Preparation, characterization and evaluation of x-MoO₃/Al-SBA-15 catalysts for biodiesel production

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Received: 7 May 2021 / Accepted: 5 November 2021 / Published online: 15 December 2021
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Abstract

Biodiesel is an alternative source of renewable energy that can be produced by a transesterification of vegetable oils. Mesoporous molecular sieves, such as SBA-15, due to high surface area and thermal stability are promising precursors for heterogeneous catalysts in the transesterification reaction. In this work, Al-SBA-15 precursor was obtained by direct hydrothermal synthesis, impregnated with different MoO₃ contents (5, 10 and 15 wt%) by the pore saturation method, and evaluated as heterogeneous catalyst in the production of biodiesel from a transesterification of soybean oil with methanol. Al-SBA-15 precursor as well as MoO₃/Al-SBA-15 catalyst were characterized for its structural characteristic by X-ray diffraction, textural characteristic by N₂ adsorption analysis, and thermal stability by thermogravimetric analysis. An experimental planning 2² + 3 CtPt was used to evaluate the influence of MoO₃ content and reaction time on biodiesel yield from soybean oil and methanol. The biodiesel content in the final product was obtained by gas chromatography. An average biodiesel yield of 96% was obtained with the catalyst 10%MoO₃/Al-SBA-15 under the following reaction conditions: 20:1 methanol/soybean oil molar ratio, and 3 wt% of catalyst loading at 150 °C in 3 h. After five consecutive reaction cycles, the biodiesel yield decreased by about 34%. The density and acidity of the biodiesel produced are within the specified values for commercialization according to international standards.

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Graphical abstract

Keywords Biodiesel · Transesterification · Al-SBA-15 precursor · MoO₃/Al-SBA-15 catalyst

Introduction

Currently, fossil fuels are the main energy source in the global energy system. However, the increase in global energy demand, uncertainties regarding the availability of oil in the future, and the environmental impacts caused by burning fossil fuels, are factors that justify the need to search for alternative sources of renewable energy to avoid an energy crisis [1–3]. In this scenario, fuels derived from vegetable biomass such as biodiesel and ethanol are alternatives as renewable sources of energy. Biodiesel is free of sulfur and aromatics, has a high flash point and a high number of cetane [4]. This biofuel can replace, totally or partially, diesel petroleum oil in automotive or stationary engines, as well as be used pure or blended with petroleum diesel in different proportions [5, 6].

Biodiesel is a mixture of mono alkyl esters produced in a transesterification reaction, in which triglycerides from different sources of vegetable oils or animal fats react with a short chain alcohol, usually methanol or ethanol in the presence of a homogeneous, heterogeneous or even enzymatic catalyst [7].

In the stoichiometric reaction of transesterification 1 mol of triglyceride reacts with 3 mols of alcohol producing 3 mols of alkyl esters and 1 mol of glycerol. Alcohol is mixed in excess to shift the reaction balance towards biodiesel, increasing its yield [8, 9]. A high methanol to oil molar ratio is usually used due to the lower contact between catalyst and reactants in the heterogeneous process than in the homogeneous one. A methanol to oil molar ratio up to 30–150 to 1 has been reported in the literature [9–12], to guarantee the highest FAMES yield [3, 7, 13]. Transesterification consists of a series of consecutive, reversible reactions, forming alkyl esters in each step as shown in Fig. 1. The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol [14].

The main process variables in the transesterification reaction are temperature, alcohol/oil ratio, reaction time, type of catalyst, water content, and free fatty acid content in vegetable oils. This study focused on catalyst preparation and evaluation for biodiesel production, taking as input variables the catalyst composition and reaction time, and biodiesel yield as response variable.

Industrially, homogeneous catalysts, such as potassium hydroxide (KOH), sodium hydroxide (NaOH) and sulfuric

Fig. 1 Consecutive steps in the transesterification reaction

acid (H_2SO_4) have been used in the transesterification reaction, with sodium hydroxide being the most used due to its low cost and high product yield. As disadvantages, the homogeneous catalysts are not recovered, but neutralized, the process is susceptible to the formation of soap due to the presence of water and free fatty acids in the reaction medium, which complicates the purification of the products, making the process expensive [15]. Thus, heterogeneous catalysts are a promising alternative to replace homogeneous ones in industrial biodiesel production, having as main advantages the easy separation of the reaction mixture by simple physical processes, the non-need for neutralization and disposal, which minimizes harmful effluents from the environmental point of view [16]; in addition, they can be regenerated and reused, are tolerant to water and organic solvents, have high thermal stability, strong acidity, and high catalytic activity [5, 17]. As disadvantages, the use of heterogeneous catalysts requires more severe reaction conditions, such as high temperatures and pressure, as well as a longer reaction time, in addition to the leaching of the active sites of the catalysts.

Among the different types, mesoporous materials are widely used in the development of catalysts, including for the production of biodiesel, due to important characteristics, such as regular pore structure, high specific surface area that can reach $1000 \text{ m}^2 \text{ g}^{-1}$, thickness pore wall of about 6 nm, thermal stability, ease of separation and regeneration. An interesting alternative for the production of heterogeneous

catalysts is the use of amorphous silica with an ordered mesoporous structure, such as SBA-15 as a support [18, 19]. The incorporation of metals in the structure of amorphous silica, such as aluminum and molybdenum, define an acidic characteristic of the mesoporous material [20].

The insertion of aluminum ions in the structure of the SBA-15 allows the creation of acidic sites that are essential for reactions catalyzed by acid [20]. Al-SBA-15 with its unique structure, surface characteristics, good thermal stability and mechanical resistance make this molecular sieve have better catalytic performance than traditional alumina catalysts throughout the reaction [21]. The literature reports that the incorporation of molybdenum in supports promotes its catalytic activity, motivating studies for its use in the transesterification reactions [22–24]. Molybdenum based catalysts are viable alternatives for transesterification, but typically suffer from poor recyclability or require high temperatures to achieve useful activity [22].

Mohebbi et al. [25] investigated the effect of MoO_3 on the esterification reaction of oleic acid by methyl route for biodiesel production, using different MoO_3 contents (5, 15, 25 and 35 wt%) impregnated in the heterogeneous mesoporous nanocatalyst B-ZSM-5. The optimum MoO_3 content was 25 wt% incorporated in the B-ZSM-5 nanocatalyst, and the optimal operating conditions were reaction time of 6 h, temperature of 160°C , catalyst concentration of 3 wt%, and methanol/oleic acid molar ratio of 20:1. The maximum conversion of free fatty acids was 98%, confirming the high

potential of the MoO_3 -impregnated nanocatalyst for industrial applications.

Ding et al. [26] synthesized and evaluated three acidic imidazolium liquids as catalysts for production of biodiesel in a transesterification of palm oil under microwave irradiation, and concluded that $[\text{HSO}_3\text{-BMIM}]\text{HSO}_4$ catalyst was the most effective for the reaction. The effect of methanol to oil molar ratio, catalyst dosage, microwave power and reaction time on yield of biodiesel was evaluated using an experimental planning. From the regression model, a maximum biodiesel yield of 99.64%, with the aid of $[\text{HSO}_3\text{-BMIM}]\text{HSO}_4$ under microwave irradiation, was predicted. The optimal reaction conditions were: mole ratio of methanol to oil 11:1, ionic liquid dosage 9.17%, microwave power 168 W, and reaction time 6.43 h. The predicted value was verified with the average yield of 98.93% from three experiments.

Pinto et al. [23] synthesized molybdenum trioxide catalysts calcined at different temperatures (200, 300, 400, 500, 600 and 700 °C), and evaluated the effect of the catalyst calcination temperature on the catalyst performance for the production of biodiesel from different vegetable oils. Different temperature, oil/alcohol ratio, reaction time and catalyst load were evaluated. The highest catalytic activity was for the catalyst calcined at 600 °C. The optimal operational conditions were 0.5 wt% of catalyst in 5 g of oil, reaction temperature of 150 °C, and a methanol/oil molar ratio of 45:1. In these conditions, the yield reached 90%, indicating that the molybdenum trioxide catalyst is effective for the transesterification reaction for biodiesel production.

Li et al. [27] synthesized $\text{SO}_4^{2-}\text{-MoO}_3\text{-ZrO}_2\text{-ND}_2\text{O}_3/\text{SiO}_2$ catalysts with different calcination times, denominating them SMZN/ $\text{SiO}_2\text{-X}$, where X is the calcination time ($X=2, 4, 6, 8$ and 12 h). The catalysts were evaluated for production of biodiesel by both esterification of lauric acid with methanol, and transesterification of triacetin and jatropha oil with methanol. A yield of 97.1% was achieved in the esterification with SMZN/ $\text{SiO}_2\text{-2 h}$ and SMZN/ $\text{SiO}_2\text{-4 h}$ catalysts. A methyl acetate yield around 92.1% was achieved with all catalysts in the transesterification of triacetin. In the transesterification of jatropha oil, yields of 75.4% and 71.2% in biodiesel were achieved with the catalysts SMZN/ $\text{SiO}_2\text{-2 h}$ and SMZN/ $\text{SiO}_2\text{-4 h}$, respectively, for a methanol/oil ratio of 9:1, 12 wt% of catalyst, temperature of 65 °C, and reaction time of 10 h.

In this work, heterogeneous catalysts with different MoO_3 contents, impregnated in a modified SBA-15 catalytic precursor by the incorporation of aluminum using direct hydrothermal synthesis were synthesized, characterized and evaluated in the transesterification of vegetable oil with methanol. An experimental design 2^2 with 3 central points was used. The effect of MoO_3 content in the catalytic support and reaction time on biodiesel yield was obtained. The catalysts $x\text{-MoO}_3/\text{Al-SBA-15}$ ($x=5, 10$ and 15 wt%) were

characterized in terms of thermal, crystalline and textural properties, as well as its activity in the transesterification reaction was proved. MoO_3 content influenced more the catalytic conversion than the reaction time, in the studied range. The $x\text{-MoO}_3/\text{Al-SBA-15}$ catalyst performance was compared to that of others catalysts for biodiesel production in the transesterification reaction reported in the literature.

The manuscript is organized with an experimental section describing the catalyst preparation and characterization, the reaction performed, and the biodiesel characterization. Results are discussed in a second section, and finally the main conclusions are presented in a final section.

Experimental

Catalyst preparation

Direct synthesis of the Al-SBA-15 catalytic precursor

The mesoporous molecular sieve Al-SBA-15 used as a catalytic precursor was synthesized from an adaptation of the methodology described by Li et al. [28] and Zhao et al. [29]. Initially, the Pluronic P123 triblock copolymer was dissolved in a stirred aqueous solution of HCl (1.6 mol L^{-1}) at 35 °C. After complete homogenization of the mixture, tetraethylorthosilicate (TEOS) was added to the reaction medium. In a beaker, aluminum nitrate ($\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$) was dissolved in a stirred solution of ethanol and HCl (1.6 mol L^{-1}) at 35 °C. The two solutions were mixed together and taken to a roto-evaporator, remaining for 24 h at 40 °C. A gel was formed with molar composition $1\text{ Si}: 0.017\text{ P123}: 4.96\text{ HCl}: 0.054\text{ Al}: 35.42\text{ EtOH}$, which was then crystallized in an oven at 100 °C for 48 h. The resulting material was cooled and then washed with deionized water to remove excess of director until the filtrate reached pH=7. The material was dried in an oven at 60 °C for 24 h. Finally, the catalytic precursor (Al-SBA-15) was activated by calcination, under synthetic air flow, from room temperature of 25 to 550 °C over 6 h, with a flow rate of 150 mL min^{-1} and ramp heating temperature of 5 °C min^{-1} .

Impregnation of molybdenum trioxide in the catalytic precursor Al-SBA-15

The incorporation of MoO_3 to the catalytic precursor was performed from ammonium heptamolybdate salt $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}]$ using the pore volume saturation impregnation method. The desired MoO_3 content in the final catalyst were 5, 10 and 15 wt%. In a typical synthesis, 1.0 g of calcined Al-SBA-15 catalytic precursor was impregnated with an aqueous solution of the molybdenum precursor, using the needed concentration to achieve the desired Mo

content assuming total incorporation [30, 31]. After impregnation, the material was dried in an oven at 60 °C for 24 h. The catalysts were calcined under the same conditions as the Al-SBA-15 catalytic precursor.

Characterization of solids

The thermogravimetric analysis was performed using a TGA-51 Shimadzu Thermogravimetric Analyzer coupled to a computer (for data storage) by the TA-60 WS collection monitor software. The samples were analyzed on a range of 30 to 1000 °C, a heating rate of 5 °C min⁻¹ and a synthetic air flow rate of 50 mL min⁻¹. The thermogravimetric analysis was used to investigate the thermal stability of catalysts and decomposition temperature of the molybdenum salt.

The structural characteristics, identifications of phases and determination of crystallite size and crystallinity of the catalyst was investigated by an X-ray diffraction method with a Shimadzu XRD-600 employing a Cu K α radiation at 40 kV and 30 mA. The crystalline size was then calculated from Scherrer's equation [32].

Fourier-transformed infrared (FTIR) spectra for the catalytic precursor and catalysts were obtained with a Spectrum 400 Perkin Elmer spectrophotometer. The analysis was performed out in the region from 4000 to 400 cm⁻¹ wave number with a resolution of 4 cm⁻¹ using a solid mixture with KBr.

Textural properties, pore volume and average pore size, and specific surface area of x_{MoO_3} /Al-SBA-15 catalysts were evaluated from N₂ adsorption isotherms and BET method [33], using a Quantachrome gas adsorption analyzer, model 3200E YOUNG.

Biodiesel production

Experimental planning

A 2² + 3 C_tP_t factorial design was used to evaluate the influence of reaction time and MoO₃ content in the catalyst on the biodiesel yield in the transesterification reaction of soybean oil. Table 1 shows the experimental levels of the independent variables used in this study.

The effects of the reaction time in the range of 2 to 4 h and the MoO₃ content in the range of 5 to 15 wt% were

evaluated. An experimental design with three levels for both variables was used, with the central point being the average of the limits of the intervals.

Minitab 17.0[®] software was used to perform statistical analysis and regression of the data. Different models (linear and quadratic) were tested and analyzed based on Analysis of Variance (ANOVA). Equation (1) describes the relationship between the dependent variable (Y) and the independent (X_n and X_m) uncoded variables, where a_n , a_{nn} , a_{nm} are the linear regression coefficients.

$$Y = a_0 + \sum_{n=1}^2 a_n X_n + \sum_{n=1}^2 a_{nn} X_n^2 + \sum_{n=1}^2 \sum_{m=n+1}^2 a_{nm} X_n X_m. \quad (1)$$

Transesterification reaction

$x_{\text{Al-SBA-15}}$ catalysts with different MoO₃ contents were used in the transesterification reaction of soybean oil and methanol with different reaction time to evaluate the catalytic potential. The reaction was carried out in a batch reactor manufactured by Parr Instruments Inc.—Model 4848. The reaction conditions were set up based on previous works and in accordance to the literature [9–12]. The reactor is an autoclave made of stainless steel with a volume of 300 mL and was stirred at a speed of 500 rpm. The reactional system containing an oil and alcohol mixture in the initial molar ratio of 1:20 and 3 wt% catalyst concentration, was sealed and heated from room temperature to 150 °C. After the reaction time, the catalyst and glycerol were separated from the products by decantation. The transesterified oils were transferred to a decanting funnel, remaining until the phases were completely formed (glycerol + alcohol, oil, catalyst). The glycerol + alcohol and catalyst phases were removed and the oil phase was washed in two steps: in the first, a solution of hydrochloric acid (HCl—Vetec) [2 M] was added to remove the excess of alcohol and catalyst; in the second step, fixed volumes of 15 mL of deionized water were added until pH ~ 7 was reached. The oil was dried with magnesium sulfate heptahydrate (MgSO₄·7H₂O—Vetec) and centrifuged for complete separation. The oil obtained was characterized for density, acidity index and methyl esters.

Reusability of the catalyst

The most active catalyst was reused under the same reaction conditions as in the first cycle. The catalyst was dried at 100 °C for 24 h and reused in four reaction cycle without regeneration.

Table 1 Levels of independent variables in the experimental planning 2² + 3C_tP_t for evaluation of the transesterification of soybean oil

Independent variable	Symbol	Levels		
		− 1	0	+ 1
Time (h)	A	2	3	4
MoO ₃ (wt%)	B	5	10	15

Biodiesel characterization

The biodiesel or fatty acid methyl ester (FAME) content was analyzed following the standard method according to EN 14103 [34] using a Shimadzu GC 2010 Plus gas chromatograph with a split/splitless injector, a flame ionization detector (FID), an AOC-20i auto-injector and a 100% dimethyl polysiloxane capillary column RTX-WAX 30 m×0.32 mm×0.25 μm (Restek Corporation). The operating conditions were as follows: FID temperature, 250 °C; the initial column temperature, 210 °C; final column temperature, 250 °C; H₂ linear velocity, 50 cm s⁻¹; and split mode injection in the ratio of 1:50. Methyl heptadecanoate was used as the standard for GC-FID. Equation (2) was used to determine the fatty acid methyl esters content, C_{FAME} (wt%).

$$C_{\text{FAME}} = \frac{(S_A - A_{\text{EI}})}{A_{\text{EI}}} \times \frac{(C_{\text{EI}} \times V_{\text{EI}})}{m} \times 100\%, \quad (2)$$

where, S_A represents sum of the peak areas, A_{EI} is the peak area of methyl heptadecanoate (internal standard), C_{EI} is the concentration (mg/mL) of methyl heptadecanoate solution (10 mg/mL), V_{EI} represents the volume (mL) of methyl heptadecanoate and ' m ' is the mass (mg) of the FAME sample.

The chromatograms in Fig. 8 show that transesterification reaction was successfully achieved and allows to calculate the individual FAME_{*i*} content using Eq. (3).

$$C_{\text{FAME}_i} = \frac{(A_{\text{FAME}_i})}{A_{\text{EI}}} \times \frac{(C_{\text{EI}} \times V_{\text{EI}})}{m} \times 100\%, \quad (3)$$

where, C_{FAME_i} is the FAME_{*i*} content (wt%); A_{FAME_i} is the FAME_{*i*} area calculated by integration of the corresponding peaks in the chromatogram.

The specific mass data were determined following the standard established by EN ISO 3675/12185 and ASTM D1298 [35], using Density Master DMA 4100 M equipment. The acidity index was determined according to the norm established by ASTM D664 and EN 14104 standards [36] by titration of the oil with a solution of ethyl ether and ethyl alcohol (2:1) using 0.1 M potassium hydroxide as the titrant.

Results and discussion

Characterization of the catalyst

Thermogravimetric analysis (TG/DTG)

The decomposition temperature of the precursor salts of aluminum and molybdenum was determined from the thermogravimetric curves shown in Fig. 2a, b.

Fig. 2 Thermogravimetric (TG) analysis of the catalytic precursor Al-SBA-15 (a) and catalyst 10MoO₃/Al-SBA-15 (b)

In Fig. 2a, there are two temperature ranges, corresponding to two mass loss events. In the first event (I), in the temperature range between 23.57 and 82.9 °C, there is a mass loss of 2.89%, which corresponds to a physical loss of water and volatile materials in the material's porous; in the second event (II) in the range of 82.95 to 383.43 °C there is a mass loss of 46.63%, due to the elimination of molecules of Pluronic P123 triblock copolymer director. The system practically reaches the equilibrium at a temperature of 500 °C.

In Fig. 2b, three mass loss events are observed. In the first event (I), in the temperature range of 23.44 to 351.69 °C, there is a mass loss of 24.28%, which corresponds to elimination of hydration water, desorption of physically adsorbed water in the porous, and the decomposition of ammonium ions present in tetrahydrate ammonium molybdate salt. The second event (II), in the temperature range of 351.69 to 756 °C, corresponds to a mass loss of 5.67% due to molybdenum oxide fusion. In the third event (III), in the temperature range of 756 to 871 °C, there is a mass loss of 5.9% corresponding to the process of sublimation of molybdenum [37].

Fig. 3 XRD pattern of the Al-SBA-15 catalytic precursor

X-ray diffractometry (XRD)

Figure 3 shows the diffractogram of the catalytic precursor Al-SBA-15. From the X-ray diffractogram in Fig. 3a, it is possible to observe the presence of peaks corresponding to the characteristic reflections of mesoporous materials with an ordered hexagonal structure of the type SBA-15. It is observed that the synthesized materials present the main reflection, corresponding to the Miller index (1 0 0), thus indicating that a material with a well-defined structure was obtained; the peaks of lower intensity are due to the reflections of the planes (1 1 0) and (2 0 0), described by Zhao et al. [29] as peaks characteristic of the hexagonal structure of the SBA-15 catalytic precursor. The ill-defined peak in the region of $2\theta = 23.71^\circ$ shown in Fig. 3b is characteristic of amorphous silica materials, which is typical of SBA-15. It is possible to notice the absence of characteristic peaks of aluminum trioxide on the surface of the mesoporous structure, indicating an effective incorporation of aluminum in the structure of SBA-15 [38].

Figure 4 shows the X-ray diffractograms of the $x\text{-MoO}_3/\text{Al-SBA-15}$ catalysts ($x = 5, 10$ and 15 wt%).

In the diffractogram shown in Fig. 4b, c peaks corresponding to the species of molybdenum trioxide were identified by comparison with the standard XRD (N° JCPDS 00-005-0508) from the library of the *International Center for Diffractional Data (JCPDS)*. In Fig. 4a, there were no peaks related to the MoO_3 species, due to the fact that these active species are well dispersed in the channels of the SBA-15 catalytic precursor. González et al. [39] investigated the crystalline and chemical structure of $\text{MoO}_3/\text{SBA-15}$ catalysts with different MoO_3 contents (5, 10, 15, 20 and 25% by mass) to evaluate their catalytic activity for the oxidation of 4,6-DMDBT; the study proved that the active species

Fig. 4 XRD pattern of the a $5\text{MoO}_3/\text{Al-SBA-15}$, b $10\text{MoO}_3/\text{Al-SBA-15}$ e c $15\text{MoO}_3/\text{Al-SBA-15}$ catalysts

may not be detected in the XRD due to the support having multiple pores, which causes the species to disperse inside the pores. It is observed that as the MoO_3 content increases, there is an increase in the intensity of the peaks, indicating the appearance of the crystalline phase corresponding to MoO_3 on the surface of the SBA-15.

Fourier transformed infrared spectroscopy

FTIR spectra of Al-SBA-15 catalyst precursor and $x\text{-MoO}_3/\text{Al-SBA-15}$ catalysts are shown in Fig. 5, in which the bands at 3381 and 1633 cm^{-1} correspond to the $\nu(\text{O-H})$ stretching vibration of adsorbed water molecules. All samples display four absorption peaks at about $1052, 967, 797$ and 447 cm^{-1} . These peaks in the catalytic precursor are attributed to asymmetrical stretching of the Si-O-Si, Si-OH, T-O (T=Si or Al) groups and the bending vibration of the Si-O-T groups, respectively. For the catalysts, the peaks in the $500\text{--}1000\text{ cm}^{-1}$ region are attributed to different stretching vibrations of Mo-O. The peaks at about 970 (all

Fig. 5 FTIR spectra of **a** Al-SBA-15, **b** 5MoO₃/Al-SBA-15, **c** 10MoO₃/Al-SBA-15, **d** 15MoO₃/Al-SBA-15

samples) and 913 cm⁻¹ (10 and 15% MoO₃ catalysts) were assigned to Mo=O_{terminal} symmetric stretching mode, indicating orthorhombic phase in MoO₃ layers, and Mo–O–Si bond, respectively. The peak at about 570 cm⁻¹ is assigned to the triply coordinated oxygen [Mo–O(3)] stretching mode, which results from the edge-shared oxygen in common with three MoO₆ octahedra. The FTIR spectra complemented the diffractograms, as it was possible to identify the MoO₃ bonds in the Al-SBA-15 structure [40, 41].

Textural analysis by nitrogen adsorption (BET)

The adsorption and desorption isotherms of N₂ of the catalytic precursor Al-SBA-15 and the catalysts *x*_MoO₃/Al-SBA-15 (*x*=5, 10 and 15 wt%) are shown in Fig. 6.

Figure 6 shows type IV isotherms with a H1 type hysteresis loop for the Al-SBA-15 support as well as for each catalyst. Leofanti et al. [33] noted that type IV isotherms are typical in mesoporous materials. H1-type hysteresis results from capillary condensation that occurs within the material's mesopores and is characteristic of materials with a cylindrical pore system. Analyzing the adsorption isotherm, three distinct regions are observed: in the first, at low pressures, for $P/P_0 < 0.2$, the N₂ adsorption occurs in the monolayer;

Fig. 6 N₂ adsorption/desorption isotherm of **a** Al-SBA-15, **b** 5MoO₃/Al-SBA-15, **c** 10MoO₃/Al-SBA-15, **d** 15MoO₃/Al-SBA-15

the second region, in the range $P/P_0 \approx 0.45$ – 0.8 , occurs the typical capillary condensation in mesoporous materials, with a hysteresis loop. In the third region, for $P/P_0 > 0.8$, multilayer adsorption occurs on the external surface of the particles [42].

The pore diameter of Al-SBA-15 incorporated with 5, 10 and 15 wt% of MoO₃ is shown in Fig. 7.

It can be seen from Fig. 7 that the support Al-SBA-15 as well as the catalysts 5MoO₃/Al-SBA-15, 10MoO₃/Al-SBA-15 and 15MoO₃/Al-SBA-15 have a uniform distribution of mesopores, with average diameters of 31.50 Å, 31.90 Å, 32.28 Å and 39.55 Å, respectively, in addition to unimodal pore size distribution.

The textural properties of the Al-SBA-15 catalytic precursor as well as the *x*_MoO₃/Al-SBA-15 catalysts (*x*=5, 10 and 15 wt%) are shown in Table 2.

From Table 2, it can be seen that the specific surface area and the total pore volume of the catalysts decrease with the increase in the MoO₃ content incorporated in the catalytic precursor, being up to 70% smaller than that of the Al-SBA-15 support. The pore diameter increased with

Fig. 7 Pore size distribution of the **a** Al-SBA-15 catalytic precursor, and **b** 5MoO₃/Al-SBA-15, **c** 10MoO₃/Al-SBA-15, **d** 15MoO₃/Al-SBA-15 catalysts

MoO₃ content, due to the higher concentration of MoO₃ on the external surface of the catalyst. Huang et al. [43], using different MoO₃ contents in the mesoporous structure of Al-SBA-15, concluded that the decrease in both the specific surface area and the pore volume is due to the migration of MoO₃ into the interior of the mesopores, as a result of the strong interaction between molybdenum trioxide and the mesoporous structure.

Factors affecting the transesterification reaction

Table 3 shows fatty acid methyl ester (FAME) yield, density and acidity index of the biodiesel obtained. A high yield of FAME was observed for all conditions of reaction time and MoO₃ content used in the experimental planning.

Effect of MoO₃ content on biodiesel yield

MoO₃ was incorporated in the catalytic precursor Al-SBA-15 with different contents (5, 10 and 15 wt%) and the catalyst obtained was evaluated in the biodiesel reaction. In the tested reaction conditions, the biodiesel yield increased 16.8 wt% with the increase of MoO₃ content from 5 to 15 wt%, for the shortest reaction time (2 h). For the longest reaction time (4 h), the increase in MoO₃ content from 5 to 15 wt% increased 7.2% the FAME yield. The latter is because the initial reaction rate is as higher as the MoO₃ content in the catalysts, and longer reaction time compensates the lower reaction rate of the catalyst with lower MoO₃ content. The highest biodiesel yield was obtained with the catalyst with 10 wt% of MoO₃ and 3 h of reaction. Thus, 10 wt% of MoO₃ incorporated in the mesoporous structure is the optimum content to guarantee an active and well-dispersed phase in the channels and on the internal surface of Al-SBA-15.

With the catalyst 5MoO₃/Al-SBA-15 the conversion was 89.2% in 4 h of reaction. From an economic point of view, even with the low MoO₃ content, the reaction time is still compatible with those reported in the literature [24, 44, 45], which makes it also a candidate, since its lower production cost compensates the greater reaction time required to achieve a high conversion.

Chen et al. [24] incorporated different Mo contents (1, 3, 5, 7 and 10 wt%) in zeolite NaBeta, evaluating them for the production of biodiesel from rice bran oil. The increase in the Mo content from 1 to 7 wt% increased the conversion from 44 to 74.8%, in the same reaction time (5 h). However, the activity of 10Mo/NaBeta catalyst decreases slightly because the active phase was not well dispersed in

Table 2 Textural properties of the catalytic precursor Al-SBA-15 and *x*-MoO₃/Al-SBA-15 catalysts (*x*=5, 10, 15 wt%)

Catalyst	S_{BET}^a (m ² g ⁻¹)	S_{ext} (m ² g ⁻¹)	$V_{\text{p}}^{\text{micro}}$ (cm ³ g ⁻¹)	$V_{\text{p}}^{\text{mes}}$ (cm ³ g ⁻¹)	V_{p}^b (cm ³ g ⁻¹)	D_{p}^c BJH (Å)
Al-SBA-15	655.48	566.67	0.03	1.02	1.07	72.36
5MoO ₃ /Al-SBA-15	523.63	447.18	0.03	0.56	0.61	53.51
10MoO ₃ /Al-SBA-15	311.08	256.36	0.02	0.51	0.58	80.83
15MoO ₃ /Al-SBA-15	199.28	163.34	0.02	0.44	0.44	89.22

^aSpecific surface area determined by Brunauer–Emmett–Teller (BET) method

^bTotal pore volume recorded at $p/p_0=0.99$

^cPore diameter calculated by Barrett–Joyner–Halenda (BJH) method

Table 3 Experimental and predicted data of FAME yield, density and acidity index of the obtained oils

Run	Factors		FAME yield (wt%)			Density (kg m ⁻³)	Acidity Index (mg KOH g ⁻¹)
	Time (h)	MoO ₃ (wt%)	Exp. ^a	Pred. ^b	Res. ^c		
1	2	5	80.13	84.39	4.26	887.7	0.92
2	4	5	88.65	84.39	4.26	883.4	0.67
3	2	15	94.31	94.83	0.52	881.9	0.89
4	4	15	95.36	94.83	0.53	881.0	0.92
5	3	10	94.94	96.24	1.30	879.6	1.85
6	3	10	97.89	96.24	1.65	879.0	0.88
7	3	10	95.89	96.24	0.35	879.4	0.91
Soybean oil						920	0.00

^aExperimental values of response^bPredicted values of response^cResidual

the channels resulting in smaller surface area. Yields above 84% were obtained with the 7Mo/NaBeta catalyst and reaction time of 8 h. Thus, a kinetic study was performed by the authors with the 7Mo/NaBeta catalyst.

Sankaranarayanan et al. [38] synthesized MoO₃/γ-Al₂O₃ catalysts with different MoO₃ contents (8, 12 and 16 wt%), and calcined them at different temperatures (800, 950 and 1100 K). The catalysts were evaluated in the transesterification of sunflower oil with methanol. The effect of various parameters, such as Mo content, calcination temperature, reaction temperature and methanol to oil molar ratio on the oil conversion was obtained. The highest activity was with the catalyst calcined at 950 K containing 16 wt% of MoO₃, for which conversion higher than 90% was obtained at 110 °C and 24 h in a batch reactor. The authors reported that the catalytic activity decreased with reuse, however it can be regenerated by recalcination.

Reaction time effect

The progress of the reaction was evaluated in the range of 2 to 4 h. For all catalysts, the conversion increased with the reaction time, confirming that the reaction is irreversible without competing parallel reactions. The largest conversion

was 98% with the catalyst 10MoO₃/Al-SBA-15, in 3 h of reaction.

Mohebbi et al. [25] using the catalyst MoO₃/B-ZSM-5 in the esterification of free fatty acids, found that the conversion increased from 91 to 96% with an increase in the reaction time from 4 to 6 h. They also observed that for reaction times greater than 6 h there was no difference in the conversion, as the esterification reaction had already reached the equilibrium.

Mapossa et al. [45] studied the nanomagnetic catalyst Ni_{0.5}Zn_{0.5}Fe₂O₄ in the transesterification of soybean oil, in the range of 1 to 4 h. It was observed that increasing the reaction time from 1 to 3 h, the biodiesel yield increased reaching 92.1%. However, from 3 to 4 h, the biodiesel yield decreased to 87.0%. The authors attributed this decrease to the reversibility of the reaction as well as to parallel reactions, such as soap production, which contribute to reduced biodiesel yield.

Chemical composition of FAME

The produced biodiesel composition is given in Table 4. C_{FAMEi} wt% was calculated from Eq. (3) and the chromatograms shown in Fig. 8. The most commonly found fatty

Table 4 Concentrations of FAME_i in the biodiesel

Biodiesel sample	C _{FAMEi} (wt.%)					
	[C16:0]	C[18:0]	[C18:1]	[C18:2]	[C18:3]	Others
1	10.31	2.27	20.69	49.55	5.93	11.25
2	11.03	2.43	22.13	52.99	6.33	5.08
3	10.99	2.66	22.97	53.27	6.12	3.98
4	13.04	2.89	22.20	52.63	6.19	3.05
5	11.48	2.55	23.41	55.50	6.53	0.52
6	11.22	2.49	22.87	54.22	6.38	2.81
7	9.23	2.51	23.06	54.65	6.43	4.12

Fig. 8 Biodiesel samples chromatograms (Acronym: C16:0—methyl palmitate; C17:0—methyl heptadecanoate (internal standard); C18:0—methyl stearate; C18:1—methyl oleate; C18:2—methyl linoleate; C18:3—methyl linolenate)

acids in biodiesel samples are: oleic (C18:1) followed by stearic (C18:0), linoleic (C18:2), palmitic (C16:0) and linolenic (C18:3) [46]. In all samples of biodiesel obtained, the

predominant fatty acids were: polyunsaturated fatty acids, linoleic (C18:2; 49–54%) and linolenic (C18:3; 5–7%); unsaturated fatty acids, oleic acid (C18:1; 20–23%) and saturated fatty acids, palmitic acid (C16:0; 9–13%) and stearic (C18:0; 2–3%). Soybean oil for biodiesel production has the following typical composition [47]: oleic (20–30%), linoleic (50–60%), palmitic (6–10%), stearic (2–5%) and linolenic (5–11%). Thus, the biodiesel produced in this work 'has a typical composition of biodiesel from soybean reported in the literature.

Density and acidity index

The acidity index and density are important properties for characterization of methyl or ethyl esters [47, 48]. The biodiesel should have a density between 850 and 900 kg m⁻³ and an acid number below 0.50 mg KOH g⁻¹. The density of each biodiesel obtained (Table 3) is within the standards established. Density values above the upper limit leads to the formation of a rich air/fuel mixture, increasing the emission of pollutants, while values below the lower limit cause loss of engine power as well as increase in fuel consumption [49]. Lôbo et al. [50] stated that the density of biodiesel is directly related to the structure of its molecules. The longer the length of the alkylester's carbon chain the greater the density. In relation to the acidity index, all results were outside the standard legal limits, which may be due to the leaching of MoO₃ into the reaction medium, as this molecule has high acidity. Then, an acidity controlling unit may be designed as part of the process.

Statistical analysis of the data

The effect of reaction time (A) and MoO₃ content (B) on FAME yield were obtained with a significance level of 5% ($\alpha=0.05$) using the Minitab 17.0® software for statistical analysis. Table 5 shows the results of Analysis of Variance (ANOVA).

The F value calculated for factor B is greater than the tabulated value, therefore, the MoO₃ content significantly

Table 5 ANOVA for the experimental planning 2² + 3 CtPt

Source	Degree of freedom	Sum of squares	Mean square	P-value	F-value	Tabulated F-value	Remarks
A	1	22.90	22.90	0.07	10.10	18.51	Insignificant
B	1	109.10	109.10	0.02	48.11	18.51	Significant
A × B	1	13.95	13.950	0.13	6.15	18.51	Insignificant
Curvature	1	75.30	75.298	0.03	33.21	18.51	Significant
Error	2	4.53	4.53	—	—	—	—
Total	6	225.78	—	—	—	—	—
$R^2 = 97.99\%$		$R = 99.00\%$					

influences the FAME yield. The values of F calculated for factor A and interaction factor $A \times B$ are smaller than the tabulated ones, therefore, they are not significant. The curvature is significant, since the calculated F value is greater than the tabulated F value, thus indicating that a quadratic model should further be used to optimize the independent variable values. The Pareto diagram depicted in Fig. 9 shows the significance of the factors with respect to the standardized effect.

As shown in Table 5, the coefficient of determination (R^2) was 97.99%, which represents the percentage of data that the model can explain. The correlation coefficient (R) was 99.00%, which indicates a strong correlation between the data.

The response surface and isocurves of FAME yield as a function of reaction time and MoO_3 content are shown in Fig. 10. It can be seen a maximum FAME yield in a region close to the central point, as well as that the minimum FAME yield occurs for the lowest MoO_3 content and the shortest reaction time.

The response surface shown in Fig. 10 corresponds to the model given in Eq. (4).

$$Y = 60.78 + 6.13A + 2.165B - 0.374A \times B + 6.63\text{CtPt} \quad (4)$$

where Y is the FAME yield.

Equation (5) is the response surface keeping every terms in the model. However, it has been seen from ANOVA in Table 5 that factor A and interaction factor $A \times B$ are not significant on the FAME yield. Thus, disregarding the non-significant terms, and readjusting the model without them, results in Eq. (4), with the coefficients of the coded model.

$$Y = 89.613 + 5.223B + 6.63\text{CtPt} \quad (5)$$

As the curvature test was significant while the interaction term $A \times B$ was not, it is not possible to conclude about the significance of the second order term included in the model given in Eq. (4). In this case, the factorial design must be extended to an experimental planning 3^2 , with the inclusion of new experimental points, and thus adjust the model given by Eq. (1), keeping all second order terms. Central composite planning is usually used to extend factorial planning. Star planning is an example of central planning based on two initial factors. In this work, only experimental planning 2^2 was carried out with the addition of 1 central point with two repetitions. The addition of axial points would imply the production of new catalysts, which was not possible for now due to the costs involved.

Reusability of the catalyst

To verify the presence of the active phase of molybdenum in the used catalyst, XRDs were carried out after the first cycle of use. Figure 11 shows the X-ray diffractograms of the $x\text{-MoO}_3/\text{Al-SBA-15}$ catalysts ($x = 5, 10$ and 15 wt%) after transesterification reaction. For $10\text{-MoO}_3/\text{Al-SBA-15}$ catalyst (Fig. 11b), it was observed that after the first use in the reaction, there was a reduction in the characteristic peaks of the MoO_3 phase. The other catalysts have the same profile as the diffractogram shown in Fig. 4. The catalytic activity was studied over five cycles of catalyst use to assess its lifetime. The FAME yield obtained for each reuse cycle of the catalyst is shown in Fig. 12. It was observed in Fig. 12 that the reused catalyst reduced its activity after five consecutive reaction cycles and the yield decreased by about 34%. Malhotra et al. [16] and Thitsartarn et al. [51] have reported that leaching of active species is a problem frequently encountered in heterogeneous catalysts.

Conclusion

The catalytic precursor Al-SBA-15 was obtained and verified from X-ray diffractograms. The catalyst $x\text{-MoO}_3/\text{Al-SBA-15}$ was obtained by incorporating MoO_3 in Al-SBA-15. Characteristic peaks of MoO_3 were identified for catalysts with 10 and 15 wt% MoO_3 contents. Thermogravimetric analysis for the catalytic precursor Al-SBA-15, as well as for salts decomposition and MoO_3 formation indicates that the calcination temperature must be up to 550°C . The adsorption/desorption isotherms of N_2 show a uniform cylindrical pore structure and unimodal pore size distribution. The density of all oils obtained from the transesterification reaction met the requirements for biodiesel, however, the acidity index of none of the oils obtained was within the alloyed limits, probably due to the leaching of MoO_3 in the oil. MoO_3 content in the catalyst influences the biodiesel yield with a significance level of $\alpha = 0.05$, based on the F test and Pareto graph. After the 5ht cycle of use, the biodiesel yield is diminished from ~ 96 to $\sim 62\%$ using the catalyst $10\text{-MoO}_3/\text{Al-SBA-15}$. That catalyst is the recommended to be used in the transesterification of soybean for biodiesel production in a competitive way with currently existing heterogeneous catalysts.

Fig. 9 Pareto chart of the standardized effects ($\alpha=0.05$)

(a)

(b)

Fig. 10 Effect of reaction time and % MoO_3 on FAME yield: **a** 3D response surface and; **b** corresponding 2D Contour plot

Fig. 11 XRD pattern of the **a** $5\text{MoO}_3/\text{Al-SBA-15}$, **b** $10\text{MoO}_3/\text{Al-SBA-15}$ **c** $15\text{MoO}_3/\text{Al-SBA-15}$ catalysts after transesterification reaction

Fig. 12 Reusability of $10\text{MoO}_3/\text{Al-SBA-15}$ catalyst (reaction conditions: $\text{MeOH}:\text{oil}$ molar ratio = 20:1, 3 wt% catalyst, 150°C , 3 h/cycle)

Acknowledgements This research was supported by the Department of Chemical Engineering—Federal University of Campina Grande. The scholarship was awarded by Coordination for the Improvement of Higher Level Education a Personnel (CAPES).

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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