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Article

Simple Niobium Catalysts Applied in Reflux and Ultrasound-Assisted Systems for Biofuel Synthesis

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Using niobium compounds as heterogeneous catalysts in biodiesel production is a promising methodology from economic and environmental viewpoints. However, the application of niobium catalysts still is a challenge due to the high temperatures and pressures for moderate biofuel yields. Therefore, easily handled and applied materials have been developed to optimize biofuel production, which is the goal of this study. Nb_2O_5 and ammonium niobium oxalate (AmNO) were activated in reflux and ultrasound-assisted system. Nb_2O_5 showed better activity under reflux, using methanol. The characterizations conclude that the Lewis-acid sites are determinant for higher conversion rather than surface area. AmNO has better activity also in the reflux system at 70 °C, against 170 °C for Nb_2O_5, reaching above 70% conversion. In addition, reactions in ultrasound-assisted systems are also appealing due to the lower time and temperature, with conversion rates above 40%. Both catalysts showed interesting results under milder conditions than those in the literature.

Keywords: ammonium niobium oxalate, niobium pentoxide, biodiesel, heterogeneous catalysis

Introduction

Biodiesel is a biodegradable and clean-burning fuel that is considered a viable alternative to current petroleum-derived diesel.[1,2] Commercial biodiesel is synthesized via liquid base-catalyzed transesterification of C_{14}-C_{20} triacylglyceride components of lipids with C_1-C_2 alcohols, into fatty acid methyl esters (FAMEs), combined with glycerol as a potentially valuable by-product.[1] Biodiesel production via transesterification requires a catalyst (homogeneous or heterogeneous) to obtain equilibrium in a practical manner.[3] Acid-based homogeneous catalysts, such as H_2SO_4 and HCl operate at high temperature, are difficult to recycle, corrosive in nature and take more time during biodiesel synthesis. Although alkaline-based catalysts such as KOH and NaOH are faster, they react with free fatty acids to form undesirable products (soap), in turn increasing pH of FAMEs and thus requiring expensive separation.[4]

Heterogeneous catalysts can lower the cost of production and make it sustainable. This is because when the catalyst is not in the same phase as reactants/products, product separation and catalyst recovery are quite easy. The development of solid base catalysts has been widely described in the literature.[3-6] However, the physical and structural properties of the catalyst need to be adequately formulated during catalyst preparation to obtain good results.[7] Several studies have proved the technical feasibility and the environmental and economic benefits of biodiesel production via heterogeneous acid-catalyzed transesterification.[3,8,9]

The niobium oxides and their compounds have a large variety of roles in catalysis, such as promoter, support, redox and acid properties.[10,11] Thus, niobium-containing materials have been proposed as effective catalysts in the dehydration of alcohols, oxidation, hydrolysis, alkylation, esterification, photocatalysis and isomerization.[12-21] Ammonium niobium oxalate (AmNO, $NH_4[NbO(C_2O_4)_2(H_2O)_x]\cdot nH_2O$) is used as a niobium precursor in the preparation of functionalized materials, including ceramics, optical lenses, high purity

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niobium oxides, tin films and catalysts. Compared with $NbCl_5$, this niobium salt is cheap, easy to handle and not sensitive to air or moisture.[12,13] Its relatively low toxicity allied to its solubility in water was used by Mendes *et al.*[12] to develop the synthesis of bis(indolyl)methanes using water or glycerol as solvent, obtaining excellent yields with easy reuse of the catalyst.

Aranda *et al.*[22] evaluated the influence of alcohol/fatty acid molar ratio (methanol or ethanol), water and catalyst concentrations, and temperature in the esterification of palm oil fatty acids using different catalysts, including various granularities of niobium(V) oxide (Nb_2O_5). Guinhos *et al.*[23] found that Nb_2O_5/H_3PO_4 and Nb_2O_5/H_2SO_4 as catalysts for the esterification showed better conversion (57%) than $Nb_2O_5.xH_2O$ and Nb_2O_5 (32-36%), using 10 g of soybean fatty acids, 4 g of MeOH, 1 h, 160 °C.

Besides the catalyst choice, the analysis of different reactor configurations and their mixture methods are important tasks. The immiscibility of the reactants is a concern in biodiesel production and intense agitations are necessary to minimize mass-transfer limitations.[24] Ultrasound-assisted synthesis is a green, rapid, economic, environmentally friendly and safe technique employed to accelerate chemical processes.[25] The chemical and physical effects of ultrasound on the transesterification reaction are explained by the radicals that are produced during the collapse of the bubble; that phenomenon induces and accelerates the chemical reaction in the bulk medium. In addition, the microturbulence generated due to radial motion of bubbles creates an intimate mixing of the immiscible reactants, increasing the interfacial area between the reactants and giving faster reaction kinetics.[26] As a consequence, the increase in reaction kinetics produces a high yield at low alcohol to oil molar ratios and reduction in reaction temperature and time.[25-27] The application of ultrasound in homogeneously catalyzed biodiesel production processes has been widely investigated[26-29] and also the effects of ultrasound when solid catalysts are used.[24,30-32]

Some published works use niobium compounds as catalysts to produce biodiesel,[23,33-36] but none of them under ultrasound-assisted reaction conditions; for this reason, the objective of this research was to test different oil sources and niobium(V) oxide and AmNO as catalysts for biodiesel production with reflux and ultrasound-assisted reaction.

Experimental

Niobium pentoxide reactions

The niobium pentoxide catalyst ($Nb_2O_5.xH_2O$) HY-340, donated by Companhia Brasileira de Metalurgia e Mineração (CBMM), was calcined in a mufla Microprocessed-Q318M for 3 h in a ceramic crucible, under normal atmosphere. Calcination temperatures were 115 and 300 °C. The catalyst was used immediately after calcination. The transesterification reactions were performed in a round-bottom flask containing 1.5 g of methanol or ethanol (> 99%), 0.5 g of vegetable oil (peanut, sunflower, canola, corn and soybean). The catalyst in ratio of 20 or 100% of the oil mass and also a polar aprotic solvent (dimethyl sulfoxide, DMSO), mass ratios were previously studied by dos Santos *et al.*[37] applying niobium pentoxide in esterification reactions of oleic acid with methanol. For the reflux system, the temperature of 170 °C was maintained for 48 h under constant stirring at 400 rpm. All solvents were properly distilled.

For the ultrasonic-assisted system, a frequency of 42 kHz and a water bath temperature at 60 °C (CRISTOFOLI) was used. Thermal treatment of 115 °C in the catalyst and the same mass proportions of oil and methanol were used with reaction times of 2, 4 and 6 h.

Ammonium niobium oxalate reactions

The transesterification reactions were made under reflux using AmNO catalyst (also donated by CBMM). However, previous thermogravimetric analysis indicated that temperatures above 70 °C must be avoided, which is going to be discussed in the results. Thus, the catalyst was used without any thermal treatment. First, a test under reflux was performed for 2 h and after a positive result, other reactions were performed for 4, 24 and 48 h, under constant stirring at 400 rpm, with mass proportions of the catalyst of 20 and 100%.

Ultrasound-assisted reactions using AmNO as catalyst, ethanol or methanol, and soybean, canola, or linseed oils were carried out under the same mass proportions of catalyst applied in the reflux reactions. The reaction conditions and solvent were the same as those used for $Nb_2O_5.nH_2O$.

^{1}H NMR analysis

All obtained products were isolated using the multiple extraction method with distilled water and hexane and further analysis by thin layer chromatography (TLC). Blank experiments were performed for all tests using AmNO and $Nb_2O_5.nH_2O$ as catalysts. After total solvent degassing, the product was prepared for ^{1}H nuclear magnetic resonance (NMR) analysis to determine the conversions of vegetable oils into biofuel. The equipment was a Varian 300 MHz and

5 mm broadband ¹H/X/D probe. The solvent used for all analyses was $CDCl_3$. The chemical shifts (δ) were plotted in parts *per* million (ppm) relative to the internal standard, 1% TMS (tetramethylsilane).

The biodiesel conversion was obtained adapting the method reported by Gelbard *et al*.[38] Thus, expressions relating the area of integration of double-doublet signals (dd) of the triacylglyceride of the vegetable oil with δ at approximately 4.2 ppm (Ao) to the singlet (s) at 3.6 ppm and a quadruplet (q) at about 3.75 ppm for the CH_2 of the biofuel (Ab) were observed, as shown in Figures S1 and S2 (in the Supplementary Information (SI) section). Some examples are available in the SI section. From this, the expressions for methyl biodiesel production (1) and for ethyl biodiesel production (2) are:

$$\text{Conversion ME } (\%) = \frac{3 \times \text{Ab}}{(3 \times \text{Ab}) + (2 \times \text{Ao})} \times 100 \quad (1)$$

$$\text{Conversion EE } (\%) = \frac{\text{Ab}}{\text{Ab} + \text{Ao}} \times 100 \quad (2)$$

Thermogravimetry analysis (TGA)

To obtain the mass loss data on heating, TGA equipment from TA Instruments model SDTQ600 was used. The compounds were weighed in an alumina crucible and subjected to a heating rate of 10 °C min^{-1} from 25 up to 800 °C, in an air atmosphere.

Infrared analysis

Infrared (IR) analyses were used to obtain vibrational information of the catalyst's chemical bonds. An ABB FTIR spectrophotometer model FTLA2000 was used for the acquisition, using the PIKE FTLA MIRacle™ accessory, an ATR (attenuated total reflection) accessory.

A study for the acid sites' characterization was performed for all catalysts by the chemisorption of pyridine. First, niobium pentoxide was purged with argon several times for surface cleaning. Then, the cleaned pre-catalyst was calcined at 115 and 300 °C. Pyridine was adsorbed on a known mass of the catalyst (20 mg) by contact with a dilute solution in $CHCl_3$ and successive degassing at beam temperature under vacuum. Further IR analyses were performed in the FTIR spectrophotometer, with the dry catalysts. The obtained data were analyzed and the assigned bands fitted by Lorentz model and then a relative (0 to 1) area comparison was performed.

Brunauer-Emmett-Teller (BET) analysis

Specific area analysis was conducted using the N_2 adsorption/desorption isotherms at 77 K, with a Quantachrome Autosorb-1 instrument. The specific surface area values were determined by the Brunauer-Emmett-Teller (BET) method,[39] using relative pressures (P/P_0) in the range of 0.05-0.31 and the pore size distributions were computed using the nonlocal density functional theory approach.[40]

X-ray diffraction

The X-ray diffraction (XRD) analyses were carried out at room temperature (23 °C) in an X-ray powder diffractometer Shimadzu XRD-6000, with radiation Cu Kα (λ = 1.5418 Å), with diffraction angle (2θ) ranging from 10 to 80° in 1° intervals, voltage of 40 kV voltage and current at 30 mA current. The obtained diffractograms were compared and analyzed using JCPDS (Joint Committee on Powder Diffraction Standards) of the International Center for Diffraction Data, available in PCPDFWIN software, version 2.3.

Results and Discussion

TGA of niobium pentoxide determined the thermal stability of the catalyst and allowed the determination of the number of water molecules *per* mol of Nb_2O_5 (Figure S3 in the SI section). The number of water molecules is directly linked with the behavior of the niobium pentoxide acting as a Lewis acid or as Brønsted-Lowry acid (leading to different catalytic pathways as showed in Scheme S1 in the SI section), as described by Nowak and Ziolek.[41] The use of chemical calculations of catalyst mass losses allowed us to determine the molecular formula of hydrated niobium pentoxide. The obtained molecular formula is $Nb_2O_5.1.8H_2O$.

IR analyses were performed to verify the loss of adsorption and hydration water as a result of increasing the temperature (Figure 1). The analyses confirmed the disappearance of the wide bands with the increase in the temperature at approximately 3200 cm^{-1} referring to the stretching of the O–H bond, and showed that at higher temperatures, the Brønsted-Lowry acid character is less accentuated than the Lewis analogues.

All Nb_2O_5 catalysts showed bands attributed to acid sites by pyridine chemisorption investigation, as presented in Figure 2. There are Lewis-acid sites PyL (LAS) at 1440 cm^{-1}, both LAS-PyL and Brønsted-acid sites PyH$^+$ (BAS) at 1485 cm^{-1} and BAS at 1542 cm^{-1}, but the PyH$^+$ band at BAS was not easy to observe (the possible

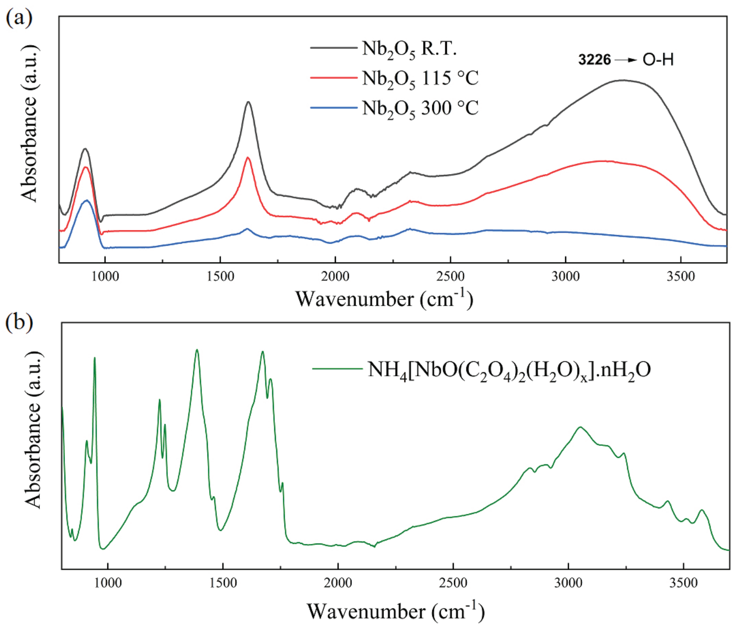

Figure 1. FTIR analysis of (a) niobium pentoxide and (b) ammonium niobium oxalate.

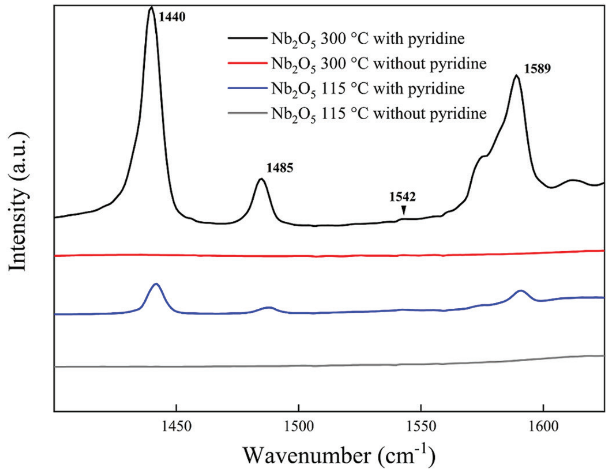

Figure 2. FTIR analysis of pyridine adsorption on $Nb_2O_5.1.8H_2O$ catalyst calcined under different temperatures to determine acid sites.

reason is the long time of heating treatment). Moreover, the integration areas of the LAS and LAS + BAS bands (Table 1) made it possible to confirm that LAS increases as the calcination temperature increases, as expected.[42]

The specific surface areas for all catalysts were obtained from the BET analysis (Table 1). From this, it was observed that when the catalyst is heated to 115 °C, there is an increase in surface area, it may occur due to the loss of adsorbed water (about 8% m/m), as presented in Figure S3 in the SI section. Meanwhile, when heated up to 300 °C, the catalyst has shown a significant decrease in its surface area, probably due to a transition from an amorphous to a crystalline phase.

Moreover, it is possible to observe from the XRD analyses (Figure 3a) that the formation of well-defined peak signals was seen when the niobium pentoxide was calcined for 3 h at 300 °C, corroborating the BET analysis. Furthermore, following the diffraction pattern described in the JCPDS database (number 37-1468), the morphology of our catalyst after thermal treatment at 300 °C is hexagonal. It was discussed by Rade *et al.*[43] that with a heat treatment at 300 °C, the niobium pentoxide still leads to an amorphous solid profile. The probable divergence in observations is that different times in the calcination of $Nb_2O_5.xH_2O$ may affect the phase organization.

The XRD analisis of AmNO showed a well-defined crystalline phase (Figure 3b). The thermal stability of AmNO was obtained from TGA under synthetic air

Table 1. Correlation between $Nb_2O_5.1.8H_2O$ LAS and BAS obtained by pyridine adsorption by FTIR analysis and the surface area obtained by Brunauer-Emmett-Teller (BET) analysis

Calcination temperature / °C	LAS	(LAS/(LAS + BAS))	Specific surface area / (m^2 g^{-1})
–	1.00	1.00	150.30
115 °C	1.40	0.88	220.00
300 °C	9.20	0.93	114.50

LAS: Lewis-acid site; BAS: Brønsted-acid sites.

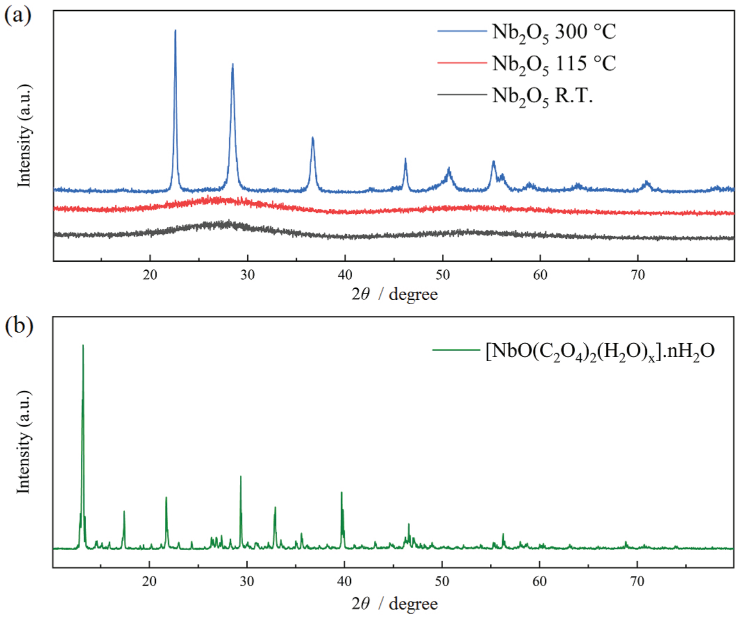

Figure 3. *Ex situ* X-ray diffraction under different heat treatments of (a) niobium pentoxide and (b) ammonium niobium oxalate.

atmosphere. The analysis showed several mass losses and was generally similar to that reported by Medeiros *et al.*[44] Loss of the adsorbed water below 70 °C is observed and this temperature was adopted for the catalyst use to avoid any degradation. From the FTIR spectrum, it was possible to observe characteristic reference bands, such as the presence of stretching assigned to N–H, O–H, C=O and Nb=O bonds, and others as already reported.[45]

Niobium pentoxide as the catalyst

The reactions under reflux (mild conditions) using niobium pentoxide as a catalyst was divided into two groups according to the alcohol, as shown in Figure 4. For all reactions, blank experiments were performed. No conversion rate was observed in the absence of the catalyst.

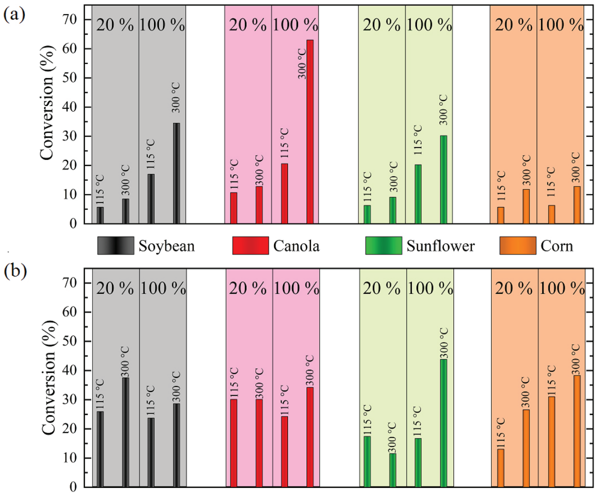

Figure 4. Conversions in (a) methyl and (b) ethyl biodiesel from soybean, canola, sunflower and corn oils using niobium pentoxide as the catalyst in a reflux system.

From the above figure, it is possible to observe differences between all the oils' conversions. Srilatha *et al.*[46] published a study on the influence of the chain length and unsaturation (presented as C_n: number of unsaturation) on fatty acids esterification using methanol and $Nb_2O_5.xH_2O$. They concluded that the reactivity decreases as the chain length and unsaturation number grows. In Figure 4, it is possible to note that the canola oil (about 54% of 18:1 and 22% of 18:2)[47] with methanol, leads to higher conversion compared to soybean (20% of 18:1 and 64% of 18:2), sunflower (17% of 18:1 and 73% of 18:2) and corn (44% of 18:1 and 48% of 18:1). Notably, when ethanol was used, the greater conversion rate was obtained with sunflower oil transesterification. In addition, all oils' conversion rates were about 30-40% in analogous conditions, this may be observed because of a smaller influence of calcination temperature using ethanol. Moreover, from the results with ethanol, it is not possible to observe the same effect of unsaturated fatty acids for the conversion with methanol. The conversion increases with bigger catalyst amounts as expected because of its higher availability in the system.

Our research group has previously tested the use of $Nb_2O_5.xH_2O$ in the esterification of oleic acid (an easier reaction compared with transesterification) reaching conversions near to 82%. From this, it was noted that without calcination and calcined above 300 °C, the reaction was not favored.[37] A similar work in the literature describes the continuous production of biodiesel through the reaction between oleic acid and ethanol, using niobic acid as a solid acid catalyst at 249 °C, obtaining yields of esters up to 70% and conversion up to 90%.[43] The same authors, using a packed bed tubular reactor, achieved 90% conversion with niobium phosphate as catalyst in the reaction using oleic acid and ethanol at 250 °C.[48]

About our results, it is also noted that when the catalyst has its morphology changed by calcination below 300 °C, better conversions were obtained. Moreover, LAS increase seems to be vital for the catalyst activity, and it is easier to improve because of its significant decrease of the surface area (small surface area means fewer active sites available, so lower conversions are expected). From catalyst's problems such as those cited, aiming to obtain better activity, many researchers have tried to improve the catalyst's design.[33-36,49-51] Studies using mixed calcium oxide and niobium oxide (CaO-Nb_2O_5) calcined at various temperatures (to produce biodiesel from palm oil and methanol) obtained conversion rates around 98%.[33] Moreover, conversion near to 89% was reported using the same mixture ratio of catalyst, 1:36 oil of macauba (*Acrocomia aculeata*) to methanol, and at 77 °C as reaction temperature.[34] Silica pellets with a loading of 12% Nb were tested by Tesser *et al.*[35] in esterification and transesterification reaching yields around 90% using soybean oil and methanol at 180 °C. Other mixed catalysts have obtained conversions up to 90% with heating above 225 °C.[36,49] Finally, our catalyst was shown to be easy to prepare and/or apply under milder conditions than those above, compared with other transesterification reactions.

Aiming to reduce the time and energy demand, the use of ultrasound-assisted systems has been studied.[24-28] Results for the ultrasound-assisted system with soybean oil using $Nb_2O_5.1.8H_2O$ are presented in Table 2. Higher conversions were observed for reactions with 4 and 6 h when the catalyst was used with a ratio of 100% mass of soybean oil. However, with 4 h and a 20% mass of catalyst, a conversion of 21.9% was obtained.

Table 2. The use of $Nb_2O_5.1.8H_2O$ under an ultrasound-assisted system with soybean oil, 60 °C, 42 kHz, varying temperature and mass proportion of catalyst/oil

time / h	Mass proportion / %	Conversion / %
2	20	–
	100	16
4	20	–
	100	21.9
6	20	16.7

Other authors reported the beneficial effects of ultrasound on biodiesel synthesis using different oils, catalysts and solvents. Stavarache *et al.*[52] studied the transesterification of vegetable oils with several alcohols using ultrasound of two different frequencies (28 and 40 kHz). They observed a reduction in reaction times (10-40 min), reduction in catalyst concentrations (2-3 times lower), and the quantity of required catalyst was 2 or 3 times lower. However, the frequencies influenced the reaction, higher frequencies (40 kHz) are much more effective in the reduction of the reaction time and lower frequencies (28 kHz) gave better yields (ca. 98%). Malani *et al.*[53] attained yields above 90% under optimized conditions of biodiesel production using a molar ratio of methanol:oil of 12.8:1, with sulfonated catalyst (8.18%, m/m) at 63 °C in a single-step process. Choudhury *et al.*[54] reported yields of 80% of FAME in the optimum experimental conditions, i.e., alcohol to oil molar ratio (ca. 7), catalyst concentration (6% m/m) at 70 °C, and ultrasound frequency of 35 kHz. Other works used an ultrasound system to improve the yield of biodiesel formation, to decrease the reaction time, or only to study the ultrasonic technique in the process of transesterification or esterification of oils.[55-58]

From the obtained results, the study can be extended to different oils using the reaction time of 4 h and varying the alcohol but applying the AmNO catalyst as seen in the next topic.

Ammonium niobium oxalate as the catalyst

In the reflux system, our first behavioral study applying AmNO as the catalyst used three different times: 4, 24 and 48 h. From those different times and varying reaction temperature and mass proportion, the conversions using soybean oil and ethanol were obtained as shown in Figure 5. The direct use of AmNO as the catalyst in transesterification has not been reported so far. Then, from the TGA analysis (Figure S4), the study was focused on reactions from 25 to 75 °C, as presented. The influence of the temperature difference was hardly observed at 4 h. However, at 24 h, the conversion increased to about 90% for both catalyst mass proportions. Surprisingly, the same behavior was observed for the time of 48 h, with an increase of about 85% in both cases. From that, it is possible to imagine a time between 4 and 24 h wherein the influence of temperature possibly remains almost constant. In addition, for all reactions at 24 and 48 h, the conversion increase varying only the mass of catalyst also seems to be constant (about 40%). To conclude, catalyst mass proportions and temperature seem to be fewer influential for conversions than reaction times.

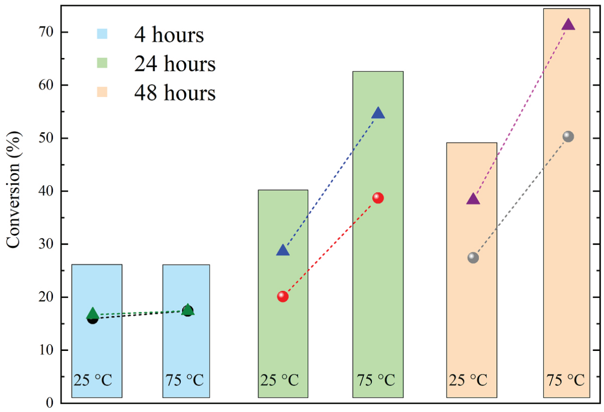

Figure 5. Conversions in ethyl biodiesel from soybean oil using ammonium niobium oxalate as the catalyst in a reflux system, varying the mass ratio (20 and 100%, catalyst/oil, represented by a sphere and triangle, respectively), temperature and reaction time.

This work has a focus on the simple use of niobium catalysts due to the excellent results presented in Figure 6, tests with pure AmNO were carried out for the transesterification of soybean and canola oils, as shown in Figure 6.

As presented before, the expected chemical compositions in canola and soybean oils are different.[47] Indeed, the canola oil showed better results for transesterification with methanol than with soybean oil. However, when ethanol is used instead of methanol, higher conversions are reached. Those results do not agree with the work of Stavarache *et al.*[52] because the use of an oil with a higher amount of unsaturation (soybean) produced the highest conversion for both alcohols, but mainly with ethanol. Many factors may explain this difference: catalyst miscibility in different solvents; activation energy, e.g., at last, the effect of increasing catalyst mass is clear for ethanol-containing reactions. This is demonstrated for soybean and canola oil, in which conversion rates increased 41.2 and 121.2%, respectively. This indicates that, in general, the utilization of pure AmNO in those oils' transesterification is favored with ethanol, oils with higher unsaturation amounts, higher reaction times and bigger catalyst mass as well. Another study using this complex catalyst (but not pure) for biodiesel synthesis was reported by García-Sancho *et al.*[59] They used an MCM-41 silica impregnated with different amounts of niobium oxalate and obtained a yield close to 80% using sunflower oil and methanol at 200 °C.[59] Our catalyst application led to a similar conversion at a lower reaction temperature.

In Table 3, for the ultrasound-assisted system, the catalyst was AmNO varying the alcohols and the mass proportions. It is possible to observe that the best result was using soybean oil, achieving a conversion of 43.2% in the production of ethyl biodiesel. The mass ratio also proved to be determining for all cases except when using methanol and canola oil. There is a 70.1% increase in the

Table 3. Ammonium niobium oxalate under an ultrasound-assisted system with soybean, canola and linseed oils, 60 °C, 42 kHz, 4 h, varying alcohol and mass proportion of catalyst/oil

Vegetable oil	Alcohol	Mass proportion / %	Conversion / %
Soybean	methanol	20	–
		100	8.3
	ethanol	20	25.4
		100	43.2
Canola	methanol	20	–
		100	–
	ethanol	20	–
		100	20.6
Linseed	methanol	20	–
		100	–
	ethanol	20	–
		100	20.6

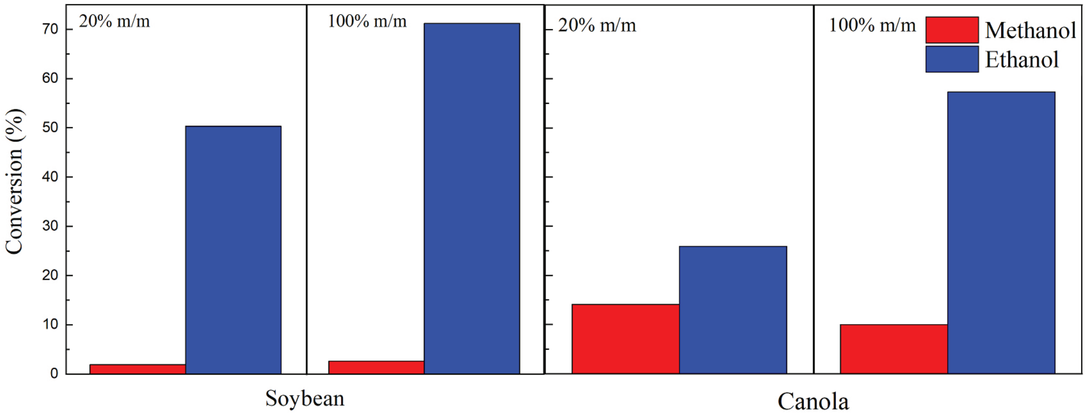

Figure 6. Conversions in biodiesel from soybean and canola oils using ammonium niobium oxalate as a catalyst in reflux system, varying the alcohol and bulk ratio of the catalyst.

conversion of ethylic biodiesel using soybean oil with the increase in mass (%) of catalyst used. The expectation of greater conversions with linseed oil (ca. 54% of 18:3)[46] was not observed. However, the use of an ultrasonic bath for 4 h and at 60 °C was promising for the production of biodiesel due to its easy handling and low energy demand.

Conclusions

$Nb_2O_5.1.8H_2O$ proved to be an easily handled catalyst and with interesting conversions of vegetable oil into biodiesel. For this catalyst, the best results were obtained using a reflux system (for methyl ester synthesis), with the conversion rate increasing as the catalyst LAS and catalyst mass grows. In addition, good results were obtained using AmNO in a reflux system, as well as in the ultrasound-assisted system. For the first use so far with the AmNO catalyst, ethyl esters are favored compared with methyl esters. Finally, both catalysts were efficient on vegetable oils' transesterification under mild conditions, 1 atm, and 170 or 75 °C for reflux system, and 60 °C for an ultrasound-assisted system.

Supplementary Information

Supplementary information (NMR spectra and TGA analyses) is available free of charge at http://jbcs.sbq.org.br as PDF file.

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