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PERFORMANCE OF RHENIUM CATALYSTS SUPPORTED ON DIFFERENT SUPPORTS (ALUMINA, NIOBIA, AND TITANIA) IN PALM FATTY ESTERS TO FATTY ALCOHOLS

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ABSTRACT

The research consists of the conversion through hydrogenolysis of palm esters to fatty alcohols. The reactions were carried out in a batch system, evaluating the variation and effects of the factors temperature (250°C and 280°C) and pressure (40 bar and 70 bar). The hydrogenation results show that the catalyst supported on Nb₂O₅ obtained better catalytic performance than the catalysts supported on TiO₂ and Al₂O₃. The best yield obtained with the catalyst Re/Nb₂O₅ was approximately 87.3% of conversion of esters and 76.24% of selectivity in fatty alcohols, at a temperature of 280°C, 70bar pressure, and 10 hrs of reaction. The performance obtained using Re/Nb₂O₅ catalyst may have been because this catalyst presents a better metallic dispersion of rhenium on the niobia surface and because this same catalyst presents a more significant amount of Bronsted acid sites than the other catalysts (Re/Al₂O₃ and Re/TiO₂). So the characterization of these catalysts is described in our previous article (Muchave et al., 2020).

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INTRODUCTION

Recently, the oleochemical industry has expanded rapidly both in the food industry and in the industrial application to produce byproducts due to decreased oil reserves and environmental problems. Vegetable oils are one of the most promising, cheap, and available types of renewable sources (Danov et al., 2017). Issues such as global warming, climate change, and depletion of fossil resources have increased the rush in technological development to promote global sustainability (Munkajohnpong et al., 2020). Therefore, in recent years, a number of studies with a view to the application of vegetable oils or their derivatives (fatty acids, glycerin, or fatty acid esters) for the production of hydrocarbons (Zhang et al., 2019; Zhang et al., 2020) and byproducts, for example, fatty alcohols (Ali et al., 2019; Muchave et al., 2020). In recent years, there has been an increase in research aimed at the production of fatty alcohols in order to find new efficient and stable catalytic systems. In addition, there is a need to establish milder conditions that can produce fatty alcohols with lower operating costs (Tamura et al., 2020).

Some of the works found in the literature to develop new catalytic systems for the production of fatty alcohols used different metals: platinum (Janampelli and Srinivas, 2020; Lawal, 2019), palladium (Janampelli and Srinivas, 2020), copper (Olcaý et al., 2010; Thakur et al., 1992), nickel (Olcaý et al., 2010; Wang et al., 2020), ruthenium (Tike and Mahajani, 2007), rhenium (Muchave et al., 2020; Rozmysłowicz et al., 2015). In addition to testing the performance of metals, the effectiveness of different supports has been tested: TiO₂(Muchave et al., 2020; Rozmysłowicz et al., 2015), Al₂O₃(Muchave et al., 2020; Tike and Mahajani, 2007), SiO₂(Wang et al., 2020), ZrO₂(Janampelli and Srinivas, 2020), Nb₂O₅(Muchave et al., 2020). Another important factor is the growing demand for fatty alcohols in the international market. The fatty alcohol market for 2020 is estimated at US \$ 5.4 billion and is expected to reach US \$ 7.0 billion in 2025. The main factors driving the fatty alcohol market are the growing demand for personal care and industrial applications (Market, 2020). The annual production of fatty alcohol is about 3 million tons (Munkajohnpong et al., 2020).

This annual production depends on two sources of raw materials: oils and fats and petroleum-based. This production depends on the conversion based on oils and fats carried out through the hydrogenation process (Huang et al., 2009; Wang et al., 2020). Most of it is through the petroleum-based raw material that involves the oligomerization of ethylene followed by oxidation (Jiang et al., 2019; Mudge et al., 2008). Therefore, this work consists of fatty alcohol production through hydrogenation of palm esters, evaluating the effect of different supports (niobia, alumina, and titania) using a rhenium-based catalyst. Organic solvents have been applied to increase the reaction rate by increasing the diffusion of reactants on the catalysts. However, in this research, no organic solvents were used in the reaction (Muchave et al., 2020).

MATERIALS AND METHODS

Reagents and Equipment: The reagents used in this work were palm ester (Agropalma SA), Perrenic Acid (HReO_4 , Sigma-Aldrich), Hydrogen 99.99% (Linde Gases), gamma-alumina ($\gamma\text{-Al}_2\text{O}_3$, SASOL), Aerioxide TiO_2 P90 (Degussa), and niobium oxide (Nb_2O_5 , CBMM). The experiments were carried out in a Parr reactor of 300 mL volume, model 4848 with stainless steel beaker, automatic temperature, and pressure control. The equipment has a gas supply system and is equipped with a stirring and speed regulation shaft.

Catalysts Preparation and Characterization: The addition of rhenium (4% of the metal content) was carried out through incipient wetness impregnation. In this case, the amount of water used to dilute perrenic acid for each support varied based on pores' volume. It was determined according to the pore volume. After impregnation of perrenic acid on all supports, the catalysts were placed in an oven for 12 hours at a temperature of 100°C. Then they were calcined at 500°C for 4 hours, a heating rate of 5°C/min, except the catalyst supported on Nb_2O_5 , which was calcined at 400°C, to avoid modifying textural properties (surface area and pore volume). These catalyst synthesis procedures and characterizations: X-ray diffraction (XRD), textural properties, programmed temperature reduction (TPR), Temperature Programmed Ammonia Desorption (TPD- NH_3), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy of pyridine (IFTR), were presented and discussed in our article, (Muchave et al., 2020). Therefore in this article, they will not be discussed.

Catalytic Hydrogenation: The experiments were carried out in a Parr Instruments reactor of 300 mL, with stainless steel beaker, automatic temperature, and pressure control. The equipment has a gas supply system equipped with a stirring and speed regulation shaft. Initially, the catalyst was reduced in an oven at 400°C for 4 hours, at a 5°C/min heating rate. Then, the substrate was placed in the reactor cup, and then the catalyst was placed in the reactor cup. Finally, the reactor was pressurized with hydrogen to remove the air. 4% of the catalyst was placed about the fatty acid ester's mass amount for each reaction. The reactions proceeded with a stirring speed of 1200 rpm to reduce external mass transfer limitations. The study of the catalysts was carried out under temperature conditions were 250°C and 280°C, pressure conditions were 40 bar and 70 bar, and time conditions were 8 h and 10 h.

Planning and Statistical Data Analysis: A factorial design with two levels was carried out (2^3). In this case, the influence of all experimental variables (Temperature, pressure, and retention time) and their interaction effects on responses was investigated. The experimental planning, Design Expert 9.6 was used. The main objective in treating ANOVA data is evaluating the model, the factors, and the interaction between the factors to verify the model's validation. The three catalysts ($\text{Re}/\text{Nb}_2\text{O}_5$, Re/TiO_2 , and $\text{Re}/\text{Al}_2\text{O}_3$).

Analysis of the products: The hydrogenation reaction products were injected through a DB 23 column, Brand J & W Scientific on a Shimadzu GC-2010 model chromatograph with a split/splitless injector and a flame ionization detector (FID).

RESULTS AND DISCUSSION

Hydrogenation of palm esters: The influence of three factors (temperature, pressure, and retention time) on all catalysts was evaluated through fractional factorial Design with two levels. The experiments were duplicated (see Tables 1, 2, and 3). The results of the evaluation of the lipid profile of the raw material (palm esters) consist of fatty acids with e-content: methyl palmitate (46.21%), methyl stearate (5.43%), methyl oleate (41.02%), methyl linoleate (7.34%). Table 1 illustrates that the time and temperature factors played a fundamental role in converting the esters into several products. The results show that both the increase in Temperature, Pressure and retention time influenced the increase in esters' conversion. The $\text{Re}/\text{Nb}_2\text{O}_5$ catalyst showed the best catalytic performance, having obtained on average of the duplicate approximately 87.3% of esters' conversion and 76.9% of fatty alcohols. This result was obtained at the temperature 280°C and 70 bar of pressure. This indicates that the higher the temperature and the reaction pressure, the greater the esters' conversion and selectivity of fatty alcohols. Similar results have been reported in the literature (Manyar et al., 2010; Rozmysłowicz et al., 2015; Sánchez et al., 2017). The selectivity of fatty alcohols was influenced by both Temperature and Pressure. The reactions carried out at a temperature of 280°C obtained greater selectivity of fatty alcohols than reactions carried out at a temperature of 250°C. On the other hand, high pressures of hydrogen (70 bar) increased the selectivity of fatty alcohols compared to the reactions performed at 40 bar.

The results also show that a longer reaction time increased the conversion of esters and increased the selectivity of wax esters (intermediate product) for reactions at 250°C and 40 bar. Time variation did not affect the selectivity of fatty alcohols but affected the conversion of esters since reactions with a long time had a greater conversion. Another aspect observed is that the increase in Temperature and Pressure promoted hydrocarbon production, although at low levels (Rodina et al., 2017; Rozmysłowicz et al., 2015). The even carbon chain hydrocarbons (C16 and C18) may have been obtained through the hydrogenation or dehydration reactions of fatty alcohols, while the odd hydrocarbons (C15 and C17) may have been obtained through the decarboxylation and decarbonylation reactions of the esters. Several reasons can be related to the good catalytic performance of the $\text{Re}/\text{Nb}_2\text{O}_5$ catalyst and the selectivity in fatty alcohols. The higher yield achieved may be related to three factors: first, Nb_2O_5 being reducible oxide, which may have increased catalyst activity; the second due to the possible presence of a considerable amount of Bronsted acid sites in the catalyst and finally, the third factor is related to more excellent metallic dispersion of rhenium on the support. The catalysts' characteristics were described in our work (Muchave et al., 2020). According to Muchave et al. (2020), the metallic dispersion of rhenium on the supports (Nb_2O_5 , Al_2O_3 , and TiO_2), based on the atomic ratio that the dispersion increases in the following order: $\text{Re}/\text{Nb}_2\text{O}_5 > \text{Re}/\text{TiO}_2 > \text{Re}/\text{Al}_2\text{O}_3$, which correspond to the following atomic ratios of 3.11, 2.69 and 0.93, respectively. The authors also demonstrated that the type of acidic sites present in the catalysts, the $\text{Re}/\text{Nb}_2\text{O}_5$ and Re/TiO_2 catalysts showed Bronsted and Lewis acidic sites. In contrast, the $\text{Re}/\text{Al}_2\text{O}_3$ catalyst only has acidic sites, Lewis. Reducible oxides promote the interaction of oxygen with metal ions at the metal-support interface. This interaction can favour the increase of the activity of the catalysts during the reaction (Manyar et al., 2010; Rozmysłowicz et al., 2015). However, research carried out by (Foo et al., 2014; Leal et al., 2019) indicates that the metallic dispersion is fundamental to explain the catalytic performance of a given catalyst in the reactions of catalytic hydrogenation. Generally, the support's properties influence the properties of the synthesized catalyst and the catalytic behaviour, defining a new structure of the prepared catalyst. (Schwab, 1970). The support will influence the electronic structure of the metallic particles in the prepared catalyst as long as the contact is sufficiently close (Bond, 1985). This explains the catalysts' different catalytic even when using the same metal (rhenium).

Re/Al₂O₃: Table 2 presents the hydrogenation results of the Re/Al₂O₃ catalyst. According to Table 2, the conversion of esters increases with increasing Temperature, Pressure, and retention time, as shown in the results of Table 1 of the Re/Nb₂O₅ catalyst. The highest conversion obtained using the Re/Al₂O₃ catalyst is on average of the duplicate of 90.4%, with a selectivity of 41.7%, obtained at 280°C and 70 bar. However, the reaction temperature did not prove to be one of the most determining factors for the selectivity of fatty alcohols; however, it was essential in converting esters. On the other hand, the results in Table 2 showed that the hydrogen pressure was indeed one of the most important factors in the selectivity of fatty alcohols. In the reactions carried out at 40 bars, it was possible to observe that reactions at 280°C obtained more excellent selectivity of fatty alcohols than the reactions carried out at 250°C. The retention time variation also influences this selectivity; reactions carried out with a 10h have higher selectivity than reactions that last for 8h. Therefore, with this result, it can be said that using Re/Al₂O₃ catalyst, the factors that affected the fatty alcohol yield were temperature and reaction time; that is, the higher the temperature or the retention time, the greater the selectivity of fatty alcohols.

In general, the catalyst did not show high conversions and was very selective in wax esters' production. According to the XPS results, the low selectivity of fatty alcohols can be attributed to the low metallic dispersion of rhenium on the alumina surface, mainly because it is characterized by a more significant amount of Lewis acid sites than the FTIR results of pyridine. However, it has a larger surface area and pore volume than the Re/Nb₂O₅ and Re/TiO₂ catalysts, considering the expected results of the catalysts (Muchave et al., 2020). Therefore, considering the effect of acidic sites and metallic dispersion, everything indicates that the Re/Al₂O₃ catalyst was more affected with low metallic dispersion. Lewis acid sites characterize it compared to the Re/Nb₂O₅ and Re/TiO₂ catalysts. The Re/Al₂O₃ catalyst obtained a better yield using solvent when compared to the solventless reactions in this article. Muchave et al. (2020), it can be seen that no organic solvent was used in this work. There was low hydrogen solubility in the substrate, high resistance to mass transport, and, consequently, limitation of the reaction rate compared to the reaction with solvent. This catalyst was the most affected of two other catalysts (Re/Nb₂O₅ and Re/TiO₂). The Re/Al₂O₃ catalyst, when using solvent, became evident eliminated the limitation of the reaction rate favoured by the greater pore volume than the other catalysts (van den Hark and Härröd, 2001; Zhilong, 2011).

Re/TiO₂. According to Table 3 regarding the Re/TiO₂ catalyst results, the increase in temperature and reaction time factors favoured greater conversion of esters and selectivity of fatty alcohols. As for the temperature evaluation, the results show that the more excellent conversion and selectivity of fatty alcohols proportionally increase the reaction time. The higher fatty alcohol yield reached at 280°C and 10 h. The reactions carried out at 70 bar presented the same profile presented for the reactions carried out at 40 bar, as shown in Table 1. The best result obtained using the Re/TiO₂ catalyst was 90.9% on average ester conversion and 56.5% on average fatty alcohols at 280°C and 70 bar. The production of hydrocarbons was observed in the reactions carried out at 280°C and 70 bars. The high chemo-selectivity of fatty alcohols obtained from the Re/TiO₂ catalyst was attributed to the high affinity of rhenium about carboxylic acid derivatives about benzene rings, based on the results of functional density theory calculations (Malinowski et al., 1998). Other authors indicate that the best performance and yield obtained using Re/TiO₂ catalyst was because TiO₂ is a reducible oxide (Rozmysłowicz et al., 2015). In general, when comparing the catalytic performance of the three (3) catalysts, it was found that the best yield was obtained in the following order Re/Nb₂O₅ > Re/TiO₂ > Re/Al₂O₃. The best yield and activity obtained in the conversion of esters and selectivity in fatty alcohols using the Re/Nb₂O₅ and Re/TiO₂ catalysts may have been due to two factors: first, because the Re/Nb₂O₅ and Re/TiO₂ catalysts have acidic sites Bronsted, while the Re/Al₂O₃ catalyst showed only Lewis acid sites. The Re/Nb₂O₅ and Re/TiO₂ catalysts showed greater metallic dispersion than the Re/Al₂O₃ catalyst. Another factor is that the two supports (TiO₂ and Nb₂O₅) are reducible oxides, as previously

discussed (Manyar et al., 2010; Rozmysłowicz et al., 2015). However, according to (Muchave et al., 2020), when using heptane as an organic solvent in the hydrogenation reactions using the catalysts (Re/Nb₂O₅, Re/Al₂O₃, and Re/TiO₂), he observed a different profile to that obtained in this work, without using a solvent. The catalysts' catalytic performance increased in Re/Nb₂O₅ > Re/Al₂O₃ > Re/TiO₂. In addition to the low performance obtained when compared to reactions with the use of solvent, in the same work, the authors obtained a higher yield in the Re/Al₂O₃ catalyst when compared with Re/TiO₂ catalyst. The authors believe that although the Re/Al₂O₃ catalyst has less metallic dispersion, more Lewis sites are due, the solvent was essential to increase the reaction rate in hydrogenation. Since the Re/Al₂O₃ catalyst has a greater pore volume, the solvent facilitated the solubility of hydrogen in the substrate and decreased the resistance to mass transport, consequently increasing the reaction rate. The metallic dispersion of rhenium on the supports also explains the yield ratio achieved by each catalyst. Moreover, the low hydrogen solubility in the substrate and high resistance to mass transport affected the reaction rate and selectivity of fatty alcohols in all catalysts.

Catalyst deactivation tests: The catalyst deactivation tests were performed only with the Re/Nb₂O₅ catalyst due to the better catalytic performance than the Re/TiO₂ and Re/Al₂O₃ catalysts. Figure 1 illustrates the results of catalyst deactivation tests. The Re/Nb₂O₅ catalyst was reused twice after the first reaction.

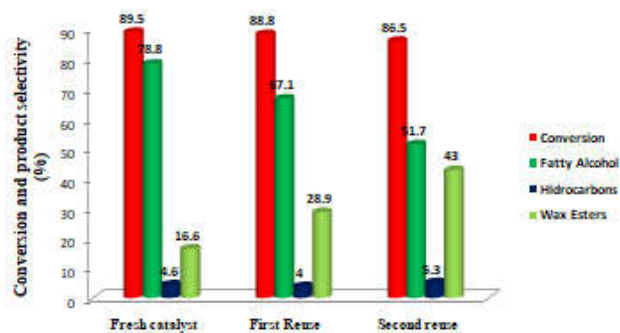


Figure 1. Show the results for ester conversion and product selectivity during the catalyst deactivation test of the Re/Nb₂O₅.

The results indicate a constant deactivation of the catalyst when comparing the catalytic performance of the first reaction to the third reaction. Quantitatively, the first obtained an average conversion of 89.5% and selectivity of fatty alcohols of 78.8%. In the second reaction, the conversion of 88.8 and selectivity in fatty alcohols of 67.1% was obtained. Therefore, there was a loss of selectivity of fatty alcohols of 11.7%, however, the conversion was statistically equal. When comparing the third reaction to the second, we had a loss in conversion and selectivity of 2.3% and 15.4%, respectively. These results indicate that although this catalyst maintains a good conversion at a temperature of 280°C and 70 bar, the selectivity of fatty alcohols decreases rapidly. This decrease in performance may be related to the partial or complete deactivation of the catalyst due to the production of water in previous reactions or possible contaminants of the raw material, for example, traces of glycerin and water. The possible contaminants responsible for the deactivation of catalysts in the hydrogenation reactions of triglycerides or derivatives (esters and fatty acids) are: water, glycerin, some peroxides, free fatty acids, glycerides derived from the use of pesticides (S, Cl and P), (Huang et al., 2009; Thakur and Kundu, 2016; van den Hark and Härröd, 2001). These contaminants from the coke are responsible for blocking the active sites of the catalysts.

The low selectivity of fatty alcohols favours the formation of wax esters; that is, the reaction of converting wax esters to fatty alcohols is increasingly slow. However, the formation of hydrocarbons remains at the same level as the first reaction. Similar results were found in the literature (Leal et al., 2019). According to Leal et al. (2019), studying the stability of Ni/Nb₂O₅ catalysts showed that after the third

reuse, the catalyst decreased its activity and selectivity in hydrocarbons. The authors demonstrated that this decrease was due to the drastic decrease in acidic Bronsted sites. Consequently, it favoured the production of fatty alcohols over hydrocarbons (Foo et al., 2014; Leal et al., 2019). The decrease in catalyst activity may have been due to the decrease in the metal surface area due to the growth of Ni particles (Leal et al., 2019). The increase of catalytic stability, according to the literature, can be achieved with the addition of a second metal. For example, (Braden et al., 2011) found that the addition of rhenium to the Ru/C catalyst increased the conversion of the substrate and the selectivity in fatty alcohols and gave the catalyst greater stability when compared to the Ru/C catalyst.

Experimental modelling and statistical analysis of data: The statistical modelling of the data was restricted only to the Re/Nb₂O₅ catalyst results, as this was the catalyst that presented the best catalytic performance compared with the other catalysts.

For the treatment of the results, the Design Expert 9.06 program was used, through ANOVA analysis of variance, to convert esters and formation of fatty alcohols (product of interest), as shown in Tables 4 and 5.

Analysis of Variance (ANOVA): The model that most described the analysis of variance for palm esters conversion data is the square root. The P-value of the model associated with the test-F statistic (P-value = 0.0001) observed in the ANOVA, Table 4 suggests that at a significance level of 5% ($\alpha = 0.05$), the model's hypothesis is statistically significant. The assessment of all factors (Temperature, pressure, and retention time) individually and the interaction between AB factors show statistical significance. However, the evaluation of the factors in a combined way found that the interactions (AC, BC) and the value of Lack of Fit proved unsuitable for the model; it is not statistically significant. The "Lack of F-value adjustment" of 0.82 implies the pure error's significance. Therefore, the lack of non-significant adjustment is good, suggesting that the model is adequate. Table 4, shows that the value of R², which was 0.985564, is in line with the value of adjusted R², which was 0.975939. Therefore, this information indicates that the data are adequate to the model. Therefore, in the F test, the R² values for the model in converting esters (87.3%) demonstrate good compatibility of the model data. The validating the experimental data's description in the model, graphs of regular data distribution (Fig 2a), and current versus predicted values (Fig 2b) were demonstrated. In these graphs in Figure 2, it is evident that the experimental points are well distributed along the line. Therefore, points observed in each sample are well arranged along the proposed line.

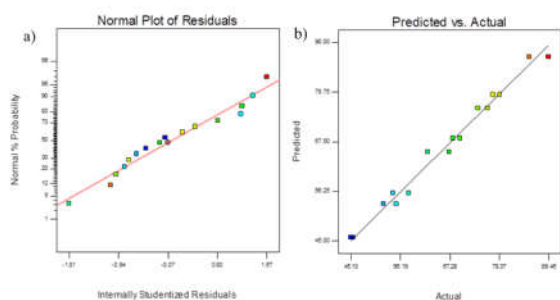


Figure 2. The figure shows: a) average probability of the reaction residues of the ester conversion; b) the distribution of Predicted vs Actual points of reaction of ester conversion

The analysis of the data's standard variance (ANOVA) provided the regression equations regarding the coded and non-coded factors (A-Temperature, B-Pressure, and C-Retention time) and their interactions for the ester conversion data.

Final Equation in Terms of Coded Factors:

$$\text{Conversion} = +8.09 + 0.68*A + 0.29*B + 0.30*C - 0.075*A*B + 9.954E-003*A*C + 0.014*B*C \quad \text{Eq.(1)}$$

$$\text{Final Equation in Terms of Actual Factors: Conversion} = -18.53741 + 0.088179*Temperature + 1.56597*Time - 4.53898E-004*Pressure - 4.99723E-003*Temperature*Time + 4.42387E-005*Temperature*Pressure + 9.37716E-004*Time*Pressure \quad \text{Eq. (2)}$$

According to Equations 1 and 2, all factors contributed to increasing esters' conversion, as demonstrated in the equations: coded and non-coded. In the coded equation, the most important factors and interactions, that is, which had the most significant contribution to the conversion of esters, follow the order A > C > B > AB > BC > AC. For the formation of fatty alcohols, the model that most described the variance analysis for the data for the formation of fatty alcohols was the linear model. The ANOVA results regarding the formation of fatty alcohols are presented in Table 5. Table 5 presents the analysis of variance (ANOVA) regarding the formation of fatty alcohols. The P-value of the model associated with the test-F statistic (P-value = 0.0001) observed in Table 5 of ANOVA suggests that, at a significance level of 5% ($\alpha = 0.05$), the hypothesis is rejected that, together, the factors have no effect, that is, the model is statistically significant. In addition to the significance of the model, it can also be seen that factors A, C and the interactions AB, AC, and ABC indicate that their terms are significant.

On the other hand, the B factor and the Lack of Fit value that was shown to be unsuitable for the model, that is, is not statistically significant. The "Lack of F-value adjustment" of 2,155 implies that the lack of adjustment is not significant about the pure error. Therefore, the lack of non-significant adjustment is good - suggesting that the model is adequate. Looking at Table 5, the value of R², which was 0.9917, is by the value of adjusted R², which was 0.98626. Therefore, this information indicates an adaptation of the experimental data to the model. Information about the statistical significance of the model, factors involved, and the R², Figure 3 was presented, which illustrates the graphs of regular data distribution and the graph of current versus predicted data for the formation of fatty alcohols. The experimental points' description is closer to the line; the closer the experimental points are to the line of the line, the more valid the model.

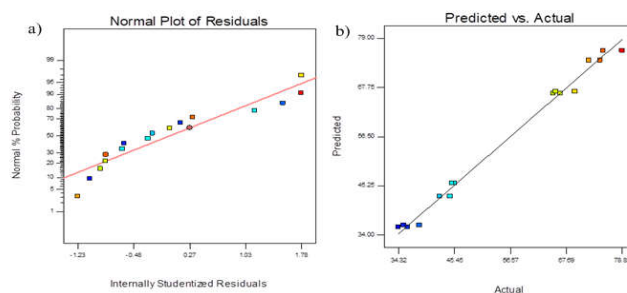


Figure 3. The figure shows: a) normal likelihood of fatty alcohol formation reaction residues; b) the distribution of Predicted vs Actual alcohol formation reaction points

The analysis of the effects of the factors and their interactions is presented through the line equations presented below.

$$\text{Final equation of the coded factors: Fatty Alcohol} = +55.56 + 2.32*A + 0.65*B + 15.33*C + 2.53*A*B - 1.84*A*C + 1.69*A*B*C \quad \text{Eq.(3)}$$

According to the straight-line equations, the order of importance of the most important factors and their interactions, that is, with greater sensitivity in the production of fatty alcohols, are C > AB > A > AC > ABC > B. Therefore, depending on the degree of importance, the variation in reaction time was the most important factor. Considering that correlation of the factors was observed, the increase in reaction time has always favoured the increase in fatty alcohol selectivity. In addition to the reaction time, the temperature proved necessary since the increase in temperature also favoured the formation of fatty alcohols. In some cases, there was the production of traces of hydrocarbons.

Table 1: Conversion and selectivity data of hydrogenation reactions using Re/Nb₂O₅ catalysts

Order	Factors			Response			
	Temperature (°C)	Time (hs)	Hydrogen (bar)	Conversion	Fatty Alcohol	Hydrocarbons	Wax Esters
1	250	8	40	45.63	38.47	0	61.58
2	250	8	40	45.1	35.37	0.9	63.73
3	280	8	40	69.6	42.56	0	57.46
4	280	8	40	67.98	44.56	0	55.65
5	250	10	40	58.1	34.32	0	65.68
6	250	10	40	54.52	36.09	0	63.91
7	280	10	40	73.6	45.46	1.44	57.46
8	280	10	40	75.81	44.96	1.03	54.01
9	250	8	70	52.4	72.2	3.3	24.5
10	250	8	70	55.31	74.44	2.95	22.61
11	280	8	70	78.5	66.5	3.7	29.8
12	280	8	70	77	65.14	2.13	32.73
13	250	10	70	62.3	65.6	3	31.4
14	250	10	70	67.13	69.43	1.22	29.35
15	280	10	70	85.1	75	4.1	20.9
16	280	10	70	89.46	78.82	4.6	16.58

Table 2. Conversion and selectivity data of hydrogenation reactions using Re/Al₂O₃ catalyst

order	Factors			Response			
	Temperature (°C)	Time (hs)	Hydrogen (bar)	Conversion	Fatty Alcohol	Hydrocarbon	Wax Esters
1	250	8	40	11	41.9	0	58.1
2	250	8	40	13.22	41.31	0.31	58.38
3	280	8	40	29.8	25.8	0	74.2
4	280	8	40	27.32	26.91	0	73.09
5	250	10	40	14.1	41.8	0	58.2
6	250	10	40	12.98	46	0	54
7	280	10	40	48.8	42.8	0	57.2
8	280	10	40	51.23	40.96	1.1	57.94
9	250	8	70	50.95	11.48	0	88.52
10	250	8	70	49.23	12.11	0	69.2
11	280	8	70	82.78	28.12	0	71.88
12	280	8	70	83.31	30.8	0	69.2
13	250	10	70	59.36	17.88	2.39	79.73
14	250	10	70	61.2	19.67	1.18	78.47
15	280	10	70	89.43	40.1	1.93	57.97
16	280	10	70	91.32	43.31	1.17	55.62

Table 3: Conversion and selectivity data of hydrogenation reactions using Re/TiO₂ catalyst

Order	Factors			Response			
	Temperature (°C)	Time (hs)	Hydrogen (bar)	Conversion	Fatty Alcohol	Hydrocarbon	Wax Esters
1	250	8	40	40.63	30.72	0	69.28
2	250	8	40	38.69	27.97	0	72.03
3	280	8	40	78.61	39.76	0.54	59.7
4	280	8	40	75.11	40.24	0	59.76
5	250	10	40	58.19	28.27	0	71.73
6	250	10	40	60.12	27.16	0	72.84
7	280	10	40	82.96	53.68	1.23	45.09
8	280	10	40	84.39	50.51	0	49.49
9	250	8	70	76.57	37.39	0	62.61
10	250	8	70	75.68	35.3	0	64.7
11	280	8	70	85.7	42.39	1.73	55.88
12	280	8	70	84.92	46.1	0.92	52.98
13	250	10	70	82.08	40.04	0	59.96
14	250	10	70	81.48	43.33	0	56.67
15	280	10	70	90.42	55.39	1.91	42.7
16	280	10	70	91.34	57.51	2.13	40.36

Optimization of the hydrogenation process: The optimum point for the model was obtained by screening experimental points and the factors used in factorial planning. This screening allowed the construction of empirical mathematical models to describe the studied system based on the studied conditions until reaching the optimum conditions. In this case, the optimization made for the conversion was of esters through the transformation of the quadratic root and the selectivity of fatty alcohols through a linear function within the established parametric conditions. The optimization result was obtained as optimal conditions of Temperature (280°C), pressure (70 bar), and retention time (10h) with a maximum conversion of 87.3% and a selectivity of fatty alcohols of 76.24%.

To estimate the defined coefficients, which seek to define the experimental data's best adjustment, the maximum values of temperature, pressure, and retention time were obtained. Therefore, once the best conditions for the process have been established to maximize the yield of fatty alcohols and minimize hydrocarbons and wax esters, surface and response graphs have been constructed that indicate the values of the factors (Figure 4). Figure 4 illustrates the ester conversion graphs' profile and the influence of factors on the catalyst's performance. Based on these profiles, it was observed that all factors had a positive influence. As previously described, the increase in any of the factors favoured the increase in conversion.

Table 4. Analysis of variance for the conversion of esters

Response	1	Conversion				
Transform:	Square root	Constant:	0			
ANOVA for selected factorial model						
Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		Mean	F	p-value	
Source	Squares	DF	Square	Value	Prob > F	
Model	10.36719	6	1.727865	102.40	< 0.0001	Hight significant
A-Temperature	7.497943	1	7.497943	444.37	< 0.0001	Hight significant
B-Time	1.376227	1	1.376227	81.56	< 0.0001	Hight significant
C-Pressure	1.398371	1	1.398371	82.88	< 0.0001	Hight significant
AB	0.0899	1	0.0899	5.328	0.0464	Significant
AC	0.001585	1	0.001585	0.0939	0.7662	Not significant
BC	0.003166	1	0.003166	0.1876	0.6751	Not significant
Residual	0.151857	9	0.016873			
Lack of Fit	0.014102	1	0.014102	0.8189	0.3919	Not significant
Pure Error	0.137755	8	0.017219			
Cor Total	10.51905	15				
Std. Dev.	0.129896		R-Squared	0.985564		
Mean	8.089426		Adj R-Squared	0.975939		
C.V. %	1.605754		Pred R-Squared	0.954374		
PRESS	0.479944		Adeq Precision	29.64381		

Table 5. Analysis of variance for selectivity of fatty alcohols

Response	2	Fatty Alcohol				
ANOVA for selected factorial model						
Analysis of variance table [Partial sum of squares - Type III]						
	Sum of		Mean	F	p-value	
Source	Squares	df	Square	Value	Prob > F	
Model	4057.5	6	676.25	180.51	< 0.0001	Hight significant
A-Temperature	85.9329	1	85.9329	22.938	0.0010	Significant
B-Time	6.8121	1	6.8121	1.8184	0.2105	Not significant
C-Pressure	3761.982	1	3761.982	1004.19	< 0.0001	Hight significant
AB	102.6169	1	102.6169	27.392	0.0005	Significant
AC	54.39063	1	54.39063	14.520	0.0042	Significant
ABC	45.76523	1	45.76523	12.216	0.0068	Significant
Residual	33.71633	9	3.746258			
Lack of Fit	7.155625	1	7.155625	2.1553	0.1803	Not significant
Pure Error	26.5607	8	3.320088			
Cor Total	4091.216	15				
Std. Dev.	1.935525		R-Squared	0.991759		
Mean	55.5575		Adj R-Squared	0.986265		
C.V. %	3.483824		Pred R-Squared	0.973954		
PRESS	106.5602		Adeq Precision	31.53145		

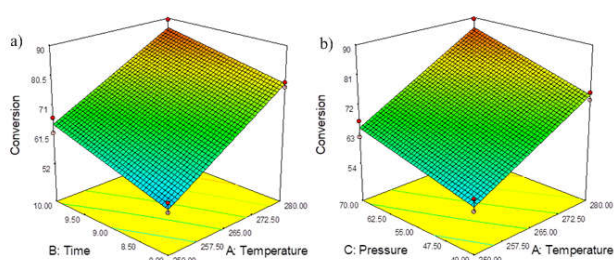


Figure 4. Represents the graphs of the response surface for the conversion of esters about the factors: a) Time (min) and Temperature (°C) and b) Pressure (bar) and Temperature (°C)

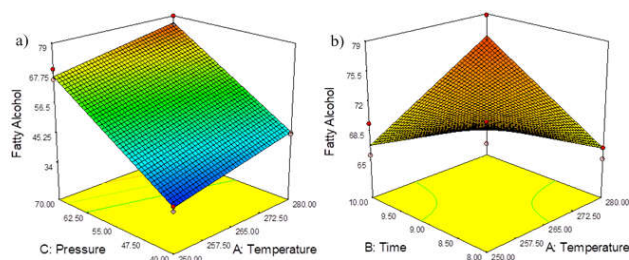


Figure 5. Represents the graphs of the response surface for the fatty alcohol yield about the factors: a) Pressure (bar) and temperature (°C) and b) Time (min) and Temperature (°C)

Based on the profiles in the graphs in Figure 5, the selectivity of fatty alcohols is dependent on the three factors (temperature, pressure, and retention time). As already described above in the conversion of esters (Figure 4), the longer the retention time, the greater the time and pressure, the greater the conversion and selectivity of fatty alcohols obtained. The better catalytic performance better yield obtained with the Re/TiO₂ and Re/Nb₂O₅ catalysts may be due to the more excellent metallic dispersion than the Re/Al₂O₃ catalyst to our XPS results (Muchave et al., 2020). Also, it may be because the supports are reducible oxides. Some studies have shown in recent years that catalysts supported on reducible oxides have a high potential for the reaction of fatty alcohol production (Tomishige et al., 2020).

CONCLUSION

The results show that the catalysts performed well in converting palm esters and product selectivity to fatty alcohols. The analysis of the factors (hydrogen pressure, temperature, and residence time) made it evident that all were fundamental for the catalysts' catalytic performance. Therefore, it was concluded that the higher the temperature, the higher the conversion rate of esters. Longer residence time influenced the increase in the selectivity of fatty alcohols. The best yield was 87,3% conversion of esters and 76,24% selectivity of fatty alcohols, achieved at a temperature of 280°C and 70 bar of hydrogen pressure using Re/Nb₂O₅ catalyst. In this way, the catalysts' catalytic performance increases in the order: a) reactions

without using a solvent: Re/Nb₂O₅> Re/TiO₂> Re/Al₂O₃. The catalysts' characterizations such as metallic dispersion, type, and quantity of acidic sites obtained in each catalyst (Muchave et al., 2020) explain the achieved efficiency. The deactivation tests showed that the Re/Nb₂O₅ catalyst has good stability, as the loss of catalytic activity remains almost stable even in the third reaction.

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DECLARATIONS

Conflict of Interest – All authors declare that they have no conflict of interest.

Availability of data and materials

All data will be made available on request according to the journal policy.

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