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Review

Biodiesel Production over Niobium-Containing Catalysts: A Review

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Abstract: Nowadays, the synthesis of biofuels from renewable raw materials is very popular. Among the various challenges involved in improving these processes, environmentally benign catalysts compatible with an inexpensive feedstock have become more important. Herein, we report the recent advances achieved in the development of Niobium-containing heterogeneous catalysts as well as their use in routes to produce biodiesel. The efficiency of different Niobium catalysts in esterification and transesterification reactions of lipids and oleaginous raw materials was evaluated, considering the effect of main reaction parameters such as temperature, time, catalyst load, and oil:alcohol molar ratio on the biodiesel yield. The catalytic performance of Niobium compounds was discussed considering the characterization data obtained by different techniques, including NH_3-TPD, BET, and Pyr-FT-IR analysis. The high catalytic activity is attributed to its inherent properties, such as the active sites distribution over a high specific surface area, strength of acidity, nature, amount of acidic sites, and inherent mesoporosity. On top of this, recycling experiments have proven that most Niobium catalysts are stable and can be repeatedly used with consistent catalytic activity.

Keywords: Niobium catalysts; biodiesel; heterogeneous catalysts

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1. Introduction

Biodiesel: Main Catalysts

The inevitable depletion of fossil fuels and the environmental problems resulting from huge emission of greenhouse gases generated in their burning have motivated the search for energy sources that are renewable and of low cost [1,2].

In this sense, the conversion of biomass resources to biofuels has risen as a potential alternative to reduce the dependence on petrol derivatives [3,4]. Among the biofuels economically viable, biodiesel has received greater attention because it can be blended into diesel without compromising its efficiency [5]. Among the several advantages of biodiesel is the possibility to use it blended with petroleum diesel. There are some types of biodiesels, such as B20 and B100, where the letter B means the percentage of biodiesel. For example, the B20 is a mixture of 20% of biodiesel and 80% of mineral diesel, in volume percent. The B100 is a pure form of biodiesel, and its applicability requires some modifications in the equipment that uses this fuel [6]. Although not viable economically as pure fuel, the use of biodiesel blended with diesel significantly reduces the dependence on petroleum, as well as the emission of greenhouses gases and particulate material. Figure 1 exposes the advantages of biodiesel B100 in relation to biodiesel B20 regarding the emission of pollutants. It is shown to reduce the emission of different harmful compounds [7]. Biodiesel can be produced through alkaline or acidic transesterification of vegetal oils or animal fats with short-chain alcohols (i.e., methyl or ethyl alcohol), generating fatty acid alkyl esters [8,9].

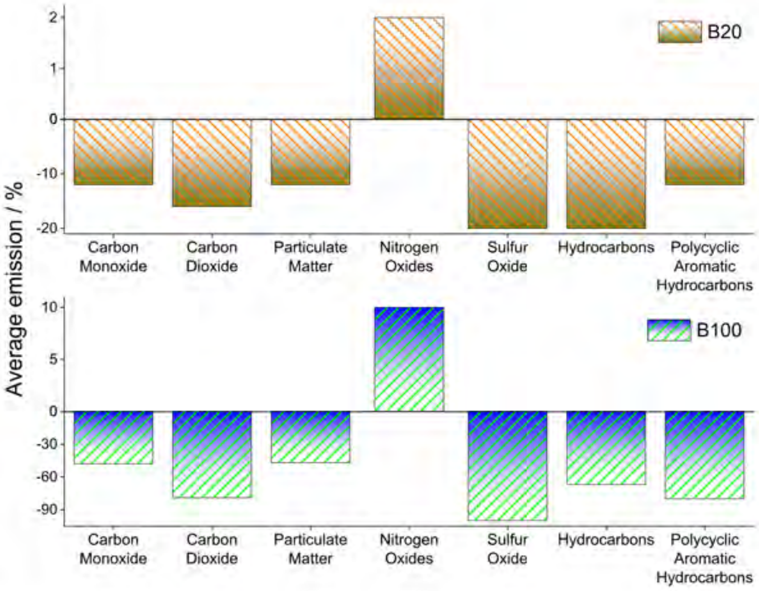


Figure 1. Pollutants average emission by the B-20 and B-100 (adapted from [7]).

Besides possessing a high flash point, high cetane number, and good lubricity, biodiesel has a closed carbon cycle, a great benefit that can minimize the impacts of CO_2 emission on the global atmosphere, as illustrated in Figures 1 and 2 [10,11].

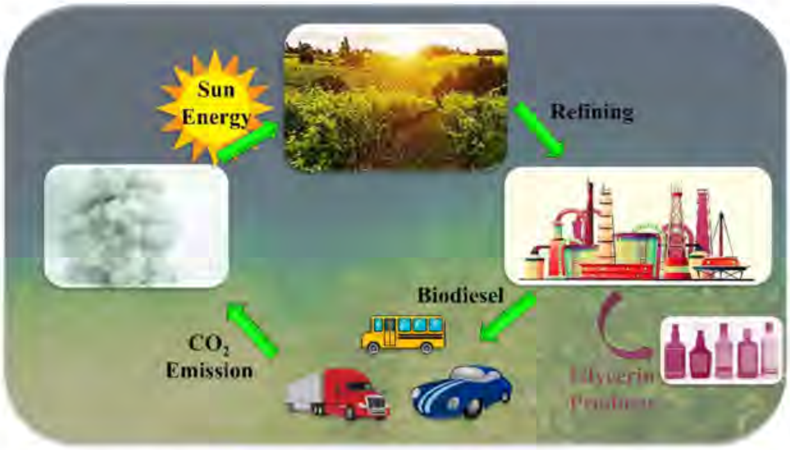


Figure 2. Closed carbon cycle for Biodiesel (adapted from [12]).

A great challenge of biodiesel production is reducing the impact of feedstock cost on its final price. Therefore, this choice becomes a crucial step to produce biodiesel at competitive prices. Figure 3 presents the percentage of costs partitioned for the process of obtaining biodiesel, highlighting that the oil feedstock is responsible for more than 70% of the costs for the production of this biofuel [13].

Vegetable oils, such as canola, palm, rapeseed, and sunflower, nonedible oils, and lipidic residues of the food industry are the desirable raw material [14,15]. To reduce production costs and minimize the concurrence with the food industry, the use of non-edible and waste cooking oils as feedstock to produce biodiesel has significantly increased and has become a good alternative to manufacture biodiesel at more competitive prices. Nonetheless, the high content of free fatty acids (FFA) present in these raw materials has motivated the search for more active and water-tolerant catalysts [16–19].

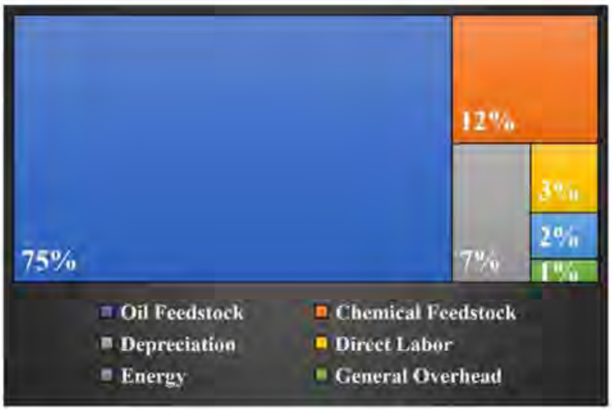


Figure 3. Percentual of the main contributions to biodiesel production cost (adapted from [13]).

The industrial production of biodiesel has been carried out in the presence of inexpensive homogeneous alkaline catalysts such as sodium or potassium hydroxides or their alkoxides. However, there are various drawbacks linked to the use of homogeneous catalysts, such as the impossibility of recovery and reuse, the large generation of effluents and residues in the steps of neutralization and products purification, the corrosion of the reactors, and the low tolerance to acidic raw material, which lead to saponification problems and difficulty to separate glycerol, an inevitable co-product [11,20,21]. Due to problems like these, the presence of water, and a high concentration of FFA in low quality oils, the use of alkaline and homogeneous catalysts becomes unfeasible. Alkaline catalysts react with FFA leading to the formation of soap. The formation of these compounds directly affects the production of methyl ester and difficult the separation of glycerol. Then, alkaline catalysts should be used only in transesterification of oils with amount lower than 0.5% of FFAs [16,21]. Although Lewis acid catalysts may be an option, they are water intolerant. Based on this, many heterogeneous catalysts composed of Nb have been developed with remarkable acidic and water tolerant characteristics [22].

Figure 4 present the scientific articles published in journals related to biodiesel production by catalytic processes from the year 2000 to now with the terms "biodiesel production" and "catalyst" in the titles of the articles.

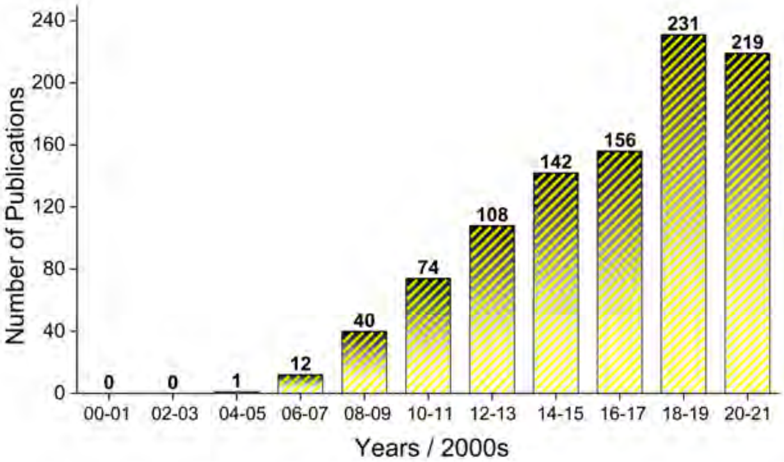
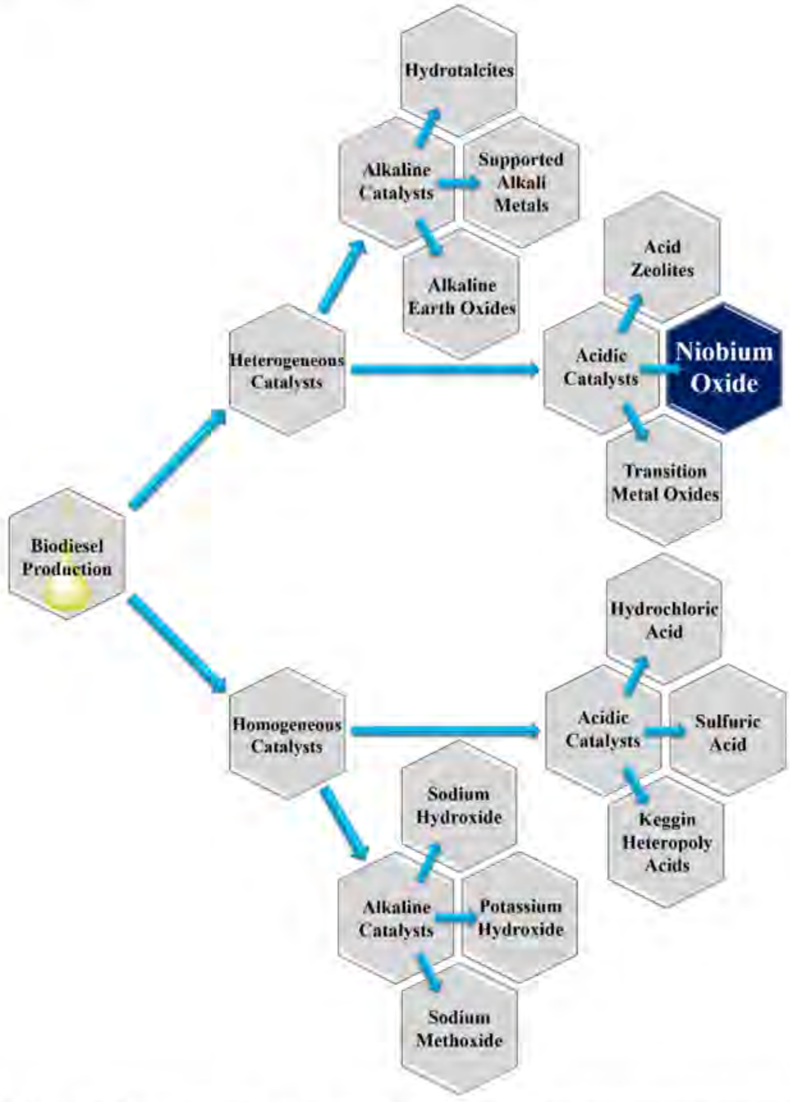


Figure 4. Number of researches related to the catalytic processes for biodiesel production since 2000. The search was made on 18 June 2021, over the database Scopus and were found a total of 983 articles for this period.

Heterogenous acidic catalysts have demonstrated to be a nice alternative to improve biodiesel production processes. Solid acidic catalysts are compatible with raw material that contain a high amount of FFAs, avoiding steps of pre-esterification, and increases the scope of feedstock that may be used to produce biodiesel, such as wasting cook oil and animal fats. Due to the possibility of reuse, the lower generation of residues and effluents and various heterogenous catalysts have been used in several processes in large scale, composing more than 80% of these industrial catalytic processes [23].

Several Niobium precursors are available, inexpensive, and very versatile, which can be used to synthesize plenty of solid catalysts with different properties, through several different routes of synthesis, such as the Pechini method, sol-gel, hydrothermal synthesis, grafting, precipitation, coprecipitation, and electrospinning. Besides the high activity, the great advantage of use of Niobium catalysts is the possibility of easy recovery and reuse. This contributes to reducing the waste generation and the cost of the process, being the industrial procedure more economically and environmentally viable [24,25]. Also, Niobium compounds are a typical example of solid acidic catalysts that have been demonstrated to be active in esterification and transesterification reactions to produce biodiesel [21,26–28].

The production of biodiesel can be performed through esterification reactions of FFAs and transesterification of triglycerides, performed in conditions of homogeneous or heterogeneous catalysis. Within these two great classes of reactions, the catalysts can be subdivided in acidic and alkaline catalysts. Scheme 1 summarizes the most common catalysts, where Niobium oxide is highlighted due to its application in biodiesel production [29–33].



Scheme 1. Summary of some common catalysts for biodiesel production [29,30].

Nb-containing compounds are used in many different areas beyond catalysis and materials science. Figure 5 shows the number of publications of articles in scientific journals containing in the titles the words “Niobium”, or “Nb”, and “catalyst”. The search was made over the database Scopus and were found a total of 511 articles for the period between the years 2000 and 2021.

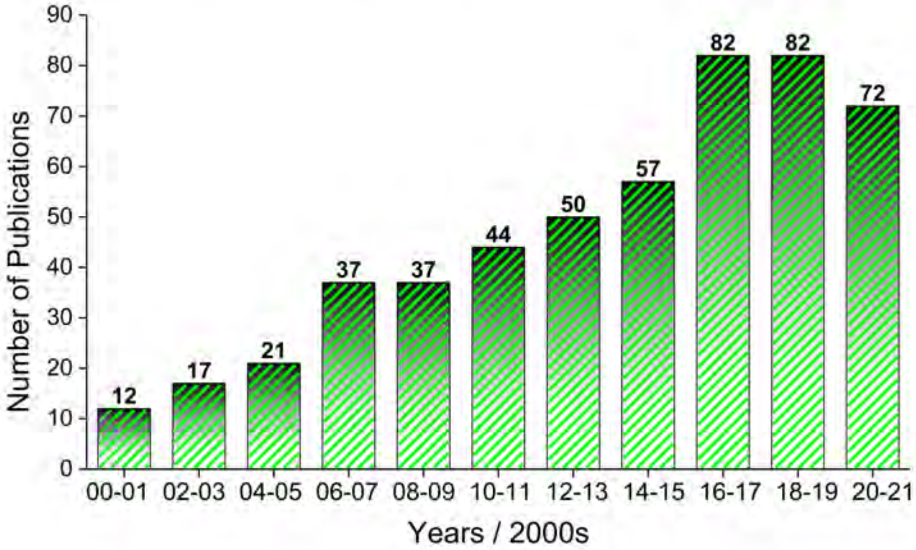


Figure 5. Number of publications related to catalytic processes involving Niobium catalysts since 2000.

It is possible to note the growing trend in the use of Niobium catalysts, which may be attributed to its versatility and specific properties that make him an active catalyst in various processes. Among the intrinsic properties of Niobium compounds, its Lewis and Brønsted acidity strength, and its structural properties allow that it could be potentially used as a heterogeneous catalyst in esterification and transesterification reactions for biodiesel manufacture. The application of Nb-containing compounds in biodiesel production routes still needs extensive research, since they have already presented a huge potential to convert triglycerides and FFAs. Brønsted and Lewis acidic sites, good thermal stability, versatility, and easy recovery and reuse are inherent properties of Niobium catalysts.

In Figure 6 a comparison between the results of esterification of oleic and stearic acids over different catalyst species is presented. The conversion achieved in reactions over catalysts with distinct acidity characteristics is shown. Niobium phosphate, Niobium oxide, sulfated Niobium oxide, aminophosphonic acid resin, organophosphoric acid with NaY molecular sieves, Zeolite Y with a Si/Al ratio 3:1 prepared using Iraqi kaolin, and sulfated titania prepared by impregnation method were described in the references cited herein, respectively [9,34–39].

The conversion results showed that all the solid acids have a great potential to be used in the esterification of saturated and unsaturated fatty acids (i.e., stearic, and oleic acids, respectively). However, the use of affordable commercially available Niobium catalysts (i.e., phosphate and oxide) avoids laborious synthesis and the problems of leaching of solid-supported or sulfated catalysts.

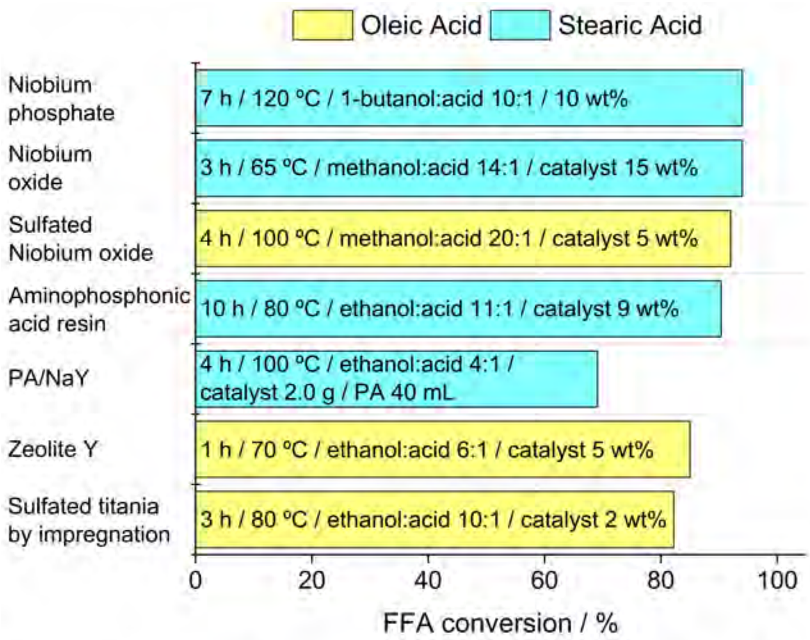


Figure 6. Comparison of conversions achieved in oleic and stearic esterification reactions over different catalysts acid solid (adapted from [9,34–39]).

2. Niobium Catalysts

2.1. Economic and Sustainability Evaluation by Using the Niobium-Containing Catalysts

The biodiesel production over solid acid catalysts has recognized advantages such as the easy recovery and reuse of catalyst, the lower corrosion and the generation of residues, and effluents in steps of the product's purification [40]. Contrary to other solid acids, Niobium catalysts display high catalytic activity and stability in the presence of water. This water-tolerance has been attributed to the Lewis acid sites, which are coordinatively unsaturated Nb^{5+} cations in NbO_4 tetrahedral units, where NbO_4-H_2O active adducts are formed that effectively preserve their positive charge [41].

Nonetheless, the cost and feasibility of the catalysts are key aspects to be considered. Niobium-based catalysts such as Niobic acid/hydrated Niobium pentoxide (i.e., Nb_2O_5 $n{\cdot}H_2O$), Niobium chloride (i.e., $NbCl_5$), and Niobium phosphate (i.e., $NbOPO_4$) are commercially available, and produced on a greater industrial scale. Brazil is the world's largest producer of Niobium, responsible for 98% of the active worldwide resources. Brazil exports most of the Niobium and produces it as commodities such as ferroniobium.

2.2. Characteristic of the Niobium Compounds

The versatility of the Niobium is corroborated by its application in a plethora of purposes. Nowadays, a remarkable growth in the various research fields and industrial sectors has been noticed. For instance, it has been used in the manufacture of metal alloys for the aerospace industry, electrical–electronic devices, medical equipment, dental implants, and mainly as catalytic materials either as an active phase or support [32,42].

The sources possible to plow of Nb are mostly located in Brazil with over 16 million tons of its ore, in 2016, which is the country with the largest world production, representing more than 90% of the world total [43].

Niobium is a transition metal belonging to group five of atomic number 41 and electron configuration [Kr] $4d^4$ $5s^1$. Its appearance is metallic gray and is resistant to many acids and high temperatures, with melting and boiling points of approximately 2477 and 4744 °C, respectively. Besides that, Niobium has a high value in metallurgical and chemical industries due to its corrosion resistance and high electrical conductivity. It is a metal that crystallizes in a unit cell of type body-centered cubic (bcc), as shown in Figure 7 [32,44].

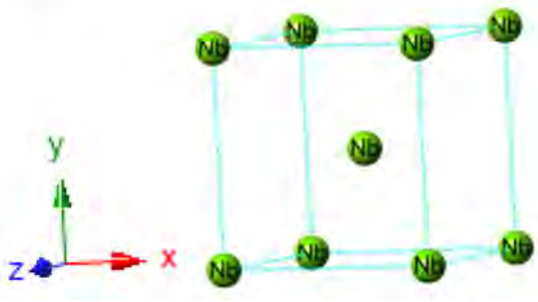


Figure 7. Crystalline structure (bbc) of the metal Niobium (adapted from [32]).

Niobium can be present in different compounds such as carbide, hydride, and oxides. There are three groups of anhydrous Niobium oxides: NbO, NbO_2, and Nb_2O_5. In Figure 8, we show the unit cells of the cubic NbO and tetragonal NbO_2 compounds [45].

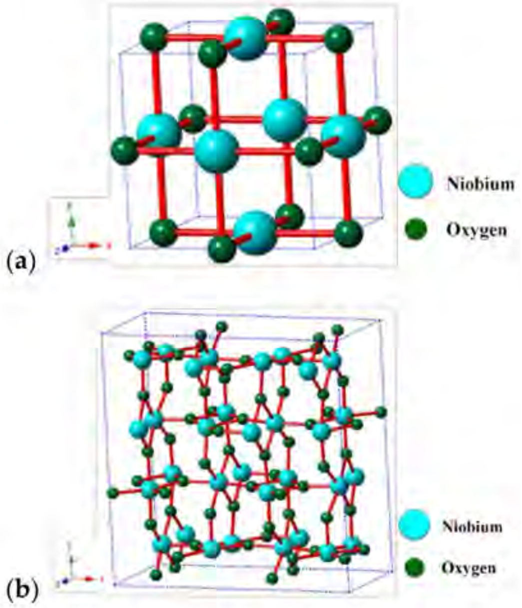


Figure 8. Crystalline structure of the (**a**) NbO and (**b**) NbO_2 unit cells (adapted from [32]).

Niobium pentoxide can occur in different phases and usually presents octahedra structure NbO_6, but due to the polymorphism, other coordination structures can be found, such as NbO_7 and NbO_8, depending on the crystalline phase, which is a consequence of the synthesis route [40]. Due to its polymorphism, Nb_2O_5 can be described in distinct phases: amorphous ($Nb_2O_5 \cdot nH_2O$), pseudo-hexagonal (TT-Nb_2O_5), orthorhombic (T-Nb_2O_5), and monoclinic (H-Nb_2O_5) [46]. The T-Nb_2O_5 and H-Nb_2O_5 phases are widely studied, the latter being the most thermodynamically stable (Figure 9) [32].

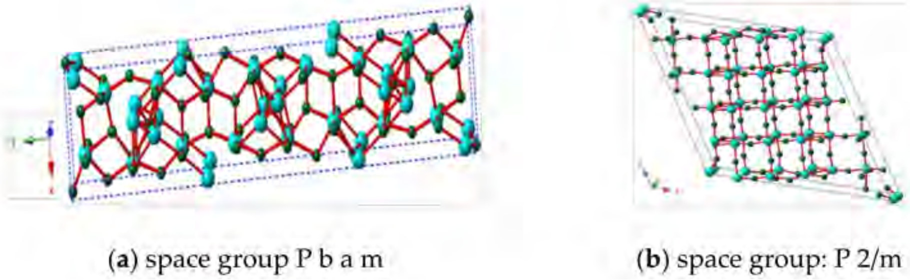
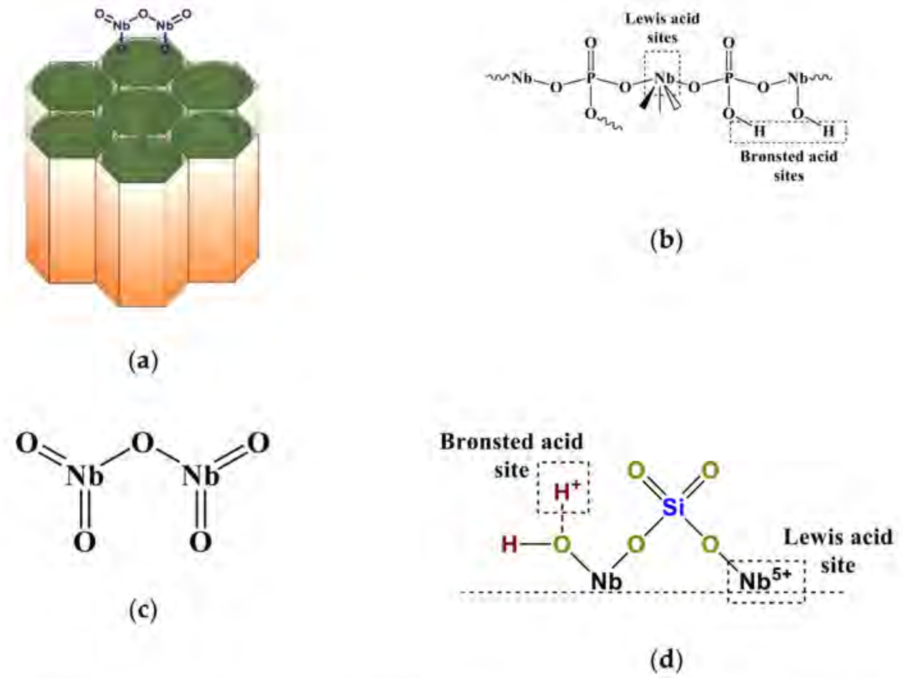

(**a**) space group P b a m (**b**) space group: P 2/m

Figure 9. Nb_2O_5 (**a**) orthorhombic and (**b**) monoclinic structures. Niobium—blue spheres; Oxygen—green spheres (adapted from [32]).

Niobium compounds have been used as solid catalysts due to their remarkable properties, such as high stability, versatility, thermal resistance, and acidity [32,42]. This last feature stands out more for the presence of Brønsted and Lewis acid sites. The Brønsted acid sites can be easily represented by OH^- clusters attached to the solid material surface. The Lewis acid sites are related to metal atoms able to receive electrons pair in their incomplete *d* orbitals. For these reasons, Niobium oxides have been used as a dopant or solid support in acid-catalyzed reactions [47–49].

There is a wide range of methodologies used to synthesize various types of Niobium catalysts. Many researchers apply Niobium pentoxide, phosphate, sulfated Niobium oxide, and different combinations of supported materials involving Niobium in various catalytic processes. As catalytic support, Nb has the function of providing a higher surface area and making the Brønsted and Lewis sites more available [50,51]. Figure 10 illustrates niobium in different solids.



(a) (b) (c) (d)

Figure 10. (**a**) Nb_2O_5 supported on MCM-41; (**b**) Niobium phosphate; (**c**) Niobium oxide; and (**d**) sulfated Niobium oxide (adapted from [4,29,35]).

Solid Niobium catalysts have been used in distinct reactions, such as epoxidation of cyclohexene [52], acetalization of glycerol to solketal [53], ethane oxidative dehydrogenation to ethene [54], furfural production from sugarcane bagasse [55], conversion of carbohydrates to 5-HMF, conversion of furfuryl alcohol and α-angelica lactone [56], and hydrogenation of CO_2 to light olefins [57]. Moreover, Niobium-containing catalysts have been used to converting biomass to biofuels [58–62].

3. Niobium-Catalyzed Processes of Biofuel Production

As stated earlier, Niobium catalysts are viewed as promising materials that can be used in a wide range of reactions due to Niobium's singular properties. Now, different reactions will be presented where various Nb-containing catalysts were used in the production of biodiesel and/or biofuel additives.

Although alkaline transesterification is faster than acid-catalyzed reactions, metal hydroxides are soluble and not easily reusable, and require neutralization steps and lead to the formation of soap, hampering the ester purification and glycerol removal [30]. On the other hand, even being slower, the acid-catalyzed reactions circumvent these drawbacks [63]. For these reasons, acid catalysts have assumed a significant role in esterification and transesterification reactions. Particularly, the nature of acid sites can be a key aspect to the successful of catalyst. At first, it is necessary that these acid sites are accessible to the substrate molecules. The main role of these acidic sites is to interact with the carbonyl oxygen of the FFA or triglyceride to generate a carbocation. This enables the nucleophilic attack by the alcohol used. Depending on the reaction type, this compound will eliminate H_2O or ROH, according to the substrate applied, leading to desired ester [64]. The esterification and transesterification reactions can briefly be exemplified in some following works.

3.1. Sulfated Niobium Oxide

Several researchers have adopted different methodologies to modify the structural, electronic, or surface properties of Niobium compounds, aiming to obtain efficient catalysts to produce biodiesel with good yield. One of the main goals is to enhance the concentration and distribution of the acidic sites on the Niobium catalyst structure [65].

Sturt et al., (2019) recently reported notable results about a Niobium oxide previously modified with sulfate groups, in which was possible to notice the increase in Brønsted acidity [35]. To compare, three catalysts were used in the esterification of oleic acid (Figure 11): pure Niobium oxide; Niobium oxide after to be calcined to 300 °C (300-Nb_2O_5); and the Niobium oxide after to be calcined and sulfated (300-Nb_2O_5/SO_4^{2-}). It is interesting to note that the sulfated catalyst provided better results in the reaction of esterification of the oleic acid to methyl oleate, reaching more than 90% of conversion. This effect can be assigned to the higher quantity of the Brønsted sites given to the sulfated Niobium catalyst [35]. Different oleic acid:methanol molar ratios and catalyst loads were used in those reactions (Figure 11).

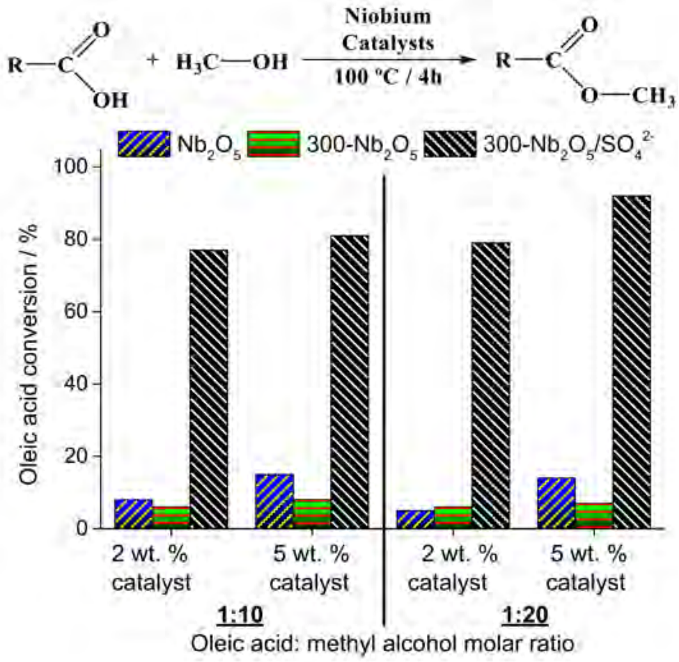
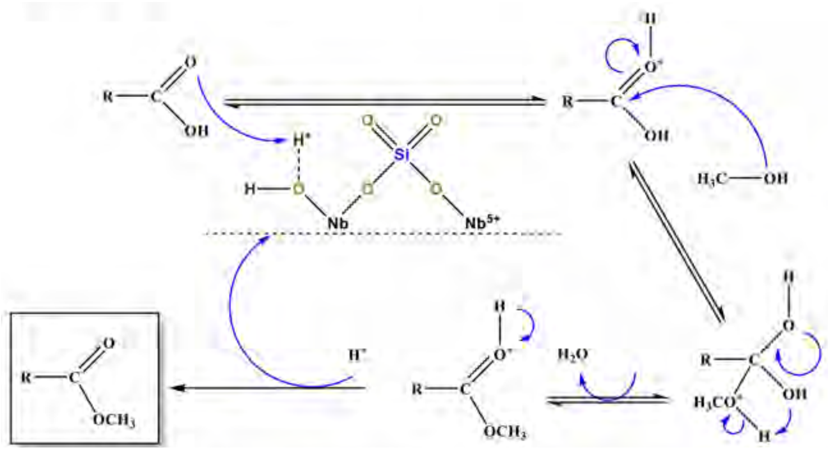
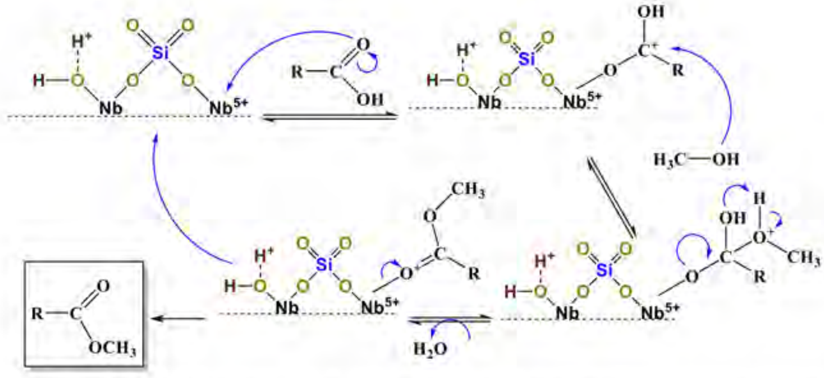


Figure 11. Esterification reaction of oleic acid with methyl alcohol over Niobium catalysts. Reaction conditions: oleic acid: methyl alcohol molar ratio (1:10 and 1:20), catalyst (2 and 5 wt%), temperature (100 °C), time (4 h) (adapted from [35]).

Schemes 2 and 3 show a mechanism proposal to illustrating the behavior of the sulfated Niobium/SiO_2 catalyst, where the authors depicted reaction pathways for Brønsted or Lewis acidic sites, respectively. These sites can act together promoting the esterification process [35].



Scheme 2. Esterification mechanism over sulfated Niobium oxide: action of the Brønsted acid sites (adapted from [35]).



Scheme 3. Esterification mechanism over sulfated niobium oxide over Lewis acid sites (adapted from [35]).

For the mechanism involving the Brønsted acidic sites (Scheme 2), firstly, the H^+ proton in the catalyst is abstracted by the oxygen electron pair from the oleic acid carbonyl. After a rearrangement step of the double bond, the carbonyl carbon is more susceptible to a nucleophilic attack of the electron pair belongs to the hydroxyl group of methyl alcohol. Afterward, the carbonylic double bond is reestablished and water is then eliminated. Afterward, the proton elimination regenerates the catalyst and resulting in the formation of methyl oleate [35].

Conversely, in the other mechanism (Scheme 3), the Niobium catalyst can act as a Lewis acid receiving a pair of electrons from the carbonyl group of the oleic acid. After that, in the same way, a carbocation can be formed and then be more susceptible to a nucleophilic attack from the hydroxyl group of the alcohol. At the end of the process, again, a water molecule is eliminated and the catalyst is reestablished through the ester formation [35].

Conceicao et al., (2016) synthesized sulfated Niobium oxide using a simple method of impregnation [66]. One of the goals was to obtain a promising heterogeneous catalyst with improved acidity to apply in simultaneous esterification and transesterification processes to produce biodiesel from palm oil. Figure 12 shows the data obtained in experiments with different catalyst loads in varied time intervals. Notably, the Nb_2O_5/SO_4 catalyst was efficient either in low or high concentrations, and within short reaction times, reaching almost 100% of the ester yield [66].

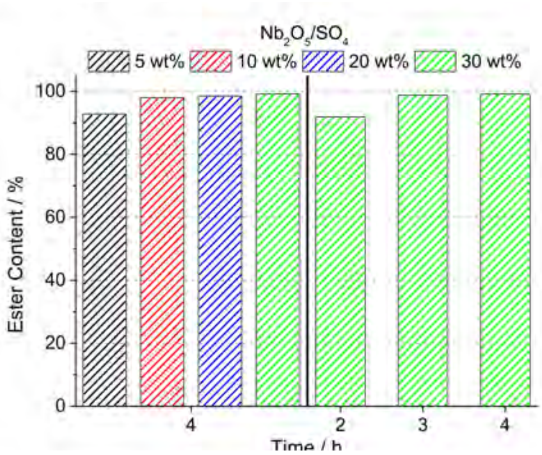


Figure 12. Effect of catalyst load in biodiesel yield measured at varied reaction time intervals. Reaction conditions: molar ratio ethyl alcohol: macaw palm oil (120:1), catalyst concentration (5–30 wt%), temperature (250 °C) (adapted from [66]).

3.2. Niobium Oxide and Niobium Phosphate

Niobium oxides and phosphates have been widely employed in many reactions, such as esterification processes, Friedel–Crafts reactions, hydrolysis, and dehydration reactions. They have attracted significant attention due to the highlighted acidic characteristics and their potential as efficient heterogeneous catalysts [67].

Commercial Niobium oxide is a material that has many important properties which make him active in different reactions. Câmara and Aranda (2011) have studied the esterification of FFAs over hydrated Nb_2O_5 (ca. 79.8% Nb_2O_5 and 19.6% water) to produce biodiesel [68]. They proposed a compatible kinetic model using the calculations of kinetic constants and determined thermodynamic parameters such as the free Gibbs energy and the variations in enthalpy and entropy, and compared with their experimental data. The results showed that the Niobium oxide was an efficient catalyst to esterify palmitic acid with ethyl alcohol to produce biodiesel, achieving conversion higher than 80% in 60 min (Figure 13). Besides that, those authors calculated the thermodynamic parameters through different temperatures (ca. 150 and 200 °C; Table 1). They have found that the palmitic acid esterification has an endothermic behavior and positive entropy variation, which decreases when hydrated ethyl alcohol (4 wt% water) was replaced by anhydrous ethanol. This behavior can be associated with the fatty acid dissociation constant and the water present in the reaction medium [68].

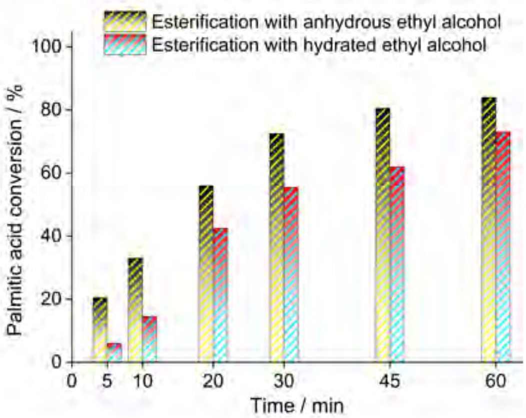


Figure 13. Palmitic acid esterification over Niobium oxide in anhydrous ethyl alcohol or hydrated (4 wt% water). Reaction conditions: alcohol: palmitic acid molar ratio (3:1), catalyst (20% wt% in relation to the fatty acid), temperature (200 °C) (adapted from [68]).

Table 1. Thermodynamic parameters for palmitic acid esterification (adapted from [68]).

Alcohol	ΔH (kJ.mol^{-1})	ΔS (J.(mol·K^{-1})
Hydrated ethyl alcohol	151.3	319.3
Anhydrous ethyl alcohol	111.7	249.8

Gonçalves et al., (2011) have assessed the behavior of the Nb_2O_5 catalyst in esterification reactions of saturated and unsaturated fatty acids (Figure 14), which were used as the model molecules [31].

Figure 14. Different fatty acids esterification with Niobium oxide in anhydrous methyl alcohol. Reaction conditions: alcohol: fatty acid molar ratio (1.2), catalyst (20 wt% in relation to the fatty acid mass), temperature (150 °C), time (30 min) (adapted from [31]).

Figure 14 outlines behavior in terms of the fatty acid conversion in 30 min of reaction. It is possible to note that the Nb_2O_5 was able to promote the esterification of unsaturated fatty acids: conversion of linoleic acid (C18:2) > oleic acid (C18:1) > stearic acid (C18:0). On the other hand, an increase in carbon chain size seems to reduce the reactivity of fatty acid in esterification reactions: lauric acid (C12:0) > palmitic acid (C16:0) > stearic acid (C18:0). It allows us to conclude that the activity is related to the polarity of the molecule, where the catalyst is most active in the presence of unsaturated acids and with smaller carbon chain sizes [31].

Niobium phosphate can be also an alternative catalyst due to its acidity characteristics [69]. To evaluate the potential of Niobium phosphate (NbP) catalyst, Bassan et al., (2013) performed a comparative study between Nb_2O_5 and NbP using lauric acid esterification as a model reaction (Figure 15) [9]. To support this discussion, those authors performed analyses of BET surface area, amount of acidic sites using NH_3-programmed temperature desorption infrared spectroscopy, and nature of acidic sites through pyridine–infrared spectroscopy analysis [9].

Although the reactions have been carried out with the same weight percent of Nb_2O_5 and NbP, the performance of Niobium phosphate was far superior; 83% of conversion against 40% achieved in the presence of Niobium oxide. The highest activity of NbP was assigned to its higher surface area and to its greater number of Brønsted acid sites [9].

Due to the better result obtained in the presence of the NbP, those authors proved the effectiveness of this catalyst in reactions with different alcohols and fatty acids. Figure 16 shows the results of lauric acid esterification with two other alcohols (i.e., methyl and ethyl alcohols) [9].

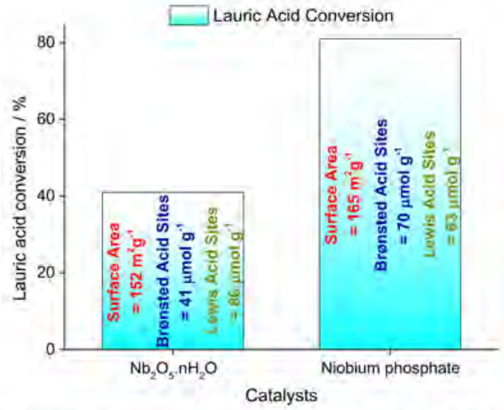


Figure 15. Lauric acid esterification with butyl alcohol over Niobium oxide or Niobium phosphate. Reaction conditions: butanol: lauric acid molar ratio (10:1), catalyst (10 wt% in relation to the lauric acid), temperature (120 °C), time (4 h) (adapted from [9]).

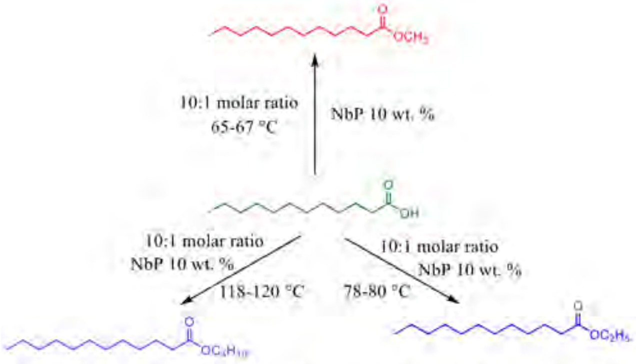


Figure 16. Lauric acid esterification with Niobium phosphate in different alcohols. Reaction conditions: alcohol: lauric acid molar ratio (10:1), catalyst (10 wt% in relation to the lauric acid), reflux temperature (methyl alcohol = 65–67 °C; in ethyl alcohol = 78–80 °C; in 1-butyl alcohol = 118–120 °C), time (4 h) (adapted from [9]).

The literature has described that the size of the carbon chain affects its reactivity in esterification reactions; in general, short carbon chain alcohols are more reactive than superior alcohols [70]. Nonetheless, this was not the only aspect varied herein; those authors performed the reactions at the reflux temperature of the alcohol. Therefore, these two aspects (i.e., temperature and size of alcohol carbon chain) were responsible for the results obtained in those experiments. The reaction carried out at the highest temperature achieved the greatest conversion; although the methyl alcohol has the lowest reflux temperature, its reaction achieved a higher conversion than ethyl alcohol because this has a carbon chain twice as long [70].

On the other hand, when the Niobium phosphate was used as the catalyst in the esterification of 1-butyl alcohol with different fatty acids, it was demonstrated to be highly efficient in all the reactions (Figure 17) [9].

As mentioned previously, one of the factors that can influence the esterification process is the fatty acid chain length. To evaluate this parameter, Srilatha et al., (2009) carried out the esterification of different fatty acids with methanol over Niobium oxide catalyst [34]. As part of their experiments, they evaluate the behavior of six different acids (Caprylic, Capric, Lauric, Myristic, Palmitic, and Stearic acids) with methanol in three distinct moments of the reactions (1, 2, and 3 h). The results are shown in Figure 18 [34].

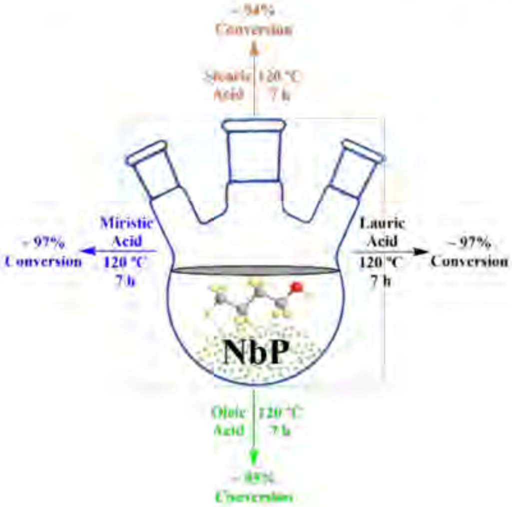


Figure 17. Fatty acid esterification with 1-butanol over Niobium phosphate. Reaction conditions: 1-butanol: fatty acid molar ratio (10:1), catalyst (10% w/w in relation to the fatty acid), temperature (120 °C), time (7 h) (adapted from [9]).

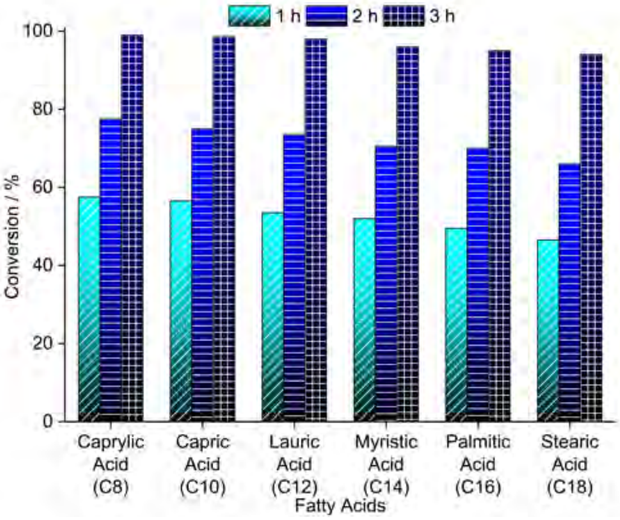


Figure 18. Different fatty acids esterification over Niobium oxide with methanol. Reaction conditions: fatty acid:methanol molar ratio (1:14), catalyst (15 wt% in relation to the fatty acid), temperature (65 °C) (adapted from [34]).

It is possible to notice that the efficiency of the reactions decreases with an increase in the carbon chain length of fatty acid for all reaction times. These experimental data agree with those reported by Natalino et al., (2014) [70].

Rade et al., (2019) studied the relationship between the acidic properties and the thermal treatment of Niobium phosphates [71]. To do this, they esterified oleic acid with ethyl alcohol in a packed bed tubular reactor. The authors considered at least two residence times to collect the samples for the reaction. These times were calculated as the times that the substrate remains in contact with the catalyst, and varied from 12 to 106 s for 0.10 and 0.80 g of catalyst, respectively [71].

Figure 19 shows the oleic acid conversion obtained in reactions over Niobium phosphate catalysts previously calcined at different temperatures, from 300 to 600 °C. The total acidity for each catalyst is as "inset" in the conversion bar. It is possible to realize that, until 500 °C, only a small variation was noticed in acidity of the catalysts treated at different temperatures. Nonetheless, the calcination at 600 °C triggered a strong decrease in the acidity of the Niobium phosphate catalyst. On the other hand, this effect had a minimum impact on the conversion; after 300 °C, the conversions remained almost constant [71].

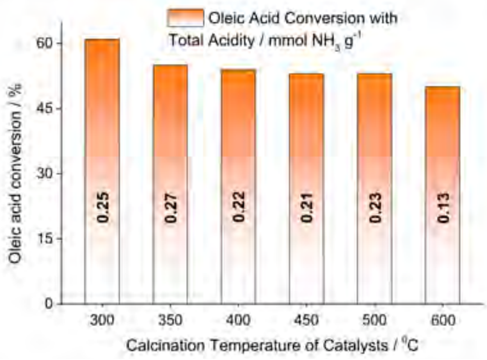


Figure 19. Oleic acid esterification with ethyl alcohol over Niobium phosphate. Reaction conditions: ethyl alcohol: oleic acid molar ratio (6:1), catalyst (0.3 g), temperature (250 °C) (adapted from [71]).

Transesterification reactions also can be explored by Niobium oxide in different oil types. This effect was evaluated by Arpini et al., (2019) [72]. Those authors submitted commercial Niobium oxide to two calcination temperatures 115 and 300 °C, to be applied in the transesterification reaction of soybean, canola, sunflower, and corn oils with methanol [72].

Figure 20 shows the results of these two catalysts in the conversions of the oils. Although the conversion values are low, less than 15%, the important aspect to highlight is the properties of the solids. According to the authors, the catalyst treated in 300 °C presented the lowest surface area; however, the same material presented a greater number of Lewis acid sites, which conforms to the reaction tendency [72]. Therefore, in this case, the surface area was a key factor in the success of the catalyst. Certainly, the different composition of oils was an important factor that impacted the conversion of the reactions.

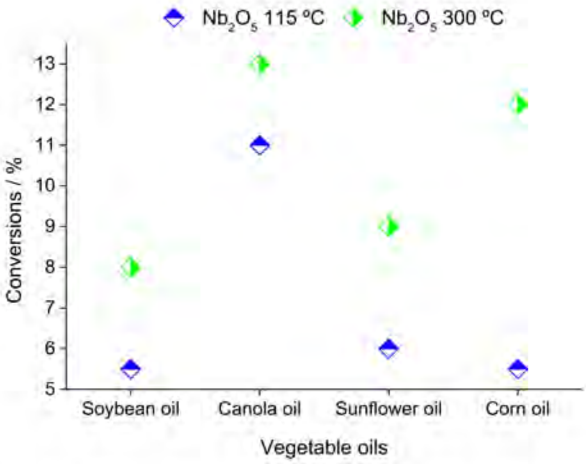


Figure 20. Transesterification of different oils with methyl alcohol over thermally treated Niobium oxides. Reaction conditions: methyl alcohol:vegetable oil molar ratio (3:1), catalyst (20% in relation to the oil mass), reaction temperature (170 °C), time (48 h) (adapted from [72]).

Melo Júnior et al., (2010) have assessed the effect of microwaves radiation in promoting the esterification of oleic acid with methyl alcohol over different metal oxides [21]. Niobium oxide and sulfated zirconia were the catalysts used in this reaction. Figure 21 shows the conversion reached in the reactions and the values of surface area and acidity for each catalyst.

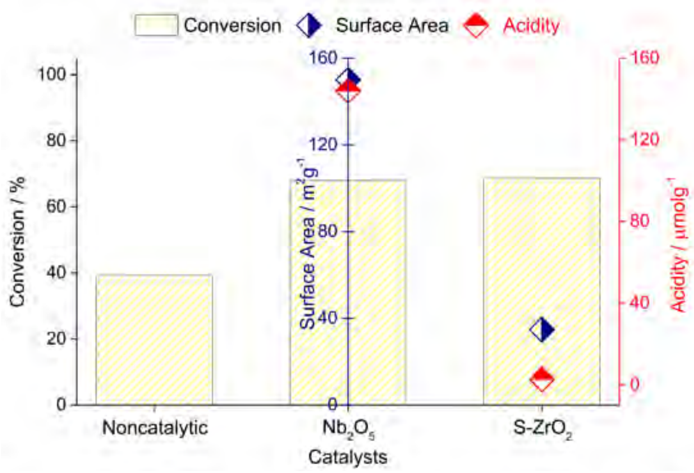


Figure 21. Oleic acid esterification reaction with methanol over Niobium oxide and sulfated zirconia. Reaction conditions: methanol:acid molar ratio (10), catalyst (5 wt% related to the oleic acid mass), reaction temperature (200 °C), time (20 min) (adapted from [21]).

The conversions of the catalysts were very similar. Conversely, Niobium oxide was much more acidic than sulfated zirconia, and the surface area value was much more expressive for Nb oxide. These results showed that the activity cannot be related to the surface area and reinforced the importance of the number and type of the acid sites on the catalyst surface [21].

The authors did not report the acid strength of the materials; nevertheless, there are other works in the literature that present some important facts related to the acid strength of the catalysts in esterification reactions. Sturt et al., (2019) and Reguera et al., (2004) evaluated the influence of this parameter in the oleic acid reactions [35,73]. In this work, Niobium phosphate obtained a better result in oleic acid decarboxylation [73]. The authors attributed this due to the stronger acid sites than the Niobium oxide and H_3PO_4 supported on Nb_2O_5 [73]. Also, in the Sturt work, it was shown that the better efficiency of sulfated niobia was in the oleic acid esterification [35]. This catalyst, in comparison to the others used in the article, presented the formation of strong Brønsted sites on the surface. The literature shows that the esterification process is effective in the presence of Lewis and Brønsted sites, which have a synergic effect. However, the Brønsted sites are more efficient [35,39,73–75]). Therefore, the remarkable behavior of sulfated zirconia can be attributed to the stronger acid sites than Nb_2O_5; these are probably Brønsted acidity sites.

3.3. Niobium as Catalytic Support and as a Dopant

Catalytic support requires some key properties, such as high surface area, availability of active sites, easy synthesis, and good stability chemical and thermal under reaction conditions. These properties should allow that the activity of a dopant may be highlighted along with the reactions, at a greater level than when the dopant is used in "solo" conditions [76].

Various inorganic materials have been used to support different dopants, and the same has occurred for Niobium compounds, which have been solid supported on different matrixes. Sancho et al., (2011) have used this strategy to increase the surface area and the availability of the active sites, supporting Niobium oxide on the mesoporous molecular sieves such as MCM-41 [28]. The activity of this Nb_2O_5/MCM-41 supported catalyst was investigated in sunflower oil transesterification reactions to produce biodiesel. Those authors used two different methodologies to synthesize the materials: initially, they incorporated Nb into the structure of mesoporous silica framework during the synthesis of support, generating a material named Nb-MCM. In the second approach, they performed the wetness impregnation of the MCM-41 silica with different Nb loads, generating catalysts identified as MCM-Nb3, MCM-Nb-5, MCM-Nb8, and MCM-Nb16, where the number represents the Nb_2O_5 wt% incorporated into the MCM silica [28].

The relationship between the surface area and acidity of the Niobium catalysts is depicted in Figure 22. The Nb-MCM was the catalyst with the greatest surface area, followed by the MCM-41 and the impregnated catalysts. For the supported catalysts obtained through the impregnation method, the surface area decreases when the load of Nb increases. This is an expected result since the density becomes higher with the incorporation of Niobium. The decrease in the acidity for the MCM-Nb16 may be assigned to the presence of Nb_2O_5 particles, which were verified by Raman spectroscopy and XRD analyses, as described by the authors [28].

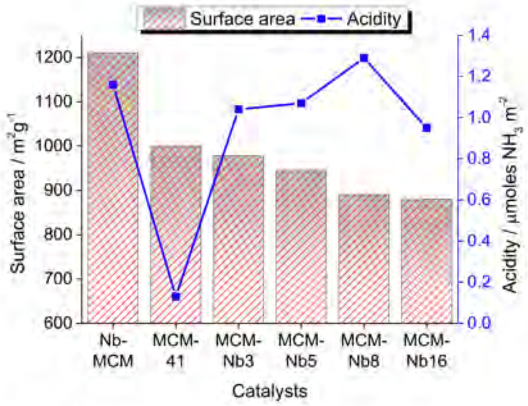


Figure 22. Effects of Nb load on the surface area and acidity of the MCM-supported catalysts. MCM-Nb3, MCM-Nb-5, MCM-Nb8, and MCM-Nb16, where the number in the names represents the wt% of Nb_2O_5 incorporated into the MCM-41 (3, 5, 8, and 16 wt%) (adapted from [28]).

All these materials were tested in reactions to produce biodiesel. It was found that the pure MCM mesoporous silica was not so active due to its weak acidity. This behavior was very similar to the non-catalytic process. Figure 23 shows that, even with the decrease in surface area, the MCM-Nb catalysts presented good results to the biodiesel yield. This result can be assigned to the increase in acidity strength triggered by the impregnation of Nb species into the material structure. From 3 to 8 wt% of Niobium, the efficiency in the reaction also improved, justified by the progressive increase in acidity strength. Despite the differences for Nb-MCM and MCM-Nb16, these catalysts were able to generate good biodiesel yields [28].

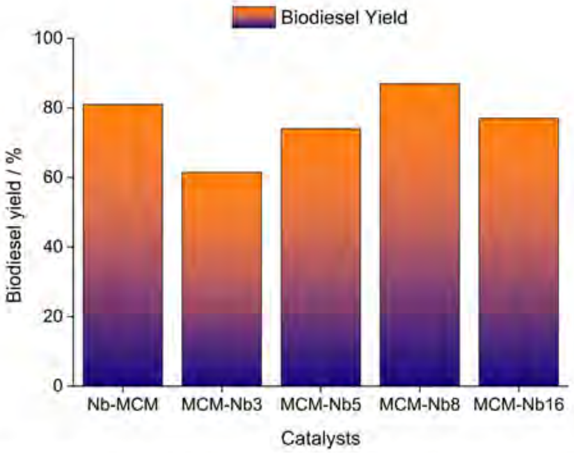


Figure 23. Effects of Niobium load on the Biodiesel production from sunflower oil over the different Niobium/MCM catalysts. In the MCM-Nb3, MCM-Nb-5, MCM-Nb8, and MCM-Nb16, the number represents the wt% of Nb_2O_5 incorporated (3, 5, 8, and 16 wt%) to the MCM-41. Reaction conditions: methyl alcohol: sunflower oil molar ratio (12:1), catalyst (5 wt% in relation to the oil), temperature (200 °C), time (4 h) (adapted from [28]).

Many catalysts can be efficient in transesterification process due to their strong Brønsted acidic sites, such as heteropoly acids (HPAs) (Figure 24). Their unique properties make the HPAs active in various reactions carried out in homogeneous, heterogeneous, or biphasic catalysis conditions. For such reasons, HPAs are attractive catalysts in acid-catalyzed reactions, such as alkylation, (trans)esterification, and etherification [77–81].

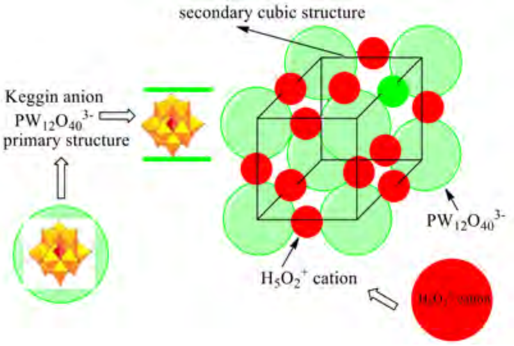


Figure 24. Primary and secondary structure of Keggin heteropolyacid $H_3PW_{12}O_{40}$ (adapted from [81]).

However, HPAs are solid with a low surface area and are soluble in polar solvents. To circumvent this drawback, Keggin HPAs have been used as the solid-supported catalysts. For instance, Srilatha et al., (2010) supported 12-tungstophosphoric acid on Niobium oxide, aiming to improve its stability and increase its surface area, thereby allowing its use as a heterogeneous catalyst [82]. The catalysts were synthesized by wet impregnation and with different $H_3PW_{12}O_{40}$ loadings (from 5 to 30 wt%). Figure 25 shows the relationship between the amount of $H_3PW_{12}O_{40}$ in all synthesized catalysts, the surface area, and the acidity represented by weak and moderate/strong sites [82].

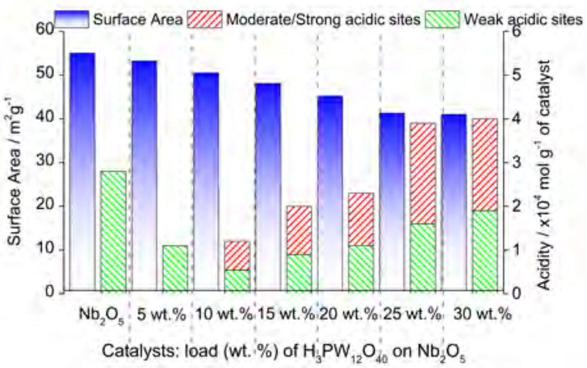


Figure 25. Relationship between the increase in $H_3PW_{12}O_{40}$ load, surface area, and acidity strength of the catalysts (loadings from 5 to 30 wt%) (adapted from [82]).

It is possible to note that the greater the load of $H_3PW_{12}O_{40}$, the smaller was the surface area of the solid-supported catalyst. This behavior can be attributed to the pore blockage by the $H_3PW_{12}O_{40}$. Conversely, in terms of acidity, a different behavior could be seen. An increase in $H_3PW_{12}O_{40}$ load leads to an increase in the strength of acidity as an increase in the number of acidic sites. The decreasing of moderate/strong acid sites and the practically constant surface area from 25 to 30 wt% of phosphotungstic acid are explained by the authors as being a possible agglomeration of particles that make inaccessible some acidic sites [82].

Figure 26 shows two connection modes in which the Keggin anion can be bonded on the Niobium oxide support, from the ligand exchange mechanism (left) or through coordination mechanism with the formation of surface complex (right) [83].

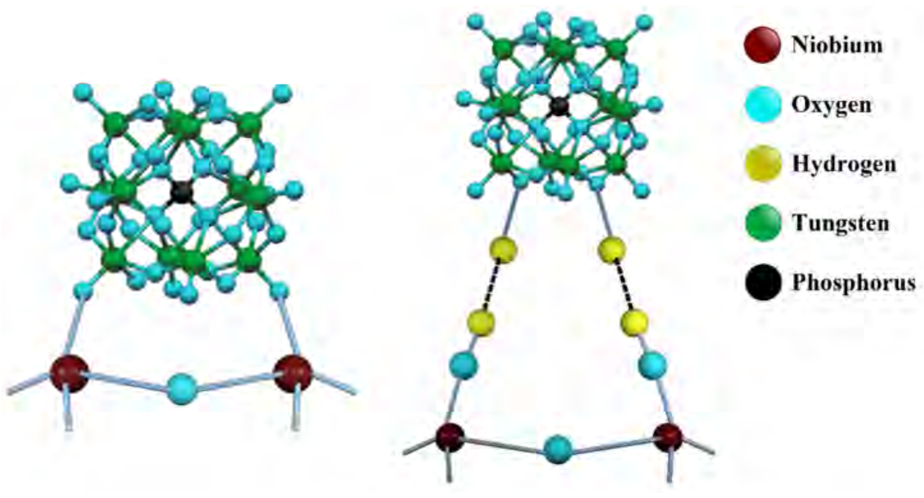


Figure 26. Supported 12-tungstophosphoric acid on Niobium oxide (adapted from [83]).

$H_3PW_{12}O_{40}/Nb_2O_5$ catalysts were used in transesterification reactions of waste cooking oil (WCO) with methanol. In Figure 27, the results of the reaction are presented, where the ester yield at 10 and 20 h are highlighted for all the Nb_2O_5-supported $H_3PW_{12}O_{40}$ catalysts. The best yields were achieved after 20 h of reaction. Likewise, an increase in load of dopant $H_3PW_{12}O_{40}$ leads to an increase in biodiesel yields until the 25 wt% $H_3PW_{12}O_{40}/Nb_2O_5$. These findings assure that the reaction is dependent on the acidity of solid catalyst [82].

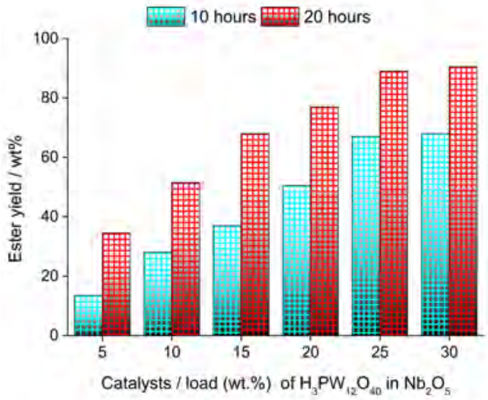


Figure 27. Ester yield on used cooking oil transesterification reaction by the $H_3PW_{12}O_{40}/Nb_2O_5$ catalysts. Reaction conditions: wasting cooking oil (0.115 mol), methyl alcohol (2.069), temperature (200 °C) (adapted from [82]).

The same research group also evaluated the impact of temperature on the 25 wt% $H_3PW_{12}O_{40}/Nb_2O_5$-catalyzed reaction (Figure 28) [64]. As can be seen, the increase in temperature favors the ester formation. Nevertheless, no significant beneficial effect was noticed at temperature higher than 200 °C in reaction carried during 20 h. It is possible that, at these conditions, the products can degrade themselves, decreasing the yield [82].

The same authors realized a stability and reusability study showing the efficacy of the 25 wt% $H_3PW_{12}O_{40}/Nb_2O_5$ catalyst in the standard conditions of the transesterification reaction [83]. Firstly, they submitted the solid by one hour in the reaction mixture and, after that, the process was continued in absence of the catalyst. Even after 10 h, there was no significant increase in the yield. For the reusability tests, the same material was used in the reaction for five cycles. They reported no relevant changes in the results for the cycles. Both tests showed the great potential of this solid due to the stability for not being detected leaching, and for the maintenance of the high activity in different subsequent reactions.

The glycerol valorization by the esterification in its acetates it is a process that allows the obtaining fuel additives (Scheme 4).

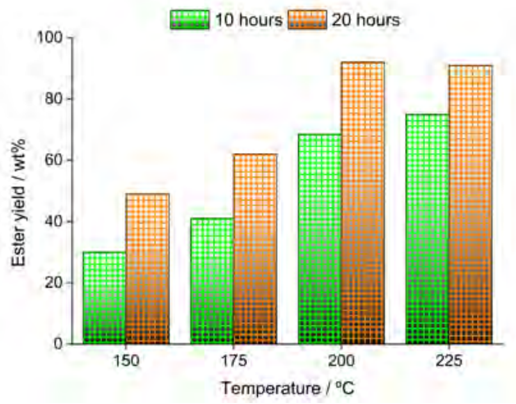
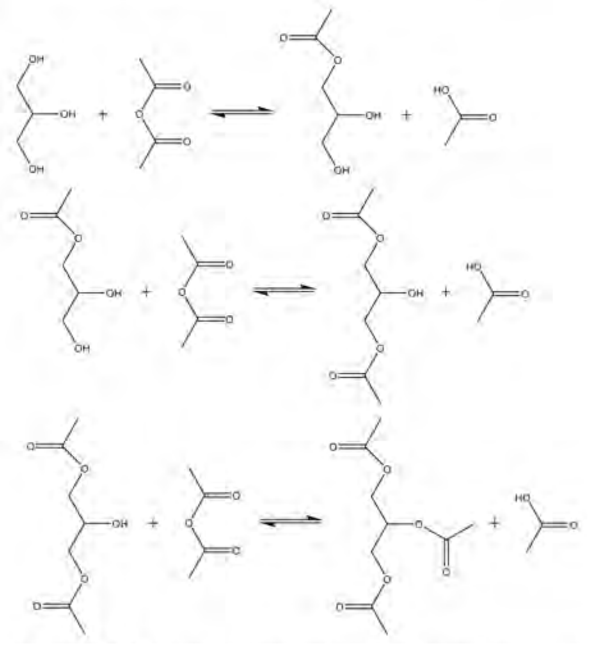


Figure 28. Ester yield obtained in wasting cooking oil transesterification reaction over 25 wt% $H_3PW_{12}O_{40}$ catalyst. Reaction conditions: used cooking oil (0.115 mol), methyl alcohol (2.069), temperature (150–225 °C) (adapted from [82]).



Scheme 4. Glycerol esterification with acetic anhydride (adapted from [84]).

Several Lewis and Brønsted acid catalysts have been used in glycerol esterification reactions in homogeneous and heterogeneous phase [84–88]. However, solid catalysts have the advantages of being easier to recovery and reuse, minimizing the generation of effluents and residues.

Figure 29 presents the conversion and selectivities for mono, di- and triacetates in reactions of esterification of glycerol carried out $H_3PW_{12}O_{40}/Nb_2O_5$ catalyst. In this procedure, we have investigated the activity of phosphotungstic acid supported on Niobium oxide, synthesized by impregnation method, and treated at temperatures of 100, 200, and 300 °C. Conversions and selectivities were evaluated by GC analysis in a Varian 450 gas chromatograph (FID detector, Carbowax capillary column) and the products were identified by mass spectrometry (CG/EM Shimazu QP5050, EI 70 eV).

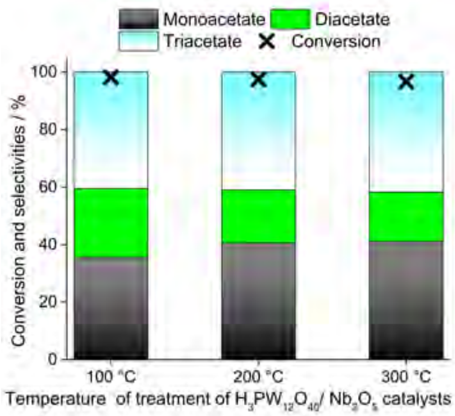


Figure 29. Conversion and selectivities in the glycerol esterification over thermally treated Niobium-supported HPA catalysts. Reaction conditions: glycerol (24 mmol), acetyl acetate (140 mmol), catalyst (30 wt. %), temperature (60 °C), time (12 h).

In Figure 29, is possible to notice that the thermal treatment had a minimum impact on the performance of catalysts, but it is important to highlight that all the reactions were efficiently performed under heterogeneous catalysis, achieving conversions of 96%.

Surasit et al., (2017) synthesized phosphotungstic acid (TPA) supported on Cesium-containing Niobium (TPA/Csx/Nb_2O_5), where "x" is the TPA/Cs molar ratio (1.0; 1.5; 1.8; 2.0; 2.3, and 2.5) and the TPA loading was 20 wt% in all catalysts [89]. Those authors assessed the activity of the catalysts in the oleic acid esterification with methanol. The Figure 30 shows the relationship between the ester yield and the acidity of the solids.

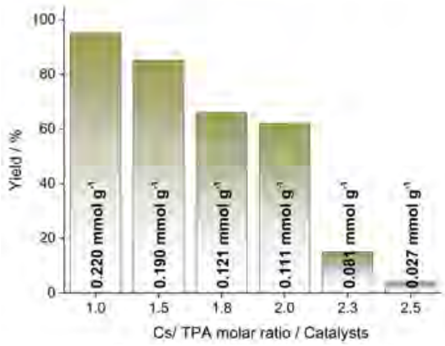


Figure 30. Yield of methyl oleate in the oleic acid esterification with methanol over different catalysts. The catalysts, in the graph, are represented by the Cs/TPA molar ratio from 1.0 to 2.5. Inside the bars, the acid site concentration of each catalyst is shown. Reaction conditions: molar ratio methanol:oleic acid (20:1), catalyst (15 wt%), temperature (65 °C), time (8 h) (adapted from [89]).

In Figure 30, it is possible to note the influence of Cs/TPA molar ratio and the amount of acid sites on the yield of methyl oleate. It follows that the ester yield is directly related to the acidity of the solids; indeed, the greater their acidity, the higher was the ester yield. The figure shows a great yield value of over 90% with a catalyst containing the lowest Cs concentration and the greatest acidity. Meanwhile, the worst result was with the Cesium catalysts containing the greatest amount of this metal and thus the lowest acidity [89].

In the same work, Surasit et al., evaluated the activity and stability of the catalyst with TPA/Cs molar ratio of 1.0. The solid showed a significant decrease in the activity only from the fifth run. This probably occurred due to deactivation by the organic residues, which were not adequately extracted. The stability of the catalyst was assessed by analysis of inductively coupled plasma-optical emission spectroscopy of aliquots collected at the end of the reaction. Low levels of Cesium and Tungsten were detected in the reaction medium after the first run, suggesting that the Niobium oxide support is reasonably stable.

Another outstanding example is the application of sulfated Niobium supported on mesoporous silica KIT-6, which was described by Subramaniyan and Arumugam (2016) [72]. Those authors carried out the transesterification of vegetable oil to fatty acid methyl esters [90]. To synthesize the catalysts, those authors used different loads of Niobium oxalate (ca. 1, 2, and 3 wt%) in relation to KIT-6. The catalysts were named as 1SNK, 2SNK, and 3SNK, according to the Niobium amount [90]. Figure 31 shows the methyl esters yield achieved in the transesterification of groundnut oil with methanol over these catalysts at temperature of 150 °C, and the surface area of the catalysts.

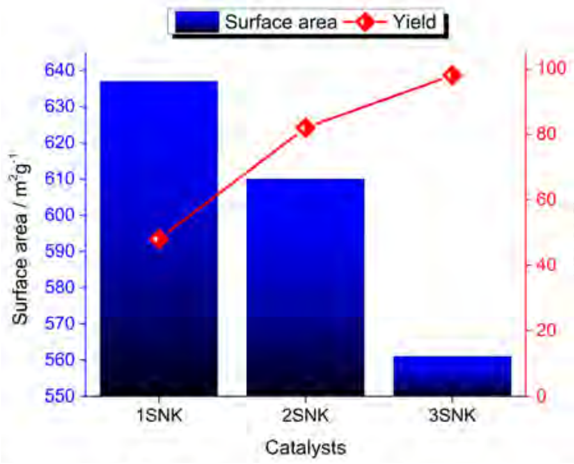


Figure 31. Yield of fatty acid methyl ester in the groundnut oil transesterification over different catalysts with methanol and the surface area of catalysts. The catalysts, in the graph, are represented by the xSNK, where x is the amount of Niobium used in the synthesis. Reaction conditions: molar ratio methanol:oil (9), catalyst (0.5 g), temperature (150 °C), time (6 h) (adapted from [90]).

The activity of the catalysts was not directly influenced by their surface area, however, the load of Niobium supported played a key aspect. The most active solid catalyst was that where the sulfated Niobium was more dispersed on the surface. Therefore, the 3SNK obtained a result of almost 100% in the yield [88].

Other result that can corroborate this behavior was presented by Tesser et al., (2015) [91]. Those authors synthesized Niobium supported on silica by the impregnation method. The catalysts were evaluated in transesterification reactions of soybean oil. The catalysts were prepared with different loading (ca. 3–12 wt%) of Nb_2O_5, being the materials designated as 3NbSi, 5NbSi, and 12NbSi. The transesterification reactions of soybean oil were carried out in stainless steel vial reactors [91]. Figure 32 shows the conversions results for the silica calcined at 900 °C and for the Niobium/Silica catalysts (3–12%).

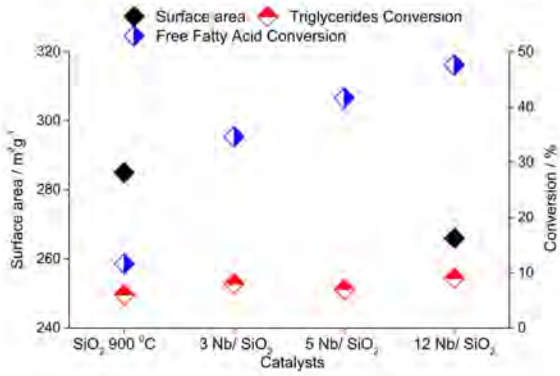


Figure 32. Conversion of triglycerides and free fatty acids of acid soybean oil over silica and Niobium/silica catalysts with methanol. Reaction conditions: soybean oil or acid soybean oil (2.00 g), catalyst (0.10 g), methanol (0.88 g), temperature (180 °C), time (1 h) (adapted from [91]).

As can be seen, for the esterification of fatty acids, the growing load concentration of Nb on the catalysts improved the conversion values. However, to the transesterification, an increase in Nb load had a minimum impact on the conversion. Although the presence of Niobium results in a lower surface area, the silica-supported Niobium catalysts were efficient in the conversion of FFAs [89].

There are many works involving the synthesis of Nb catalysts interacting with mesoporous silica support. Silva et al., (2017) synthesized efficient catalysts of Niobium supported on SBA-15 and applied them in propanoic acid esterification with methanol [90]. Those authors evaluated the behavior calcinated at different temperatures and containing Brønsted and Lewis acid sites at varied proportions. The catalysts were synthesized with different Nb loadings on the support, 2–32 wt%. Figure 33 shows the performance of the 2 wt% Nb/SBA-15 catalyst in propanoic acid esterification. The Brønsted:Lewis (B/L) ratio and the calcination temperatures to which the material was subjected are included in Figure 33. The activity was expressed in the initial rate of the reaction normalized with the Niobium content [90].

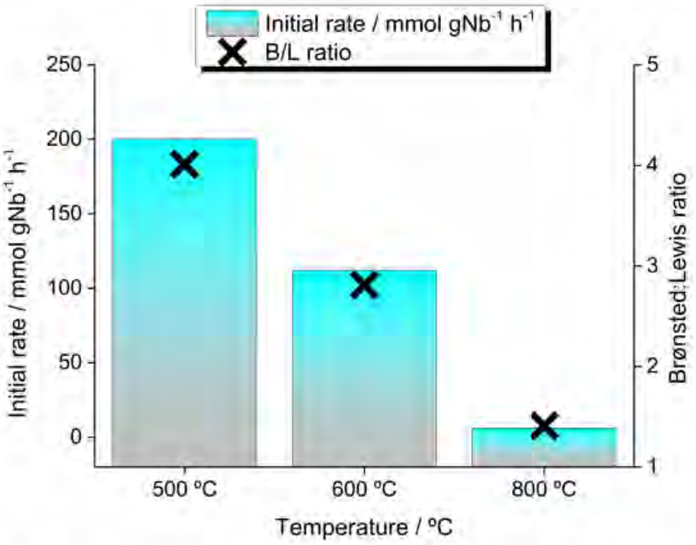


Figure 33. Effect of the B/L ratio and calcination temperature of catalyst in esterification of propanoic acid with methanol over Niobium supported on SBA-15 (2 wt% Nb/SBA-15). Reaction conditions: Methanol: propanoic acid molar ratio (30), catalyst (50 mg), temperature (60 °C), dihexylether as internal standard (0.12 mL) (adapted from [92]).

In Figure 33, it is possible to see the direct relationship between the efficiency in the reaction and acidic properties of the catalyst with the thermal treatment. The treatment temperature plays a strong role in the acidic parameters, varying the amount of acid sites on the surface. These results show the strong dependence from Brønsted sites, since the higher the calcination temperature, the lower the B/L ratio, and this reveals a decrease in the performance in the reaction. According to the authors, this phenomenon can be explained by the recrystallization of the niobia due to high treatments temperatures, decreasing the Niobium species dispersion on the support surface [92].

3.4. Others

In recent years, the literature has reported many works showing the development of a huge types of Nb catalysts applied in different reactions. These catalysts have distinct structure and properties that can perform interesting activities and selectivities in a plethora of reactions [93].

In addition to reactions to produce biodiesel, modified materials can be applied for the productions of additives to compose the biofuel. The triacetylglycerol can be obtained from glycerol esterification with acetic acid and can be very useful to improve some properties of the biodiesel, such as viscosity, cold resistance, and can be an anti-knock agent. Trejda et al., (2012) synthesized different Niobium catalysts incorporated on mesoporous molecular sieves of SBA-15 type and functionalized with MPTMS (i.e., (3-mercaptopropyl)trimethoxysilane). The catalysts were designated with the numbers 32 or 64 to show the TEOS/Nb molar ratios, and with the numbers 1, 5, or 10 to show the Si/MPTMS molar ratios [94].

In Figure 34, it is possible to notice that the presence of the MPTMS leads to a decrease in the surface area, while the increase in Nb load leads to an increase in the acidic sites [92]. Interestingly, in the same work, we can verify the positive effect of the Nb presence in the catalysts (Figure 35). The materials without Nb showed a good potential in the conversion of glycerol; however, the Niobium silicates were better in this esterification reaction, reaching conversion values over 90%, being more selective for diacetylglycerol and triacetylglycerol [94].

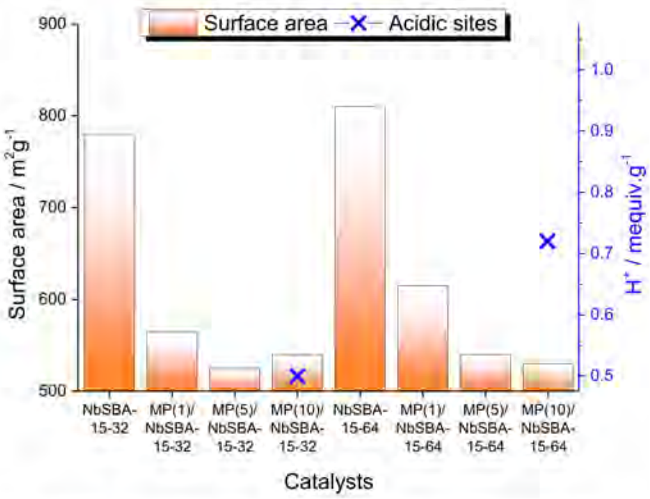


Figure 34. Variation of surface area and acidity in relation to the amount of MPTMS ((3-mercaptopropyl)trimethoxysilane), and Niobium load in the different niobiosilicate catalysts; 32 or 64 show the TEOS/Nb (tetraethyl orthosilicate/Nb) molar ratios; 1, 5, or 10 in the parentheses show the Si/MPTMS (MPTMS = (3-mercaptopropyl)trimethoxysilane) molar ratios and SBA-15 is the mesoporous molecular sieves (adapted from [94]).

Niobium can compose a wide range of catalysts derived from well-known structures. A good example was described by Katada et al., (2009) [95]. The authors synthesized heteropoly acid-derived solid acid catalysts with Nb in the structure.

Figure 36 presents a scheme of the reaction of triolein transesterification with ethanol into ethyl oleate over a Keggin anion-derived catalyst substituted by Nb. Moreover, the yield of ethyl oleate obtained in reactions with different heteropoly acids is presented in Figure 35, with and without Niobium in their composition, and the information about the solubility [95].

According to the authors, all the catalysts showed good activity for this reaction. For the insoluble catalyst, its reproducibility was confirmed in different preparations and applied in subsequent reactions under the same conditions. The reaction with this catalyst achieved a yield of ethyl oleate between 41 and 50%. For the catalysts that were partly or totally soluble, the yield of ethyl oleate exceeds 70% [95].

The results obtained by the catalyst $H_4PNbW_{11}O_{40}/WO_3$-Nb_2O_5 proved to be satisfactory and promising for the solid to be used in industry, achieving yields higher than those obtained in reactions over SO_4^{2-}/ZrO_2 catalysts. Moreover, these catalysts have greater durability than ion-exchange resin. Additionally, despite the activity being comparable with that of the Cesium solid catalyst, they are easier to reuse than the latter, which is difficult to recover because the particles that compose the material are very fine, making it difficult to separate from the liquid [95].

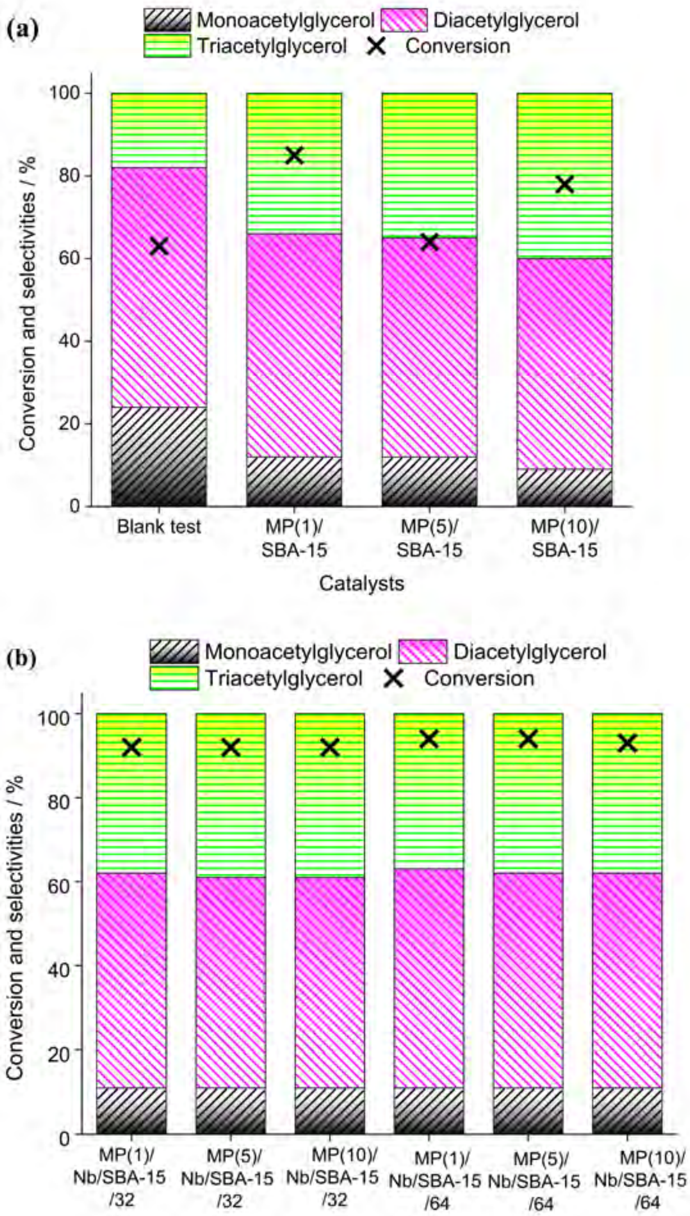


Figure 35. Conversion and selectivities for the glycerol esterification over silicates and Niobium silicates under nitrogen atmosphere, (**a**) over catalysts without Nb and (**b**) over Nb catalysts; 32 or 64 show the TEOS/Nb (tetraethyl orthosilicate/Nb) molar ratios in the synthesis of gel; (1), (5), or (10) show the Si/MP (MP = (3-mercaptopropyl)trimethoxysilane) molar ratios, and SBA-15 is the mesoporous molecular sieves. Reaction conditions: molar ratio glycerol:acetic acid (1:9), catalyst (100 mg), temperature (150 °C), time (4 h) (adapted from [94]).

Wong and co-authors (2014) showed that mixed oxides containing CaO and Nb_2O_5 can be used for biodiesel production, in transesterification reactions of palm oil [10]. The authors evaluated the effect of calcination temperature of catalyst in the yield of the esters [11]. The mixed oxides were calcined in temperatures between 300 and 800 °C. Figure 37 shows the behavior of each solid in the biodiesel yield in relation to the surface area and basicity in terms of CO_2 desorbed [11].

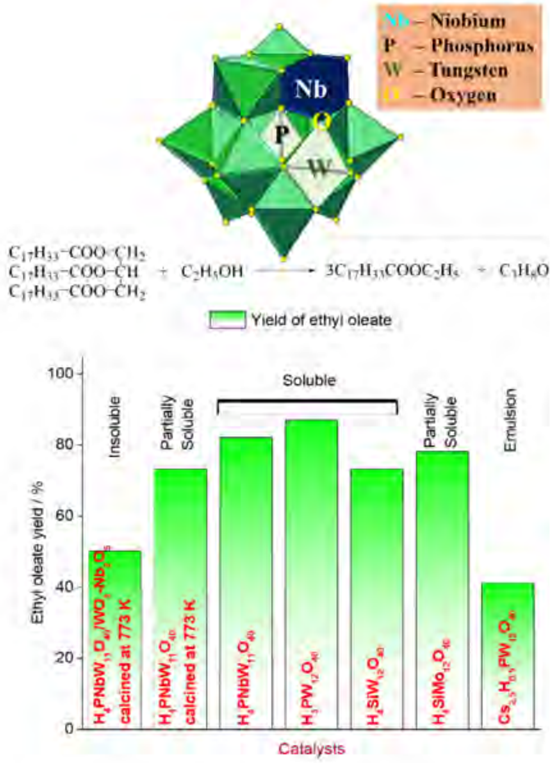


Figure 36. Schematic representation of the biodiesel production reaction catalyzed by the Keggin anion composed of Nb and yield of ethyl oleate by different heteropoly acids. Reaction conditions: molar ratio methanol:triolein (50), catalyst (0.2 g), temperature (100 °C), time (8 h) (adapted from [95]).

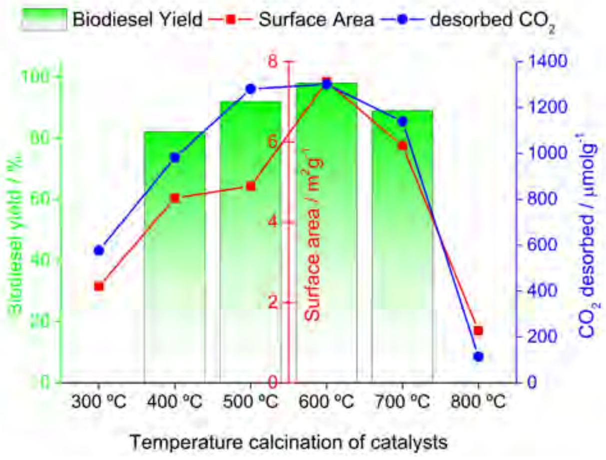


Figure 37. Palm oil transesterification catalyzed by CaO/Nb_2O_5, represented by the calcination temperature, in methanol. Reaction conditions: molar ratio methanol: palm oil (12), catalyst (3 wt%), temperature (65 °C), time (2 h) (adapted from [11]).

It can be seen at 300 and 800 °C of calcination temperature that the catalysts did not present results for biodiesel production. This can be explained according to the presence of $CaCO_3$ and $Ca(OH)_2$ in lower calcination temperatures, <600 °C, and the dominant phase of $CaNb_2O_6$ in higher calcination temperatures, 700 and 800 °C. These phases decrease the availability of CaO active sites. In contrast, for the other calcination temperatures, the biodiesel yields gradually increased with the thermal treatment until 600 °C, together with the surface area and basicity. As stated by those authors, the increase in the calcination temperature until 600 °C provided a raise in surface area and basicity, contributing to the reactant diffusion and the availability of the basic active sites [11].

The efficiency of different species of Niobium oxides were put to the test in the esterification of oleic acid and transesterification of soybean oil with methanol under refluxing. Pietre et al., (2010) compared the behavior of Niobium oxide with the same solid treated with sulfuric and phosphoric acids [96]. The catalysts were designated as Nb_2O_5, $NbSO_4$ and NbPO, with surface areas of 119, 21.2, and 53.4 m^2g^{-1}, respectively. Figure 38 exposes the activity of the three solids in the esterification and transesterification yields obtained by those authors [77].

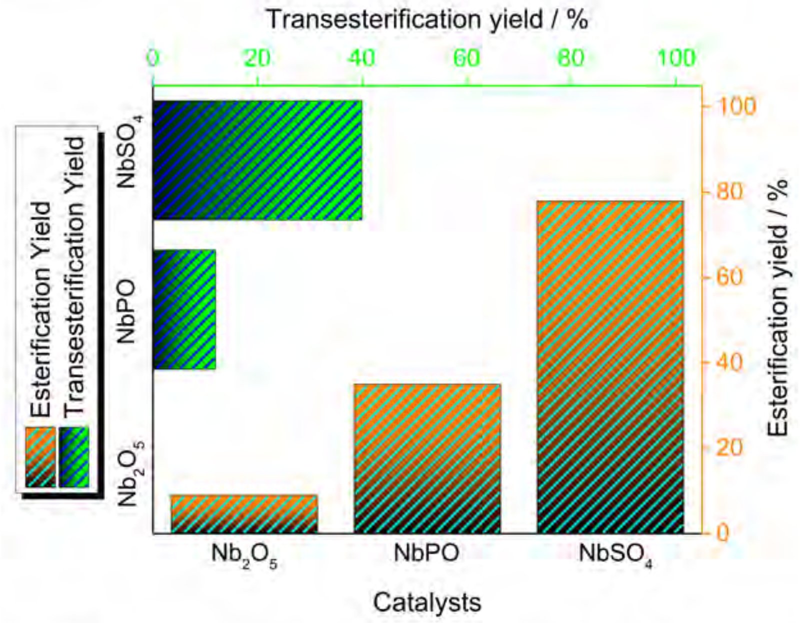


Figure 38. Esterification and transesterification yields catalyzed by Niobium catalysts in methanol. Reaction conditions: soybean oil (12.00 g), oleic acid (4.00 g), methanol (7.00 mL), catalyst (0.30 g), temperature (70 °C), time (5 h) (adapted from [96]).

An interesting profile can be noticed in relation to these different reactions; the catalytic performance was superior in esterification reactions. This can be explained due to phase distributions in the systems. In the esterification reaction, the oleic acid was dissolved in methanol, but in the other reaction existed three phases: catalyst (solid), soybean oil (liquid), and methanol (liquid). It is important to say that the $NbSO_4$ was the most active in both processes, followed by the NbPO and Nb_2O_5. One more time, as shown in this review, the behavior of these materials obeys their acidity, where, according to those authors, the total number of acid sites in $NbSO_4$ is greater than the other catalysts, being twice and eight times more acidic than the catalyst treated with phosphoric acid and the untreated catalyst, respectively [96].

As proven by many works published in the literature, Niobium compounds can play an important role in a diversity of reactions. A good example is the Nb catalysts applied in oleic acid conversion to produce hydrocarbons in the range of diesel oil (C14–C18). Reguera et al., (2004) developed a work where Nb_2O_5, $NbOPO_4$, and H_3PO_4/Nb_2O_5 were used as catalysts in a fixed bed and continuous flow reactor [73]. The last catalyst was obtained through the wetness impregnation of H_3PO_4 on the Nb_2O_5.

Figure 39 shows the conversions after 30 and 60 min, conversion sample 1 and conversion sample 2, respectively. The surface area and total acidity of the catalysts are also presented in Figure 39. The $NbOPO_4$ was the most active catalyst for this reaction, followed by the impregnated catalyst and Nb_2O_5, respectively. It is easy to see that the treatment with H_3PO_4 improves the efficiency of the Niobium oxide due to the increase in its acidity, although it has lowered its surface area [73].

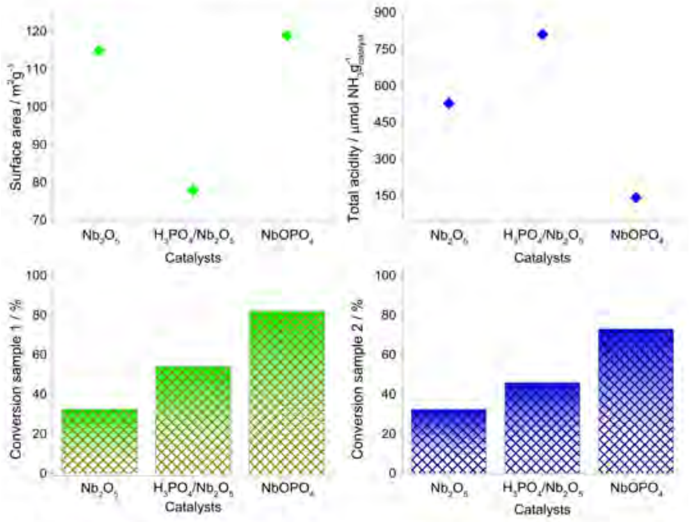
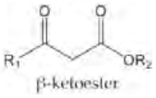


Figure 39. Oleic acid descarboxilation by Niobium catalysts and its surface area and total acidity. Reaction conditions: reactant flow (20.5 g h^{-1}, catalyst (5 g), temperature (350 °C), time (sample 1 = 30 min; sample 2 = 60 min) (adapted from [73]).

However, the most interesting detail is that the best result was achieved in reactions over $NbOPO_4$ catalyst, which has the lowest acidity. The authors explained that the TPD analysis measure the total of acid sites, but is not sufficient acid to efficiently decarboxylate the oleic acid; only the strong acid sites, presented mostly in the $NbOPO_4$ catalyst, can do it [73].

Table 2 summarizes others relevant data referent to the application of Nb catalysts in esterification and transesterification processes. The exhibition of these results reinforces the need to further explore the potential of Niobium-containing compounds in these types of reactions where there is a dependency on stable materials and singular surface properties to reach satisfactory conversion and yield values.

Table 2. Application of Niobium catalysts in different esterification and transesterification reactions.

Catalyst	Substrate	Reaction Conditions	Conversion [a]/Yield [b] (%)	Ref.
$NbOPO_4$ (5% based on FFA mass)	Oleic Acid	Oleic acid: dimethyl carbonate molar ratio (1:5)/250 °C/3 h	83 [a]	[97]
Nb_2O_5 (10% weight of β-ketoester)		1- *t*-butyl alcohol/8 h $R_1 = R_2 = CH_3$ 2- Glycidol/5.5 h $R_1 = R_2 = CH_3$ 3- *n*-butyl alcohol/5.5 h $R_1 = R_2 = CH_3$ * β-ketoester (1 equiv) and alcohol (2 equiv)	1—93 [a]/60 [b] 2—80 [a]/76 [b] 3—100 [a]/98 [b]	[98]
Nb_2O_5 small pellets (2% *w*/*w* in relation to fatty acid)	Fatty acid mixture (real vacuum distillated palm oil)	Anhydrous methanol: fatty acid mixture molar ratio (3)/130 °C/1 h	82 [a]	[99]
Nb-TCPP-SBA-AM [c] (0.01 g)	Levulinic acid	Acid: methanol molar ratio (1:5)/60 °C/6 h	74 [a]/59 [b]	[100]
$Na/NbOPO_4$ [d] (2% of oil mass)	Vegetable oil	Oil: methanol mass ratio (1:12)/65 °C/3 h	98.5 [b]	[101]
$NbOPO_4$ (10% *w*/*w*)	Oleic acid	Methyl acetate:oleic acid molar ratio (10:1)/240 °C/2 h	79.05% *w*/*w*	[102]
1- $NbOPO_4$ (5% *w*/*w*) 2- Nb_2O_5 (5% *w*/*w*)	Macaw oil	Methyl acetate: macaw oil (30:1)/250 °C/2 h	1—86.93 [a] 2—74.64 [a]	[103]
SO_4^{2-}/Nb_2O_5 (5% *w*/*w*)	Andiroba oil	Anhydrous ethanol: oil molar ratio (120)/ 260 °C/7 h	66.7 [a]	[104]
1- Nb_2O_5/HNO_3 2- Nb_2O_5/H_3PO_4 3- Nb_2O_5/H_2SO_4	Soybean fatty acids	Soybean fatty acids (10 g)/methanol (4 g)/ 160 °C/1 h	1—40 [a] 2—57 [a] 3—57 [a]	[105]
$HNbMoO_6$ (0.1 g)	Lactic acid	Lactic acid (0.05 mol)/*n*-butanol (0.25 mol)/343 K/5 h	35.1 [b]	[106]

[a] Conversion; [b] Yield; [c] Niobium incorporated *meso*-tetra-(4-carboxyphenyl)-porphyrin grafted by the surface amine groups present on functionalized SBA-15; [d] Synthesized with regulation of the pH = 4.

4. Conclusions

Herein, we report the recent advances achieved in the development of Niobium-containing heterogeneous catalysts as well as their use in routes to produce biodiesel. The efficiency of different Niobium catalysts in esterification and transesterification reactions of lipids and oleaginous raw materials was evaluated. The catalytic activity of Niobium compounds was discussed based on characterization data obtained by different techniques, such as NH_3-TPD, BET, and Pyr-FT-IR analysis. The effects of main reaction variables, such as temperature, time, catalyst load, and oil:alcohol molar ratio, on the biodiesel yield was evaluated. In general, the high catalytic activity is assigned to its properties, such as their mesoporosity, distribution of active sites over a high specific surface area, strength of acidity, nature, and number of acidic sites. We hope that the progresses reported herein can be useful in the development of new solid acid catalysts for the biodiesel industry.

Author Contributions: Conceptualization, D.C.B. and M.J.d.S.; methodology, D.C.B. and M.J.d.S.; investigation, D.C.B. and M.J.d.S.; writing—original draft preparation, D.C.B. and M.J.d.S.; writing—review and editing, D.C.B. and M.J.d.S.; visualization, D.C.B. and M.J.d.S.; supervision, M.J.d.S.; project administration, M.J.d.S.; funding acquisition, M.J.d.S. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: There are no conflict to declare.

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