the Na/SBA-15 (2.5) was suspended in 10 mL of the solution to obtain an optimum ratio of 400 $mg_{enzyme}/g_{support}$ [15]. The suspension was maintained with gentle agitation at room temperature for 24 h, then centrifuged to remove the supernatant and washed twice with 10 mL of 25 mM phosphate buffer pH = 8. The determination of the non-immobilized protein content was carried out by a Bradford test [28]. The hybrid material obtained from the enzymatic immobilization was named as L_{PF}/Na/SBA-15 (2.5).

2.7. Transesterification reaction

The reactions were carried out in screw vials placed in an orbital shaker at 180 rpm, 37 °C and a 1:4 sunflower oil to ethanol molar ratio, and they were started when the biocatalyst was added. Samples were taken at different times to be analyzed by HPLC.

2.8. Chromatographic analysis

The analysis were performed with a PerkinElmer 200 series HPLC with UV–vis detector, equipped with a solvent delivery unit with gradient of elution, a KNAUER Vertex Plus (250 mm × 4.6 mm, 5 μm) Eurospher II 100-5 C18 P. The software used was Total Chrom. The wavelength of the UV detector was set at 205 nm, the column temperature was maintained at 30 °C and the flowrate was 1 mL/min. For chromatographic runs, a stepwise method was used: 100% of methanol in 0 min, 50% of methanol and 50% of 5:4 2-propanol/n-hexane in 10 min maintained with isocratic elution for 10 min [29].

All reactions were performed at least in duplicate and the results were expressed as mean values (the percentage differences between the values were always less than 5% of the mean).

3. Results and discussion

3.1. Na/SBA-15 characterization

The structural and textural characterization of the mesoporous support was made by SAXS, TEM and high angle XRD.

The SAXS spectrum of the Na/SBA-15 (2.5) support shows the presence of well-defined peaks that can be indexed to the (1 0 0), (1

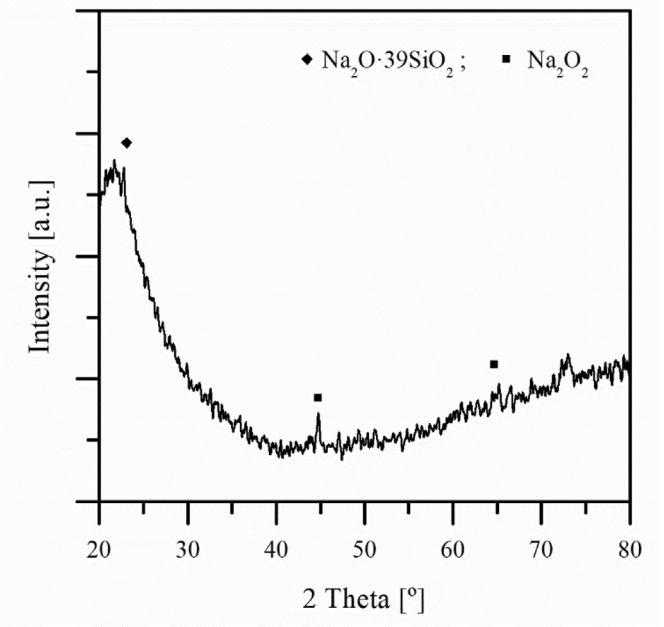

Fig. 2. XRD profile of Na/SBA-15 (2.5) support.

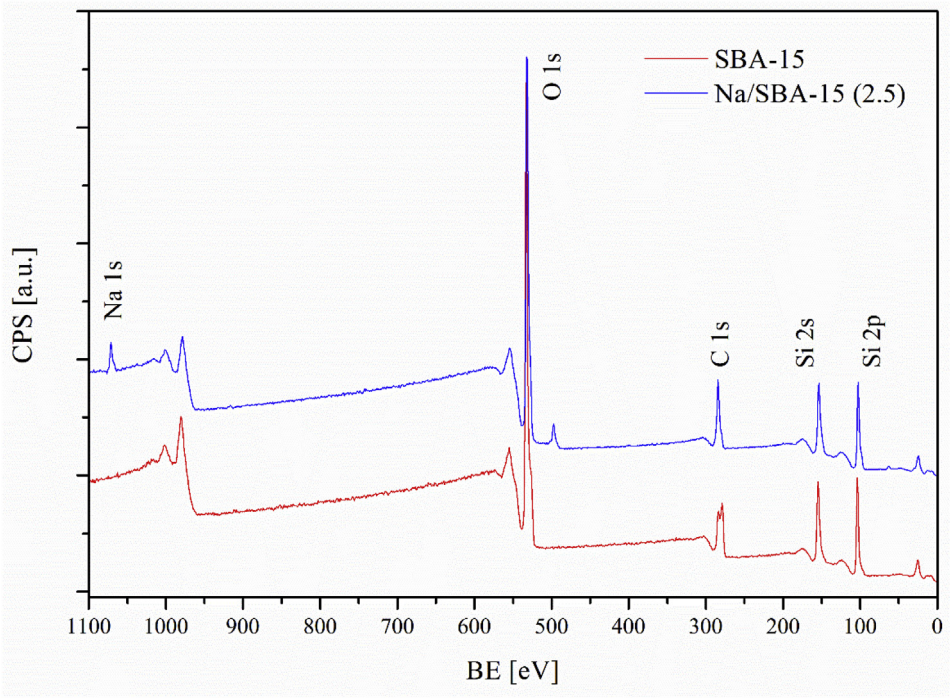

Fig. 3. XPS pattern of SBA-15 (Red) and Na/SBA-15 (2.5) (Blue). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

1 0), and (2 0 0) planes. These peaks are associated with the presence of a highly ordered porous structure with a hexagonal pore arrangement (Fig. 1A). Fig. 1B shows Na/SBA-15 TEM image, where well-ordered parallel nanotubular pores can be observed along the axis, showing a good structure of the obtained solid. Thus, the regular hexagonal array of uniform channels in which each pore is surrounded by six neighbors could be clearly observed.

These results demonstrated that the hexagonal array of the original mesostructured SBA-15 silica is preserved throughout chemical modification of its surface with sodium. In order to study the chemical composition of the material, sodium content was determined by ICP, obtaining a 2.20 wt%. Sodium oxide species on SBA-15 were observed in the high angle XRD profile (Fig. 2). This pattern shows the typical peak for the amorphous silica (~22°) [30], besides hinted peaks attributed to Na_2O_2 species [31,32]. Peaks corresponding to other species such as Na_2O, NaO_2 cannot be detected, indicating that if they exist, they are amorphous clusters or nanoparticles too small to be detected by this technique [33]. According to the XRD analysis, the different oxides species would be finely dispersed on the silica support [30]. This also agrees with the lower specific surface corresponding to Na/SBA-15(2.5), 357 m^2/g, compared to 794 m^2/g of SBA-15.

Then, XPS spectra of the support and Na/SBA-15(2.5) are showed in Fig. 3. The corresponding bending energies are summarized in Table 1. C 1s signal was adjusted at 284.8 eV. O 1s signal can be mostly assigned to the siliceous support contribution (Si–O of SiO_2). The lower binding energy for Na/SBA-15(2.5) (531.3 eV)

Table 1
Bending energies and superficial composition determined by XPS for Na/SBA-15(2.5).

Na/SBA-15(2.5)	Si 2s	Si 2p	O 1s	C 1s	Na 1s
Superficial composition (wt%)	28.25	33.91	35.48	0.00	2.36
Bending energy (eV)		102.0	531.3	284.6	1070.4

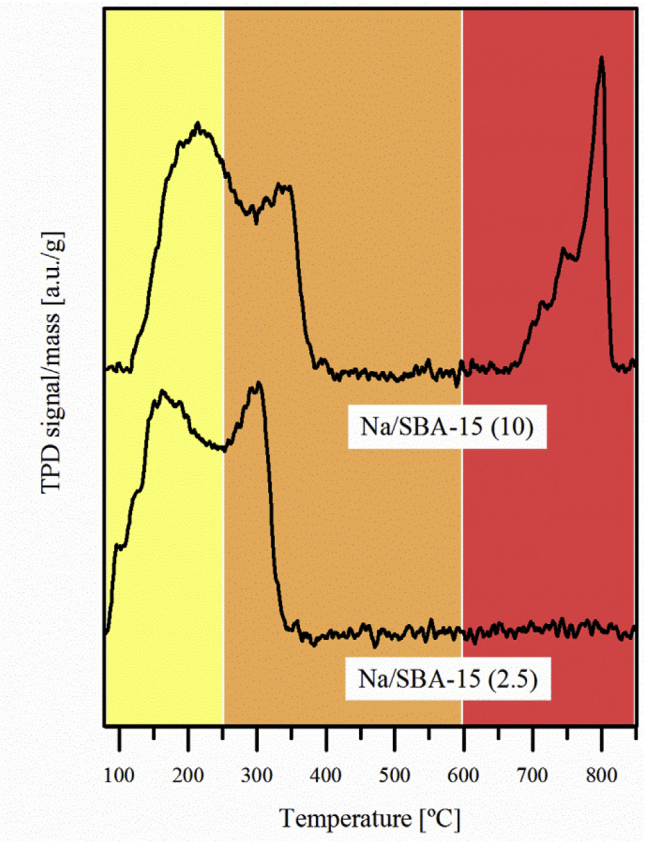

Fig. 4. CO_2-TPD profiles of Na/SBA-15 (2.5) and SBA-15 (10) supports.

compared to the pure support (533 eV) may be due to the formation of Si–O–Na bonds after sodium impregnation and calcination, which can stabilize the metal oxides and silicates on the support surface [34,35]. In the Si 2p region, a lower binding energy (102.0 eV) respect to the support (103.5 eV) can also be detected, suggesting the existence of the interaction between the SBA-15 and metal species. Finally, the presence of Na is evidenced by the signal at 1070.4 eV, which is absent in the support spectrum [34].

The surface composition is also showed in Table 1. It should be noticed that the difference between sodium content determined by XPS respect to that obtained by ICP (2.20 wt%) is about 7%.

It is known that loading sodium or calcium on the SBA-15 support grants its basicity. This basicity favors the lipase activity creating a synergic effect with the support [15]. To confirm the sodium modified solid basicity, Na/SBA-15(2.5) was analyzed by CO_2 temperature-programmed desorption. Fig. 4 shows the obtained profile in comparison with a solid modified with higher sodium concentration (Na/SBA-15(10)). On the graphic, three regions can be defined depending on the type of sites present on the solid. Desorption from 80 °C to 250 °C corresponds to the presence of low basic strength sites (yellow zone). Thus, the observed band in this region would correspond to the interaction of CO_2 with the support SiO_2 species [36]. Then, desorption between 250 °C and 600 °C corresponds to medium basic strength sites, as sodium silicate species (orange zone) [36]. Finally, the band appearing from 600 °C onwards evidences the presence of high basic strength sites. These sites may be attributed to finely dispersed sodium oxides on the catalyst surface, considered as super base [37].

As it can be observed, both solids show bands corresponding to low and medium basic strength sites. However, only Na/SBA-15(10) shows a band corresponding to high basic sites [35]. In a previous report, the highest activity of lipase immobilized on Na/SBA-15(2.5) was already observed. Nevertheless, when the metal loading increases, the lipase activity decreases. It could be due to the appearance of high basic strength species, as it is shown for the solid with a 10 wt% theoretical sodium loading. The super basic character of these species could create an alkaline environment that causes the enzyme denaturation. It is known that ionic interactions can affect the stability of the enzyme native state, decreasing its activity. Thus, the optimum activity of the lipase was achieved in presence of medium basic strength species or sites on the SBA-15 surface at a theoretical sodium loading of 2.5 wt% [15].

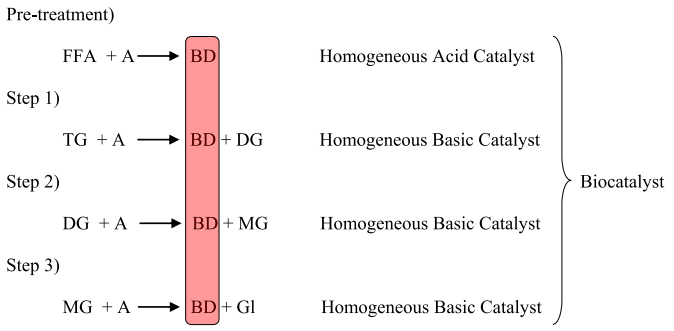

Fig. 5. Homogeneous catalysis vs. biocatalysis. Stages of the biodiesel reaction using triglycerides and free fatty acids as raw material. FFA: Free Fatty Acid, TG: Triglycerides, DG: Diglycerides, MG: Monoglycerides, BD: Biodiesel, GL: Glycerin, A: Ethanol.

3.2. Transesterification reaction

The *Pseudomonas Fluorescens* lipase immobilized on characterized solid (Na/SBA-15(2.5)) was tested in the transesterification reaction of the following oils: sunflower, waste frying, residual soybean and *J. hieronymi*, with commercial ethanol (96% v/v). As it is showed in Fig. 5, biodiesel (BD) and glycerin (GL) would be the expected products if the reaction had a 100% yield (step 3). However, if the reaction is not completed (steps 1 and 2), monoglycerides (MG) and diglycerides (DG) are obtained as reaction intermediates. Moreover, the scheme should include the esterification reaction (pre-treatment) in case the raw material contains free fatty acids, such as *J. hieronymi* oil and residual soybean oil (Fig. 6) [5,19,21,22].

Fig. 6 exposes the HPLC chromatograms of the four above mentioned oils. In this, regions were assigned to the four types of compounds that can be determined by the technique (TG, DG, MG and FFA) according to their retention time, without differentiating between the esters arising from different fatty acids. Triglycerides (16–19 min), diglycerides (9–14 min) and monoglycerides (4.5–6.5 min) in minor proportion can be identified in the *J. hieronymi* oil, waste frying oil and commercial sunflower oil. Meanwhile, a peak corresponding to free fatty acids appear in the residual soybean oil (2–4 min), where they represent about 79 wt%

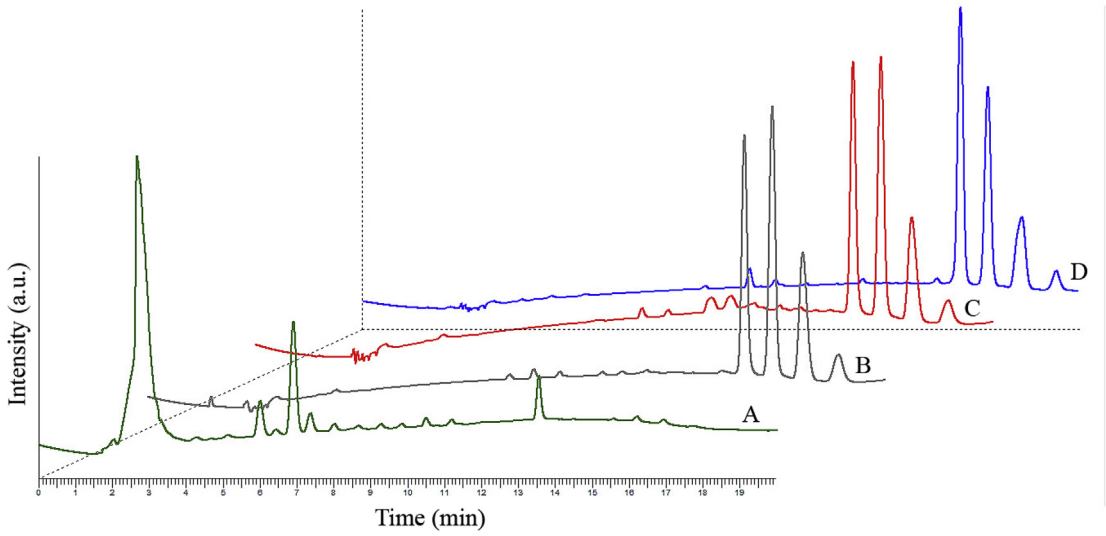

Fig. 6. Chromatograms of the raw oils: A) Residual soybean oil, B) *J. Hieronymi* oil, C) used frying oil, D) sunflower oil.

[38].

These results are in agreement with their high acid value (mass of KOH necessary to neutralize the free fatty acids present in 1 g of sample), summarized in Table 2: 76.81% for the residual soybean oil and 4.07% for *J. hieronymi* oil. The large amount of free fatty acids in the residual soybean oil comes from the purification processes of crude soybean oil, as mentioned in the introduction. Meanwhile, non-edible oils, such as *J. hieronymi* are often contaminated with FFA due to the agro-climatic and the processing conditions of the oils extraction and their storage [41]. According to Freedman et al. [42], the maximum acid value of oil to be used in homogeneous process for biodiesel production must be lower than 1 wt%. For this reason, an acid catalyzed esterification is necessary to convert the free fatty acids into methyl esters, and thus, reducing the acidity to an acceptable value [41]. In addition, these oils must undergo a prior treatment to reduce their water content, since the allowed one is 600 ppm [25]. This is because the water inhibits the transesterification reaction when using NaOH as catalyst and, together with FFA, leads to parallel reactions of saponification with the consequent formation of soaps [31]. As it can be seen in Table 2, all studied samples exceed that maximum value.

On the other hand, the waste frying oil has a lower percentage of triglycerides respect to commercial sunflower oil. This is because during the frying process, triglycerides can be partially hydrolyzed by the water present in food, increasing the free fatty acids concentration, and therefore, the acid value (see Table 2) [43].

However, considering that lipase has an esterification/transesterification activity (even with high water content [15,44]), if a biocatalyst is employed, the biodiesel production could be carried out in a single stage using the mentioned oils (Fig. 5).

Herein, using a batch reactor the activity of the L_{PF}/Na/SBA-15(2.5) biocatalyst was determined. As it can be appreciated in Fig. 7, after 48 h of reaction, the biocatalyst was able to produce biodiesel with the four mentioned oils. According to the achieved biodiesel yields, sunflower oil (FAEE yield: 95.6 wt%), which is considered as food, could be replaced by alternative oils such as waste frying oil (FAEE yield: 91.4 wt%) or *Jatropha hieronymi* oil (FAEE yield: 89.7 wt%) which are non-edible and almost lead to similar biodiesel yields.

The biocatalyst even showed a very good esterification/transesterification activity in the case of residual soybean oil, leading to a biodiesel yield of 76.0 wt% from a raw material mainly composed by free fatty acids, and without any previous treatment.

The decrease in biodiesel yields when employing J. *hieronymi* and residual soybean oils could be due to the large water amount, 1185 and 5221 ppm, respectively (Table 2). This may be due to the fact that lipase activity decreases when the water content exceeds the optimum water activity point, as other authors have already mentioned [14,15].

4. Conclusions

In this work, the developed L_{PF}/Na/SBA-15 biocatalyst was employed to produce biodiesel from alternative renewable substrates. Its potential to transesterify and/or esterify the starting oily feedstock with commercial ethanol (96% v/v) has been confirm.

Table 2
Physicochemical characterization of the raw materials used.

Feedstock	Density [g/cm^3]	Triglycerides content [wt%][a]	Diglycerides content [wt%][a]	Monoglycerides content [wt%][a]	Acid value [mg_{KOH}/g_{oil}][b]	FFA content [wt %][c]	Water content [ppm][d]
Sunflower oil	0.94	92.58	3.48	1.33	0.11	0.05	631
Used frying oil	0.94	80.06	16.57	1.31	0.21	0.11	671
Residual soybean oil	0.96	2.43	5.53	4.20	153.72	76.91	5221
J. Hieronymi oil	0.92	94.12	4.03	0.63	8.14	4.07	1185

[a] Measured by HPLC.
[b] Determined according to the European standard EN 14104: 2003.
[c] Calculated from the acid value [45].
[d] Determined according to the standard ISO 12937: 2000.

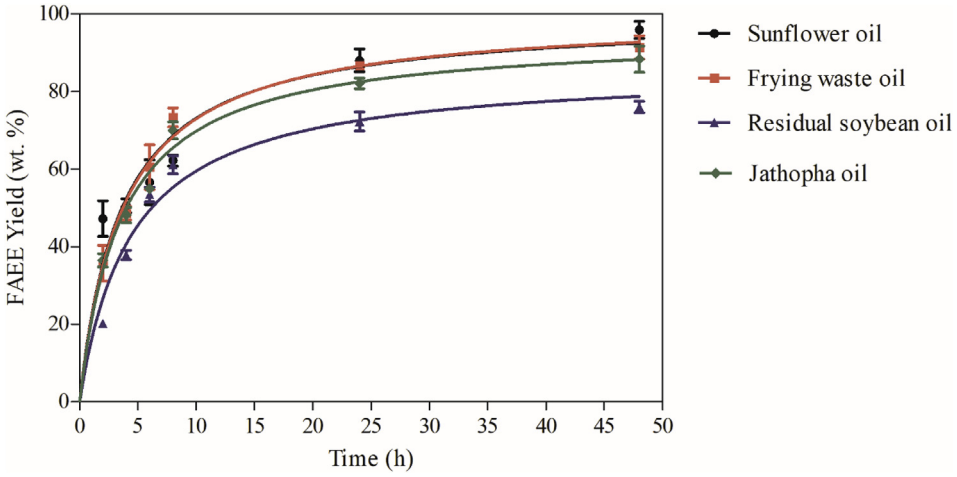

Fig. 7. Transesterification activity of the biocatalyst L_{PF}/Na/SBA-15 in a batch reactor versus different substracts: sunflower oil, used frying oil, residual soybean oil and *J. Hieronymi* oil. Reaction conditions: 48 h reaction, 37 °C, 80 rpm, 1:4 oil/ethanol (96% v/v) ratio, 400 $mg_{protein}/g_{support}$.

Yields between 76 and 96 wt% were obtained with the four tested oils (commercial sunflower oil, non-edible *J. hieronymi* oil, waste frying oil and residual soybean oil) without the need for any previous treatment. These results also encourage a bioprospecting of new plant species with oilseeds (native of semiarid and arid ecosystems), which promise the production of second-generation biofuels.

Author contributions statement

Gabriel O. Ferrero: Conceptualization, Methodology, Investigation, Resources, Writing—original draft preparation, Visualization, Supervision, Project administration, Funding acquisition. **Edgar M. Sánchez Faba:** Methodology, Investigation, Writing — review and editing. **Adriana A. Rickert:** Methodology, Resources, Writing — review and editing. **Griselda A. Eimer:** Conceptualization, Resources, Writing — review and editing, Supervision, Project administration, Funding acquisition

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.

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References

[1] Comisión Europea, Un marco estratégico en materia del clima y energía para el período 2020-2030, COM, 2014, pp. 1–21, 15 final, (2014, http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:52014DC0015.
[2] R. Luque, J.C. Lovett, B. Datta, J. Clancy, J.M. Campelo, A.A. Romer, Biodiesel as feasible petrol fuel replacement: a multidisciplinary overview, Energy Environ. Sci. 3 (2010) 1706–1721, https://doi.org/10.1039/c0ee00085j.
[3] A. Barragán-Escandón, J. Terrados-Cepeda, E. Zalamea-León, The role of renewable energy in the promotion of circular urban metabolism, Sustain. Times 9 (2017) 1–29, https://doi.org/10.3390/su9122341.
[4] C.S. Wassell, T.P. Dittmer, Are subsidies for biodiesel economically efficient? Energy Policy 34 (2006) 3993–4001, https://doi.org/10.1016/j.enpol.2005.09.024.
[5] H. Sulistyo, M.F. Almeida, J.M. Dias, Influence of synthetic antioxidants on the oxidation stability of biodiesel produced from acid raw Jatropha curcas oil, Fuel Process. Technol. 132 (2015) 133–138, https://doi.org/10.1016/j.fuproc.2014.12.003.
[6] T.L. Chew, S. Bhatia, Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery, Bioresour. Technol. 99 (2008) 7911–7922, https://doi.org/10.1016/j.biortech.2008.03.009.
[7] S. Yan, C. Dimaggio, S. Mohan, M. Kim, S.O. Salley, K.Y.S. Ng, Advancements in heterogeneous catalysis for biodiesel synthesis, Top. Catal. 53 (2010) 721–736, https://doi.org/10.1007/s11244-010-9460-5.
[8] G.O. Ferrero, M.F. Almeida, M.C.M. Alvim-Ferraz, J.M. Dias, Glycerol-enriched heterogeneous catalyst for biodiesel production from soybean oil and waste frying oil, Energy Convers. Manag. 89 (2015) 665–671, https://doi.org/10.1016/j.enconman.2014.10.032.
[9] Y.M. Sani, W.M.A.W. Daud, A.R. Abdul Aziz, Activity of solid acid catalysts for biodiesel production: a critical review, Appl. Catal. A Gen. 470 (2014) 140–161, https://doi.org/10.1016/j.apcata.2013.10.052.
[10] J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, J.D. Méndez Díaz, M.S. Polo, J.R. Utrilla, Selection of heterogeneous catalysts for biodiesel production from animal fat, Fuel 94 (2012) 418–425, https://doi.org/10.1016/j.fuel.2011.10.069.
[11] A. Corma, From microporous to mesoporous molecular sieve materials and their use in catalysis, Chem. Rev. 97 (1997) 2373–2420. http://www.ncbi.nlm.nih.gov/pubmed/11848903.
[12] G.A. Eimer, L.B. Pierella, G.A. Monti, O.A. Anunziata, Synthesis and characterization of Al-MCM-41 and Al-MCM-48 mesoporous materials 78 (2002) 65–75.
[13] A. Salis, M. Pinna, M. Monduzzi, V. Solinas, Comparison among immobilised lipases on macroporous polypropylene toward biodiesel synthesis, J. Mol. Catal. B Enzym. 54 (2008) 19–26, https://doi.org/10.1016/j.molcatb.2007.12.006.
[14] A. Salis, M.S. Bhattacharyya, M. Monduzzi, V. Solinas, Role of the support surface on the loading and the activity of Pseudomonas fluorescens lipase used for biodiesel synthesis, J. Mol. Catal. B Enzym. 57 (2009) 262–269, https://doi.org/10.1016/j.molcatb.2008.09.015.
[15] G.O. Ferrero, H.J. Rojas, C.E. Argaraña, G.A. Eimer, Towards sustainable biofuel production: design of a new biocatalyst to biodiesel synthesis from waste oil and commercial ethanol, J. Clean. Prod. 139 (2016) 495–503, https://doi.org/10.1016/j.jclepro.2016.08.047.
[16] S.K. Narwal, R. Gupta, Biodiesel production by transesterification using immobilized lipase, Biotechnol. Lett. 35 (2013) 479–490, https://doi.org/10.1007/s10529-012-1116-z.
[17] K. Kato, R. Irimescu, T. Saito, Y. Yokogawa, H. Takahashi, Catalytic properties of lipases immobilized on various mesoporous silicates, Biosci. Biotechnol. Biochem. 67 (2003) 203–206, https://doi.org/10.1271/bbb.67.203.
[18] S. Cesarini, F.I. Javier Pastor, P.M. Nielsen, P. Diaz, Moving towards a competitive fully enzymatic biodiesel process, Sustain. Times 7 (2015), https://doi.org/10.3390/su7067884.
[19] S. Fracchia, V. Miranda, A.A. Rickert, Seed oil evaluation of the desert plant *Jatropha Peiranoi* and its potential as feedstock for biofuel vol. 60 (2016) 163–167.
[20] H.J. Berchmans, S. Hirata, Biodiesel production from crude Jatropha curcas L. seed oil with a high content of free fatty acids, Bioresour. Technol. 99 (2008) 1716–1721, https://doi.org/10.1016/j.biortech.2007.03.051.
[21] S. Shah, M.N. Gupta, Lipase catalyzed preparation of biodiesel from Jatropha oil in a solvent free system, Process Biochem. 42 (2007) 409–414, https://doi.org/10.1016/j.procbio.2006.09.024.
[22] S.G. Bojan, S. Chelladurai, S.K. Durairaj, Batch type synthesis of high free fatty acid Jatropha Curcus oil biodiesel- India as supplying country, J. Eng. Appl. Sci. 6 (2011) 73–78.
[23] F. Yagiz, D. Kazan, a.N. Akin, Biodiesel production from waste oils by using lipase immobilized on hydrotalcite and zeolites, Chem. Eng. J. 134 (2007) 262–267, https://doi.org/10.1016/j.cej.2007.03.041.
[24] M. Tudorache, A. Negoi, B. Tudora, V.I. Parvulescu, Environmental-friendly strategy for biocatalytic conversion of waste glycerol to glycerol carbonate, Appl. Catal. B Environ. 146 (2014) 274–278, https://doi.org/10.1016/j.apcatb.2013.02.049.
[25] E. Santacesaria, G.M. Vicente, M. Di Serio, R. Tesser, Main technologies in biodiesel production: state of the art and future challenges, Catal. Today 195 (2012) 2–13, https://doi.org/10.1016/j.cattod.2012.04.057.
[26] P.T. Vasudevan, M. Briggs, Biodiesel production–current state of the art and challenges, J. Ind. Microbiol. Biotechnol. 35 (2008) 421–430, https://doi.org/10.1007/s10295-008-0312-2.
[27] L.A.K. Amano, Lipase AK"Amano", Amano Labs, 2008, pp. 1–2.
[28] M.M. Bradford, A rapid and sensitive method for the quantitation of microgram quantities of protein utilizing the principle of protein-dye binding, Anal. Biochem. 72 (1976) 248–254, https://doi.org/10.1016/0003-2697(76)90527-3.
[29] M.S. Carvalho, M.A. Mendonça, D.M.M. Pinho, I.S. Resck, P.A.Z. Suarez, Chromatographic analyses of fatty acid methyl esters by HPLC-UV and GC-FID, J. Braz. Chem. Soc. 23 (2012) 763–769, https://doi.org/10.1590/S0103-50532012000400023.
[30] J. Tantirungrotechai, P. Thananupappaisal, B. Yoosuk, N. Viriya-empikul, K. Faungnawakij, One-pot synthesis of calcium-incorporated MCM-41 as a solid base catalyst for transesterification of palm olein, Catal. Commun. 16 (2011) 25–29, https://doi.org/10.1016/j.catcom.2011.09.002.
[31] S. Kumar, B. Kishore, N. Munichandraiah, Electrochemical studies of non-aqueous Na–O $_2$ cells employing Ag-RGO as the bifunctional catalyst, RSC Adv. 6 (2016) 63477–63479, https://doi.org/10.1039/C6RA13596J.
[32] J. Mao, Q. Gu, D.H. Gregory, Revisiting the hydrogen storage behavior of the Na-O-H system, Materials (Basel) 8 (2015) 2191–2203, https://doi.org/10.3390/ma8052191.
[33] V.R. Elías, G.O. Ferrero, R.G. Oliveira, G.A. Eimer, Improved stability in SBA-15 mesoporous materials as catalysts for photo-degradation processes, Microporous Mesoporous Mater. 236 (2016) 218–227, https://doi.org/10.1016/j.micromeso.2016.09.001.
[34] W. Xie, L. Zhao, Heterogeneous CaO–MoO3–SBA-15 catalysts for biodiesel production from soybean oil, Energy Convers. Manag. 79 (2014) 34–42, https://doi.org/10.1016/j.enconman.2013.11.041.
[35] E.M. Sánchez Faba, G.O. Ferrero, J.M. Dias, G.A. Eimer, Thermo-chemically tuning of active basic sites on nanoarchitectured silica for biodiesel production, Mol. Catal. (2018) 1–8, https://doi.org/10.1016/j.mcat.2018.08.013.
[36] H. Sun, J. Han, Y. Ding, W. Li, J. Duan, P. Chen, H. Lou, X. Zheng, One-pot synthesized mesoporous Ca/SBA-15 solid base for transesterification of sunflower oil with methanol, Appl. Catal. A Gen. 390 (2010) 26–34, https://doi.org/10.1016/j.apcata.2010.09.030.
[37] B.S. Lin, H.K. Jia, Y. Chun, J. Yang, N.G. Fang, Y. Wang, H.Z. Jian, G.Z. Zhi, New attempt at directly generating superbasicity on mesoporous silica SBA-15, Inorg. Chem. 47 (2008) 4199–4208, https://doi.org/10.1021/ic702223b.
[38] D. Nicola, Edinburgh Research Explorer Development and Optimization of a Method for Analyzing Biodiesel Mixtures with Non-aqueous Reversed Phase Liquid Chromatography Development and Optimization of a Method for Analyzing Biodiesel Mixtures with Non Aqueous Reversed, 2008.
[39] A. Dijkstra, J. Segers, Production and refining of oils and fats, third ed., in: F.D. Gunstone, J.L. Harwood, A.J. Dijkstra (Eds.), Lipid Handb. With CD-ROM,

third ed., CRC Press, Abingdon, 2007, pp. 143–262, https://doi.org/10.1201/9781420009675.ch3.
[40] J.B. Woerfel, Soybean oil processing byproducts and their utilization, in: D.R. Erickson (Ed.), Pract. Handb. Soybean Process. Util., first ed., Elsevier, Urbana, 1995, pp. 297–313, https://doi.org/10.1016/B978-0-935315-63-9.50021-8.
[41] L.C. Meher, C.P. Churamani, M. Arif, Z. Ahmed, S.N. Naik, Jatropha curcas as a renewable source for bio-fuels—a review, Renew. Sustain. Energy Rev. 26 (2013) 397–407, https://doi.org/10.1016/j.rser.2013.05.065.
[42] B. Freedman, E.H. Pryde, T.L. Mounts, Variables affecting the yields of fatty esters from transesterified vegetable oils, J. Am. Oil Chem. Soc. 61 (1984) 1638–1643, https://doi.org/10.1007/BF02541649.
[43] J.M. Dias, M.C.M. Alvim-ferraz, M.F. Almeida, Comparison of the performance of different homogeneous alkali catalysts during transesterification of waste and virgin oils and evaluation of biodiesel quality 87 (2008) 3572–3578, https://doi.org/10.1016/j.fuel.2008.06.014.
[44] A. Salis, M.F. Casula, M.S. Bhattacharyya, M. Pinna, V. Solinas, M. Monduzzi, Physical and chemical lipase adsorption on SBA-15: effect of different interactions on enzyme loading and catalytic performance, ChemCatChem 2 (2010) 322–329, https://doi.org/10.1002/cctc.200900288.
[45] J. Salimon, B.M. Abdullah, N. Salih, Hydrolysis optimization and characterization study of preparing fatty acids from Jatropha curcas seed oil, Chem. Cent. J. 5 (2011) 67, https://doi.org/10.1186/1752-153X-5-67.