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Biowax Production from the Hydrotreatment of Refined Palm Oil (RPO)

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Abstract: In this study, conditions were determined to obtain a solid wax with a waxy ester content of more than 25% from the hydrotreating of palm oil. The experiments were conducted in a pilot-scale fixed-bed reactor. The influence of temperature, liquid hourly space velocity (LHSV), and pressure on the conversion of triglycerides were evaluated using a nickel molybdenum catalyst (NiMo/Al₂O₃). The variables were evaluated between 240 and 260 °C, 1 and 2 h^{−1} and 41 and 55 bar, respectively. Based on these results, the best conditions were T:240–260 °C; P: 90 bar; LHSV: 1.5 h^{−1}; hydrogen/oil ratio 472 LN/L with a conversion around 60 wt%; and a selectivity towards waxy esters of 40 wt%. These conditions were then validated with a second catalyst (NiMoB/Al₂O₃), yielding a triglyceride conversion of about 60 wt% and a waxy ester concentration of around 30 wt%.

Keywords: biowax; refined palm oil; hydrotreatment



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1. Introduction

Waxes are generally defined as “a greasy, tacky solid with varying degrees of brightness, viscosity and plasticity, which melts easily” [1]. Waxes can refer to fatty components obtained from vegetal, animal, or mineral origin. They also can be classified as natural or synthetic. The latter are low molecular weight waxes derived from the polymerization of raw materials, such as methylene, ethylene, and alpha-olefins. Natural waxes refer to animal and vegetable origins, which can be chemically modified by methods, such as hydrogenation and esterification. This study focuses on producing waxes from vegetable oil, specifically palm oil. Vegetable oils are a promising source for making environmentally friendly alternative waxes due to their abundance and inherent biodegradability [2].

Waxes from vegetable oils can be obtained by transforming these oils into solid or semi-solid fats, waxes, and paraffins through microbial processes or partial or total catalytic hydrogenation. Each biowax application requires different physical and chemical properties that must be fulfilled by the product obtained [3–8].

The reactions that take place during the hydrotreatment of vegetable oil are shown in Table 1. The main reactions are: break down of the triglycerides into the constituent fatty acids, partial hydrogenation of unsaturated fatty acids, the formation of fatty alcohols and the production of esters from the esterification of free fatty acids and fatty alcohols [9].

Several studies have reported that the selective hydrogenation of high molecular weight hydrocarbons and triglycerides is achieved with NiMo catalysts more than CoMo catalysts. CoMo catalysts promote the hydrogenolysis of bond C-O, while NiMo catalysts promote the C-C hydrogenolysis of the triglycerides and fatty acids. The hydrogenation of carbon–carbon double bonds of unsaturated fatty acids occurs at a lower temperature than oxygen removal reactions (decarboxylation, decarbonylation, and hydrodeoxygenation) [10–12].

Most studies in the hydrotreating of vegetable oils are related to obtaining liquid products. For example, the production of green diesel using mono or bimetal catalysts, such as NiMo or CoMo, at temperatures between 300 °C and 400 °C and pressures within

the range of 34 bar and 55 bar [9,12–18]. For example, the production of biojets, using a bifunctional catalyst [19–24], at 330–550 °C and 48–62 bar, to promote the complete hydrodeoxygenation of fatty acids and triglycerides. Other studies focus on obtaining lubricants by processing vegetable oil at 130–160 °C and 0.015–0.1 psig with NaOCH₃ or H₂SO₄ catalyst. However, there are few studies related to solid waxes. Guzman et al. [10] developed a process that employs catalysts to obtain solid waxes rich in high molecular weight paraffins at conditions around 140–260 °C and 870–90 bar.

Table 1. General reactions in partial HDT of RPO. Modified from [9] and [10].

Reactions	Reaction Type	ΔH^0_{Rxn} [kJ/mol]
TAG + 3H ₂ → FFA + C ₃ H ₈	Hydrogenolysis/Hydrogenation	≈ −220 to −331
FFA + 2H ₂ → FA + H ₂ O	(Initial reactions)	≈ −41
FFA + H ₂ /2H ₂ → HFFA	Hydrogenation	≈ −110 *
FFA/HFFA → P _{C−1} + CO ₂	Decarboxylation (DCO ₂)	≈ −7 to −10 *
HFFA/FFA + H ₂ /2H ₂ → P _{C−1} + H ₂ O	Decarbonylation (DCO)	≈ 32 to 35 *
HFFA/FFA + H ₂ /2H ₂ → P + H ₂ O	Hydrodeoxygenation	≈ 107
FFA/HFFA + FA → WE + H ₂ O	Esterification	≈ −15

TAG: Triglycerides, FFA: Free Fatty Acids (unsaturated or saturated), FA: Fatty Alcohols, HFFA: Hydrogenated Free Fatty Acids, WE: Waxy Esters, P: Paraffins, C−1: minus one carbon in the paraffin. * Estimated in ASPEN-HYSYS V12.1.

The studies discussed previously show that both the catalyst and the operating conditions determine the type of product obtained from the vegetable oils hydrogenation. These process variables have a remarkable impact on the chemical composition of the obtained wax. In particular, they could change the conversion of triglycerides (TGA) into fatty acids (FFA), waxy esters (WE), fatty alcohols (FA), and paraffins (P) [10,25–27]. Thus, it is possible to select conditions to produce a palm wax with attractive physical-chemical properties for its use in cosmetic formulations [6,10,26,28–33].

The current study aims to determine the main process variables in the hydrotreating (HDT) of refined palm oil (RPO) with NiMo catalysts. Triglyceride conversion is expected to be greater than 50%, while the chemical composition of the waxes obtained includes a varied range of chemical families. (paraffins, fatty acids and alcohols, waxy esters, mono/di, and triglycerides) instead of one predominant family. The interest is to have a solid wax that can be used in cosmetics formulation, so it is intended to have a waxy esters concentration higher than 25 wt%.

2. Materials and Methods

2.1. Feed and Reagents

The main characteristics of the vegetable oil used in this study for the hydrotreating tests are given in Table 2. This palm oil has been previously treated by degumming, bleaching, and deodorization processes [34].

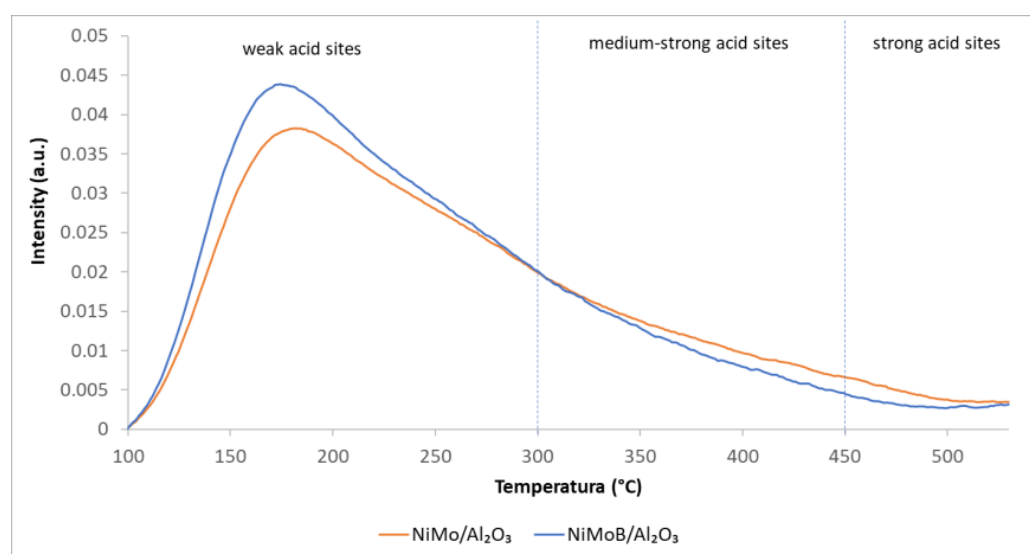
The hydrogen used in the hydrotreating of the RPO is of grade 5 purity (99.999%), and the 99.999% pure nitrogen is used for hermeticity tests in the pilot plant.

2.2. Catalysts

The catalysts consist of nickel-molybdenum sulfide particles dispersed on an alumina support with phosphorus as a dopant in the trilobe form. One of the catalysts contains boron (NiMoB/Al₂O₃), and the other does not (NiMo/Al₂O₃). The presence of Boron implies an improvement in the acidity of the catalysts, specially through weak acid sites, as shown in Figure 1. The acidity of the catalyst is an important parameter to take into account since it favors esterification reactions; this work seeks to increase the content of this chemical group in the wax obtained. No additional information on catalyst properties is given for confidentiality reasons.

Table 2. General Properties of the RPO.

Characteristic	Analytical Method	Units	Refined Palm Oil (RPO)
Density (15 °C)	ASTM D 1298	g/mL	0.8944
Molecular weight		g/mol	659.5
Melting Point	NTC 213	°C	26.2
Acid Number	ASTM D 664	mg KOH/g	0.18
Iodine Value	NTC 283	g I ₂ /100 g	49.7
Fe Content	ICP-OES	ppm	<3.33
P Content	ICP-OES	ppm	<5.47
Na Content	ICP-OES	ppm	<5.07
K Content	ICP-OES	ppm	<1.27
Mg Content	ICP-OES	ppm	<0.17
Ca Content	ICP-OES	ppm	<4.95

**Figure 1.** NH₃-TPD of catalyst Reference 1 (NiMo/Al₂O₃) and Reference 2 (NiMoB/Al₂O₃).

2.3. Experimental Set-Up

The process conditions were tested in a continuous pilot unit with a fixed bed reactor with an electrical heating system and pressure and level control (see Figure 2). The feed (RPO) went through the reactor, and the effluent passed to a high-pressure separator. Finally, the product stream passes through a low-pressure phase separator to segregate the liquid phase from the gas phase. The gas stream was transferred to a wet gas flowmeter. The gas effluent (gas sampling) was analyzed by gas chromatography using the standard procedure UOP 539. The liquid product (wax) was sent to the product tank. The entire liquid recovery system was heated to 50 °C to keep the product in a liquid state. The collected product was left at room temperature, turning into a solid state. This product was analyzed by gas chromatography coupled with a mass detector. This made it possible to identify the distribution of chemical families. The NTC 283 method was used to establish the iodine value.

2.4. Catalytic Evaluation

In both cases, 90 cm³ of catalyst was loaded into the reactor. First, the catalyst was dried in situ with a nitrogen flow at a temperature of 120 °C for one hour. The catalyst was activated by injecting a mixture of hydrocarbons blend (C with 2.5 v/v% of dimethyl disulfide (DMDS)) into the reactor under the presence of hydrogen at a pressure of 30 bar and a temperature of 350 °C. The sulfidation was carried-out until a major breakthrough of the H₂S concentration in the outlet gas stream was observed. Once the catalyst was

activated, a stabilization stage was performed for 72 h, in which the operating conditions were imposed for 14 h with a non-spiked hydrocarbon. Then, a purge with RPO was performed for 24 h to remove any trace of the stabilization feed from the unit. Finally, the catalytic evaluation was carried out for 30 h.

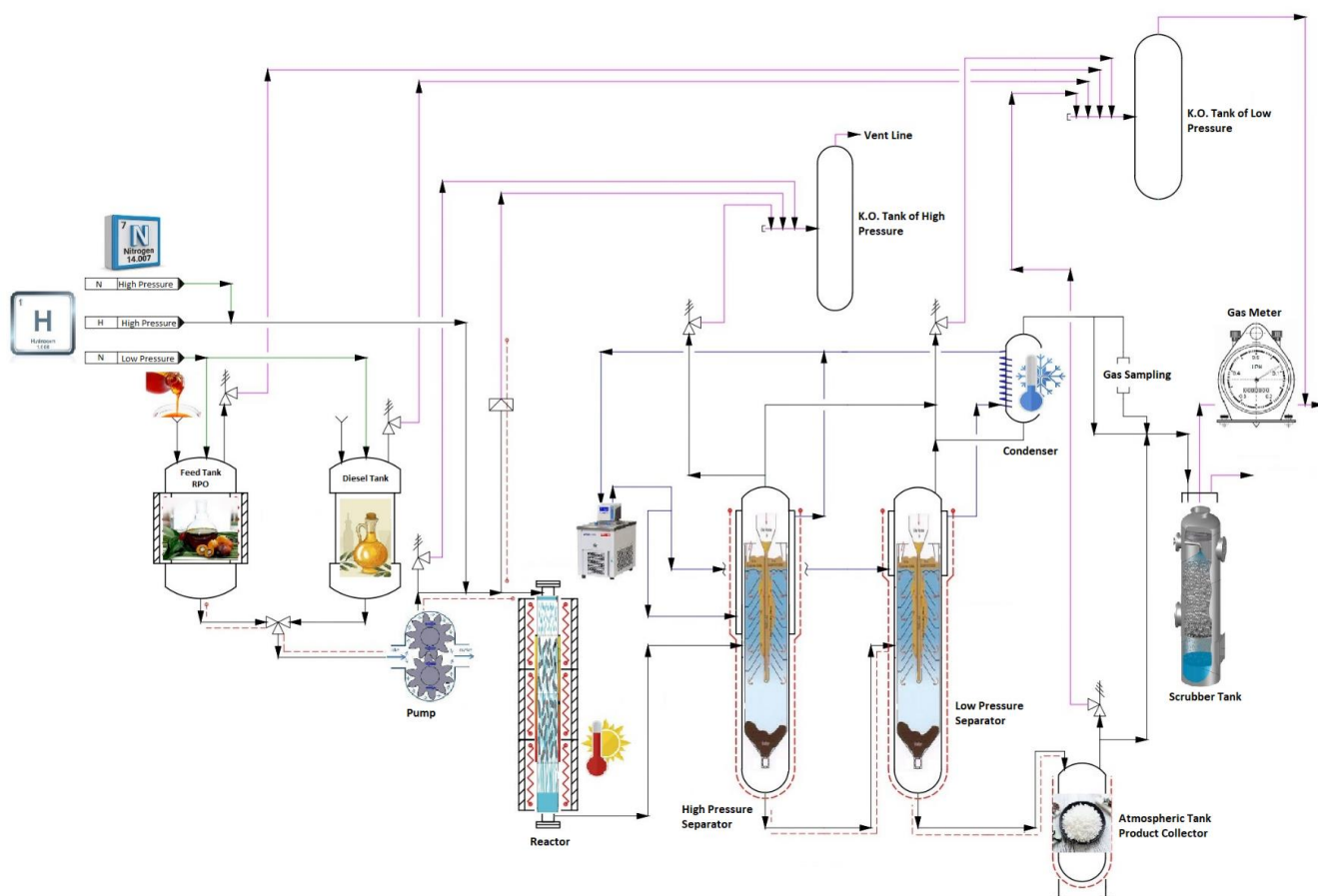


Figure 2. Process Flow Diagram of the HDT Pilot Plant.

The effect of temperature, pressure, and LHSV on both the conversion and the distribution of chemical families, was assessed. The conditions for each experiment are indicated in Table 3. These conditions were selected according to the process patented by ECOPETROL S.A. [11].

The catalyst performance was assessed by calculating the triglycerides (TAG) conversion according to Equation (1), and the selectivity of the process toward the waxy esters was determined by Equation (2).

$$\% \text{Conversion} = (\% \text{TAG}_{\text{Feed}} - \% \text{TAG}_{\text{Pro}} / \% \text{TAG}_{\text{Feed}}) \times 100 \quad (1)$$

$$\text{Selectivity} = [\% \text{WE}_{\text{Pro}} / (\% \text{TAG}_{\text{Feed}} - \% \text{TAG}_{\text{Pro}})] \times 100 \quad (2)$$

where:

%TAG_{Feed}: Percent of Triglycerides in the feed;

%TAG_{Pro}: Percent of Triglycerides in the product;

%WE_{Pro}: Percent of Waxy Esters in the product.

Table 3. Test conditions for Reference 1 ((NiMo/Al₂O₃) and Reference 2 (NiMoB/Al₂O₃) catalysts.

Catalyst	Catalyst Bed [cm ³]	Feed	Temperature [°C]	Pressure [bar]	LHSV [h ⁻¹]	Volumetric Ratio @[LN/L]
Reference 1 (NiMo/Al ₂ O ₃)	90	Refined Palm Oil (RPO)	250 260	55	2	472
Reference 1 (NiMo/Al ₂ O ₃)	90	Refined Palm Oil (RPO)	250	41 55 90	2	472
Reference 1 (NiMo/Al ₂ O ₃)	90	Refined Palm Oil (RPO)	250	55	1 1.5 2	472
Reference 2 (NiMoB/Al ₂ O ₃)	90	Refined Palm Oil (RPO)	240 250 260	55	1,5	472

2.5. Chromatographic Analysis

The condensed products were characterized by GC-MS in an Agilent 7890A gas chromatograph configured with Mass Detector (5975C MSD) and Flame Ionization Detector (FID) with a Programmable High-Temperature Injection Port. For the chromatographic separation, a SIMDIS-HT column (5 m × 0.53 µm × 0.15 µm) was used, with a working temperature from 40 °C to 390 °C, covering a distillation range from 36 °C to 652 °C, equivalent in carbon number of n-paraffins C5 to C72.

To analyze the reaction products in the solid state (wax), the samples were diluted in carbon disulfide at a ratio (98:2), and 2 µL of this dilution was injected into the chromatograph.

3. Results and Discussion

3.1. Operational Conditions Test for Reference 1 Catalyst (NiMoB/Al₂O₃)

3.1.1. Temperature Effect on the Hydrotreatment of Vegetable Oils

Figure 3 shows the conversion and selectivity as a function of the reaction temperature.

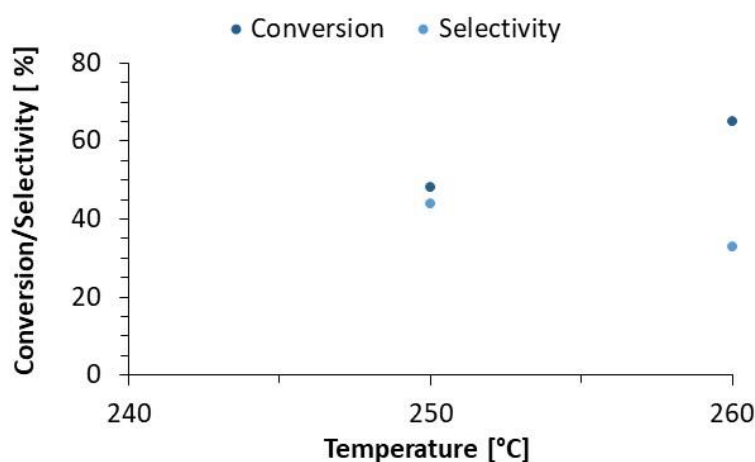


Figure 3. Conversion and selectivity at 55 bar and LHSV: 2 h⁻¹, as a function of temperature for catalyst reference 1(NiMo/Al₂O₃).

Increasing temperature from 250 °C to 260 °C increases triglyceride conversion by 17% and decreases selectivity to waxy esters by 11%. A higher reaction temperature favors the reactions presented in Table 1 (hydrogenolysis/hydrogenation) [10,35], which leads to a further transformation of triglycerides in different chemical families, whose distribution is shown in Figure 4.

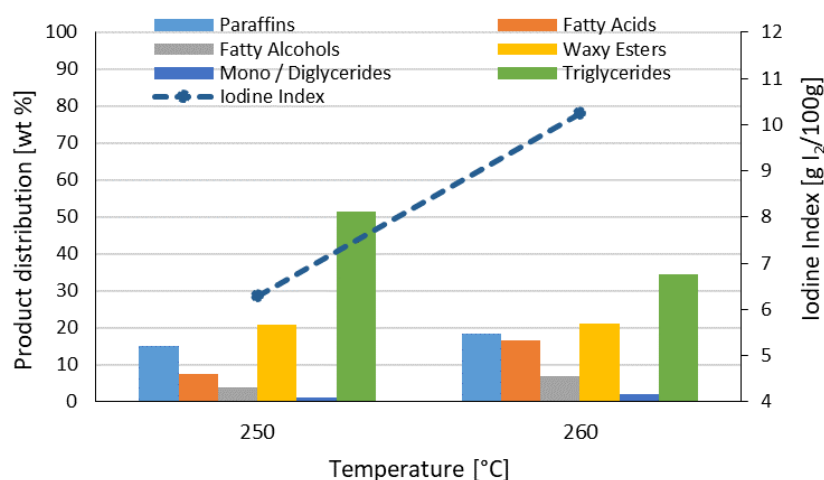


Figure 4. Composition of the reaction product (wax) at 55 bar and LHSV: 2 h^{−1} as a function of temperature for catalyst, Reference 1, (NiMo/Al₂O₃).

With the increase in reaction temperature, a rise in the concentration of fatty acids is shown through hydrogenolysis/hydrogenation reactions of triglycerides. These are the initial reactions to transform oxygenate compounds in the chemical families, shown in Figure 4. A slight increase in paraffin concentration was also observed, primarily due to decarboxylation (DCO₂) and decarbonylation (DCO) reactions, followed by hydrodeoxygenation of fatty acids. The content of fatty alcohols increases slightly due to hydrogenolysis reactions of the C=O bond of fatty acids [10,35–37], which is also favored in this temperature range [10].

The increase in the formation of paraffins is principally associated with decarboxylation reactions (DCO₂), as suggested by the increase in CO₂ concentration in the gas stream (Table 4). The CO is characteristic of decarbonylation reactions, and its concentration in the gas does not increase substantially with the reaction temperature rise. These are common reaction pathways to produce paraffin from vegetable oils. [14,35–37].

Table 4. Oxygenated byproducts as a function of reaction temperature.

Temperature [°C]	CO ₂ [Vol. Molar%]	CO [Vol. Molar%]
250	10.63	1.0
260	12.04	1.3

The iodine value is a measure of the degree of unsaturation of the liquid product. The increase in this value from 6 g of I₂/100 g for the reaction at 250 °C to 10 g of I₂/100 g for the reaction at 260 °C may be related to the higher formation of fatty acids, which, by their chemical nature, have a higher iodine value than the other chemical families that compound the wax, such as paraffins, alcohols, esters, and triglycerides.

These results show that the increase in temperature affects the conversion and selectivity of the RPO hydroprocessing, favoring the conversion of triglycerides and reducing the selectivity towards waxy esters. In addition, a product with a higher iodine value is obtained. This implies that biowaxes with different compositions can be obtained by varying the reaction temperature by 10 °C.

3.1.2. Pressure Effect on the Hydrotreatment of Vegetable Oils

Figure 5 illustrates the conversion and selectivity concerning the total pressure. the reaction conditions are temperature: 250 °C, LHSV: 2 h^{−1} y R: 472 LN/L.

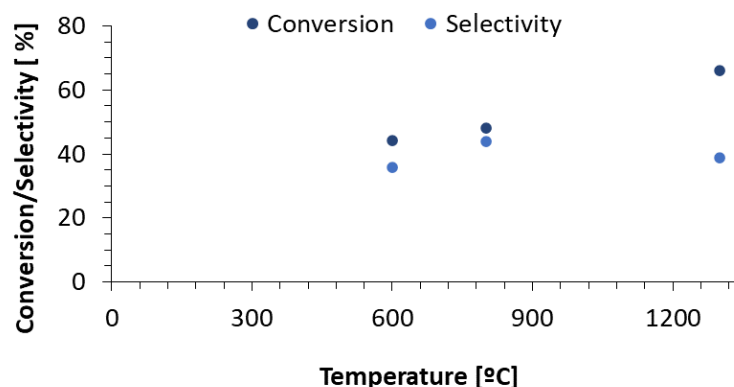


Figure 5. Conversion and selectivity at 250 °C and LHSV: 2 h^{−1} as a function of pressure for catalyst, Reference 1, (NiMo/Al₂O₃).

Figure 5 shows that at 41 bar, the triglyceride conversion was 44%; it reaches 48% by increasing the pressure to 55 bar, and finally, a conversion of 66% is obtained at 90 bar. This indicates that the conversion increased proportionally with the pressure since this variation implies a higher availability of hydrogen in the reaction system; therefore, the hydrogenolysis/hydrogenation reactions were promoted. Regarding selectivity, there is no evidence of a change in the production of waxy esters due to the increase in the total pressure.

Figure 6 shows the composition of the chemical families in the wax and the iodine number as a function of the total pressure. The increase in triglyceride conversion is reflected in higher production of fatty acids, which increase their concentration by 6% for the biowaxes obtained at 90 bar. This could be, once again, due to the higher availability of hydrogen in the reaction system, which, together with the catalyst used (NiMo), promotes both the hydrogenation of the unsaturated compounds in the raw material and the rupture of the C-C bond in the triglycerides to produce fatty acids. The subsequent reactions for the formation of fatty alcohols, hydrogenation of the C=O bond, and the breakup of the C-O bond are also favored, producing an increase of 5% of these compounds for the reactions at 90 bar of pressure. [10,12,26,38]. The waxy esters concentration in the biowax obtained by the RPO hydrotreatment increases linearly with the total pressure increase. This increase could be due to the higher production of fatty acids and alcohols favored by the reaction conditions [10], which are the precursors of waxy esters [9,12,38].

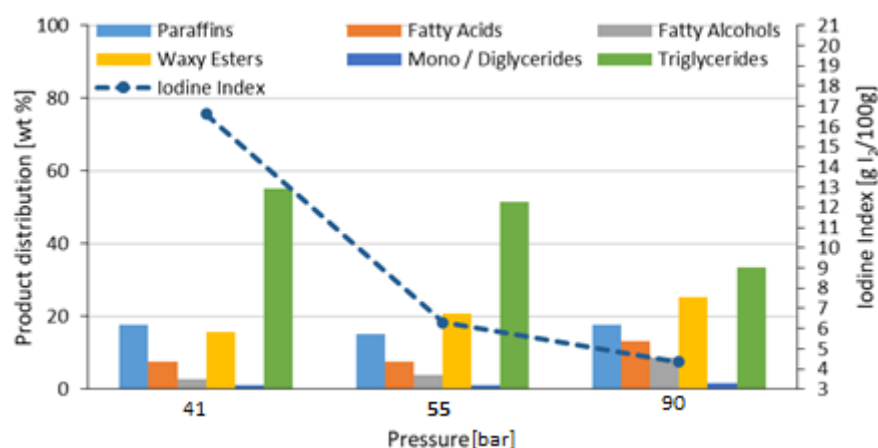


Figure 6. Composition of the reaction product (wax) at 250 °C and LHSV: 2 h^{−1} as a function of pressure for catalyst, Reference 1, (NiMo/Al₂O₃).

The concentration of paraffins does not change appreciably in biowaxes with the changes in total pressure. This could indicate that the increase in the partial pressure of

hydrogen makes the process more selective towards the formation of fatty alcohols from hydrogenolysis of the C=O bond in the fatty acids and, subsequently, the formation of the waxy ester, which is favored in this range of operation conditions according to Le Chatelier's equilibrium principle [39,40]. Table 5 shows the analysis results of the reaction gases according to the possible routes for the paraffins formation.

Table 5. Oxygen byproducts as a function of total pressure.

Pressure [bar]	CO ₂ [Vol. Molar%]	CO [Vol. Molar%]
41	9.40	1.01
55	10.63	1.00
90	11.32	1.10

Table 5 shows that the production of paraffins occurs mainly by decarboxylation (DCO₂) and decarbonylation (DCO) reactions. In addition, the increase in the total pressure does not have a notable effect on these paraffin production routes since there is no significant variation in either CO₂ or CO concentration in the reaction gases.

The changes in the distribution of the chemical families in the biowaxes cause the properties of the final product to be modified, which can be evidenced in the reduction in the iodine number as the pressure increases. Hydrogenating the double and triple bonds of compounds present in vegetable oil increases the production of saturated compounds [10,35].

According to these results, the change in total pressure notably influences triglyceride conversion, but its effect on selectivity towards waxy esters is not significant. Additionally, there is no evidence of an appreciable increase in the iodine number when the total pressure increased from 55 bar to 90 bar. Instead, the total pressure of 55 bar represents a less demanding requirement in terms of the materials and thickness used in the construction of a production plant, which would decrease the investment cost (CAPEX) in the case of a possible scaling up of the process.

3.1.3. Liquid Hourly Space Velocity Effect on the Hydrotreatment of Vegetable Oils

Figure 7 shows the conversion and selectivity as a function of space velocity. The reaction conditions are temperature: 250 °C, pressure: 55 bar, and R: 472 LN/L.

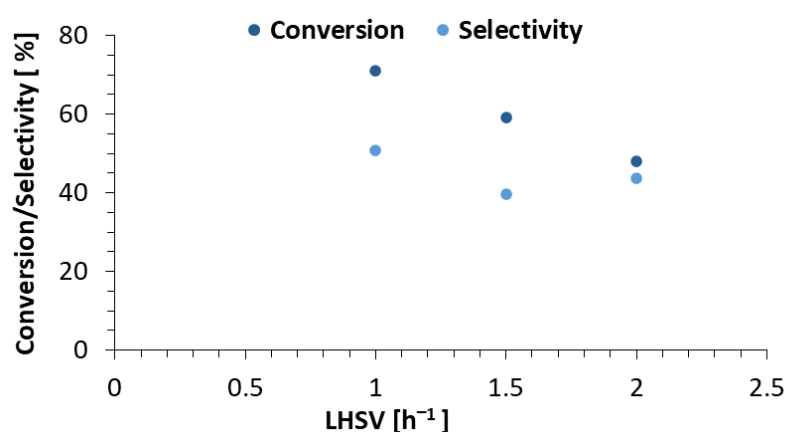


Figure 7. Conversion and selectivity at 250 °C and 55 bar as a function of LHSV for catalyst, Reference 1, (NiMo/Al₂O₃).

The increase in the LHSV affects the conversion of triglycerides. The conversion decreases by 23% when it goes from 1 h⁻¹ to 2 h⁻¹ due to the higher space velocity and the decrease in contact time between the palm oil and the catalyst. Selectivity is reduced by around 6% by the increase in LHSV. We can explain it by the fact that the esterification reaction is slower than the reactions for obtaining other compounds, such as paraffin [41].

Figure 8 shows the composition of the chemical species in the product as a function of the LHSV.

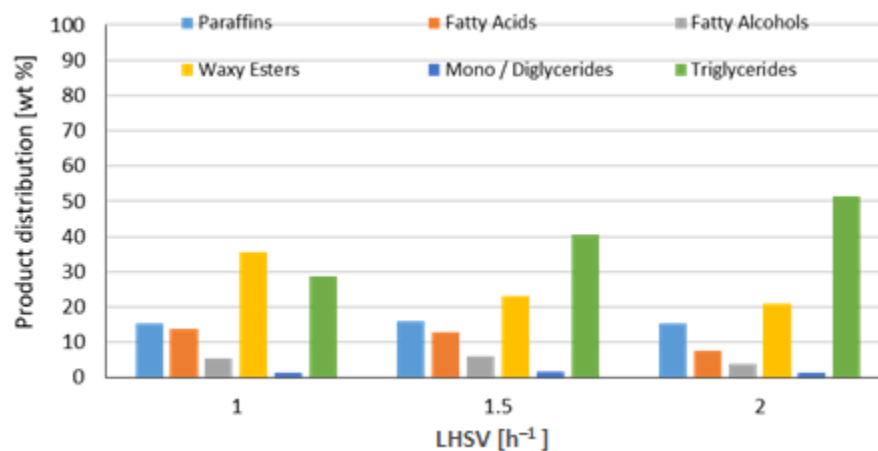


Figure 8. Composition of the reaction product (wax) at 250 °C and LHSV: 2 h^{−1} as a function of LHSV for catalyst, Reference 1, (NiMo/Al₂O₃).

Figure 8 shows that as the liquid hourly space velocity increases, the triglyceride content in the reaction product increases from 28% to 51%. The opposite behavior was observed for the waxy esters, which passed from 36% to 21%, and the content of fatty acids decreased from 14% to 7%. There is no appreciable change in the content of paraffin and fatty alcohols when the spatial velocity varies.

According to these results, the transformation of triglycerides to fatty acids decreases by reducing the contact time between the palm oil and the catalyst. Therefore, is suggested to use an LHSV less than or equal to 1.5 h^{−1}. The esterification reactions occur slower than paraffin formation; this can be seen by the little variation in paraffin content for the different spatial velocities evaluated. It can be deduced that fatty alcohols are the limit reagent for the esterification reaction since their concentration is always lower than that of fatty acids [38,42,43].

Table 6 shows the analysis results of the reaction gases based on the possible deoxygenation routes that can occur to produce paraffin (DCO, DCO₂, and HDO), fatty alcohols by hydrogenolysis of the C=O bond, and waxy esters [10,26].

Table 6. Oxygen byproducts as a function of LHSV.

LHSV [h ^{−1}]	CO ₂ [Vol. Molar%]	CO [Vol. Molar%]
1.0	14.61	1.37
1.5	10.86	1.16
2.0	10.63	1.00

The formation of paraffin is higher by the decarboxylation route (DCO₂), which is favored by the increase in the residence time of the palm oil in the catalytic bed. Regarding decarboxylation, no considerable influence of space velocity on its production was observed [9,10,13].

Additionally, as seen in Figure 9, an increase in the concentration of light compounds at lower LHSV was observed, accordingly with the carbon numbers distribution from C5 to C12 in the biowax obtained. These catalytic hydrocracking reactions are mainly promoted by acid sites present in the solid; in the Reference 1 catalyst (NiMo/Al₂O₃), this is attributed to the presence of phosphorus as a dopant in the support, which is commonly used to improve metal dispersion without significantly affecting its hydrogenating activity and reducing deactivation by coke formation during hydrotreating [44].

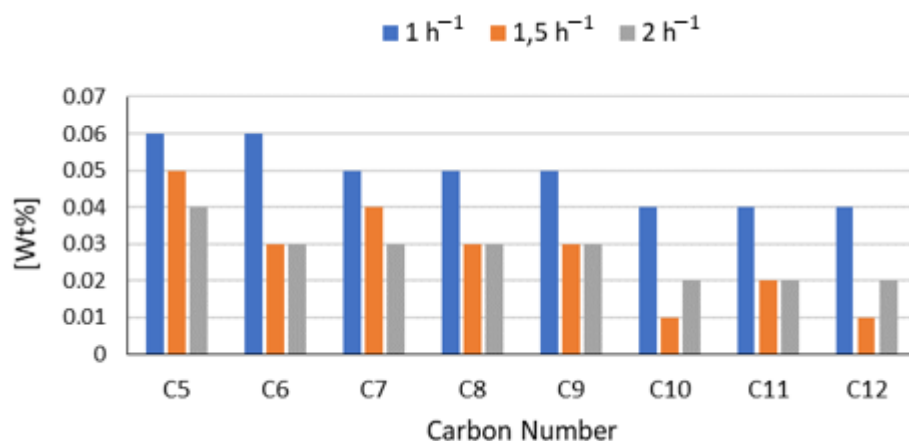


Figure 9. Lightweight carbon distribution as a function of LHSV (NiMo/Al₂O₃).

This increase may affect the overall balance of the process because of possible losses due to volatile or gaseous compounds. Hence, it is recommended to use a space velocity of 1.5 h⁻¹, which achieves a good compromise between conversion, esters content, and the reduction in possible mass losses related to the formation of light compounds and gas products. This also promotes the productivity of a possible industrial plant since a higher flow of feed oil per day would be processed compared to the amount to be processed with a space velocity of 1 h⁻¹.

3.2. Effect Test of the Selected Operational Conditions in the Reference 2 Catalyst (NiMoB/Al₂O₃)

The Reference 2 catalyst differs from the Reference 1 catalyst because of the presence of boron as an additional doping agent in the support. For the tests, temperatures of 240 °C, 250 °C, and 260 °C were evaluated for a pressure of 55 bar, an LHSV of 1.5 h⁻¹ and an H₂/Oil ratio of 472 LN/L. Figure 10 shows the conversion and selectivity towards waxy esters by hydrotreatment of refined palm oil.

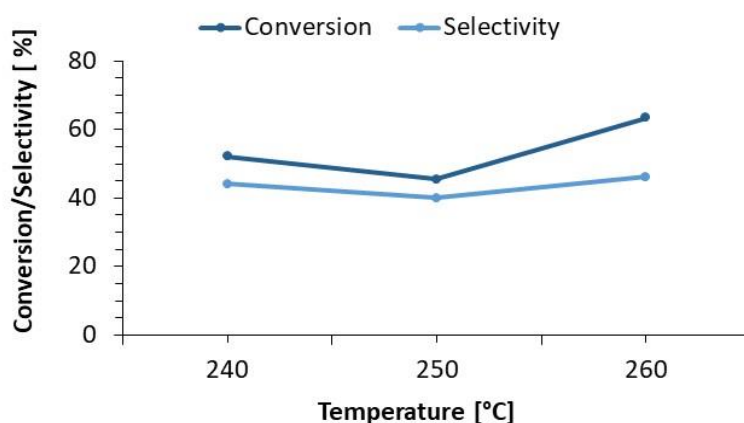


Figure 10. Conversion and selectivity at 55 bar and LHSV: 1.5 h⁻¹ for catalyst, Reference 2 (NiMoB/Al₂O₃).

As observed in Figure 10, the reference 2 catalyst follows the same behavior as the previously evaluated catalyst, i.e., with increasing temperature, the conversion increases due to the kinetics of the reactions. Concerning selectivity, negligible change was seen due to the increase in reaction temperature, despite the increase in triglyceride conversion at 260 °C. This may be due to the presence of boron in the catalyst, which helps to maintain the distribution of the chemical families in the product almost constant.

When comparing the conversion at 250 °C and LHSV of 1.5 h⁻¹ of the Reference 2 catalyst (46%wt) regarding the Reference 1 catalyst (59%wt), a difference of 13%wt is

observed. The lower conversion obtained with the Reference 2 catalyst could be related to the presence of boron, which provokes changes to the surface and acid properties of the catalyst. These modifications promote the esterification reactions at these process conditions [44,45], and, as it was mentioned before, these reactions are slow, and therefore a minor triglycerides amount are converted at the same time on stream. The previous is in concordance with the percentage of waxy esters present in the waxes obtained, which for the Reference 1 catalyst, was 23.23%wt and for the catalyst with Boron was 28.9%wt. Figure 11 presents the carbon distribution of the waxes obtained with the two catalysts, it is noticed that there are more light carbons between C13 and C21 with the Reference 2 catalyst. This can be related to the higher acid sites of this catalyst (Figure 1), as is known that the addition of boron improves the alumina acidity, resulting in increased cracking reactions [46].

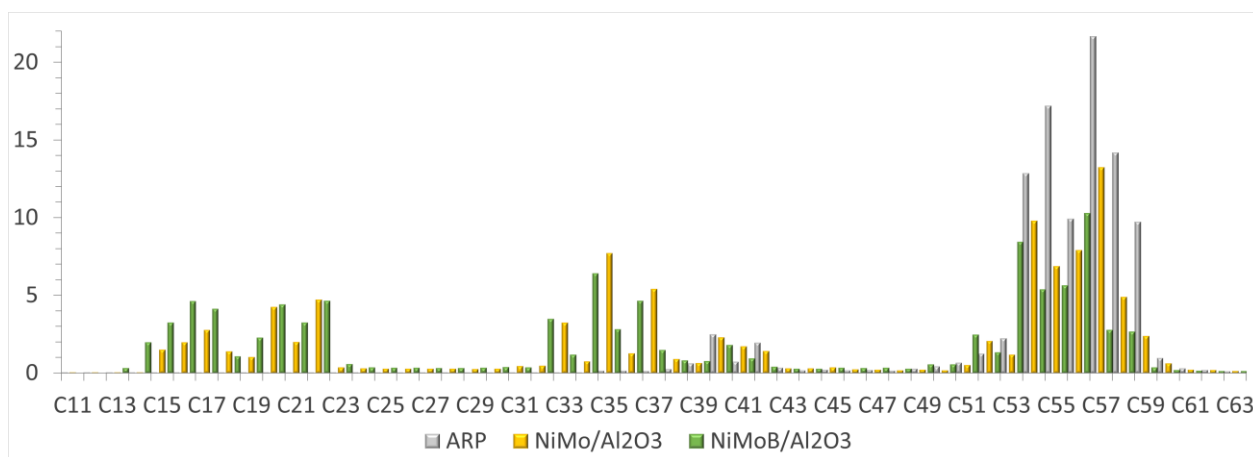


Figure 11. Carbon distribution of the RPO and the waxes obtained with the Reference 1 (NiMo/Al₂O₃) and Reference 2 catalysts (NiMoB/Al₂O₃).

Regarding the composition of the reaction products (Figure 12), it was observed that the content of triglycerides is reduced when the reaction temperature reaches 260 °C, dropping to 47 wt%. This increase in conversion corresponds to a 10% increase in the paraffin content and a higher content of waxy esters of around 6%, concerning the values obtained at 240 °C. For all the reaction temperatures evaluated, no appreciable content of fatty alcohol is observed in the product obtained, which may be due to the higher density of acid sites in the Reference 2 catalyst that promote the esterification reaction of fatty acids and alcohols. Additionally, it is verified that the fatty alcohol is the limit reagent for this reaction since the esterification occurs until these compounds are exhausted, leaving unreacted fatty acids.

The behavior of the distribution of chemical families for the Reference 2 catalyst may be related to the content of boron in the support, which allows for the keeping of the concentrations of the reaction products, which are almost constant in relation to the concentration of the waxy ester and the conversion of triglycerides [45]. When the reaction temperature increases to 260 °C, an appreciable change in the concentration of the paraffin is observed and the concentration of the waxy ester. Similar behavior is reported by Guzman et al. [10]. They attribute it to the slight exothermicity of the esterification reaction, which, at the indicated reaction conditions, allows this distribution of products to be achieved, but at higher reaction temperatures (>260 °C), a much more significant increase in paraffin and reduction in waxy esters in the product can be observed.

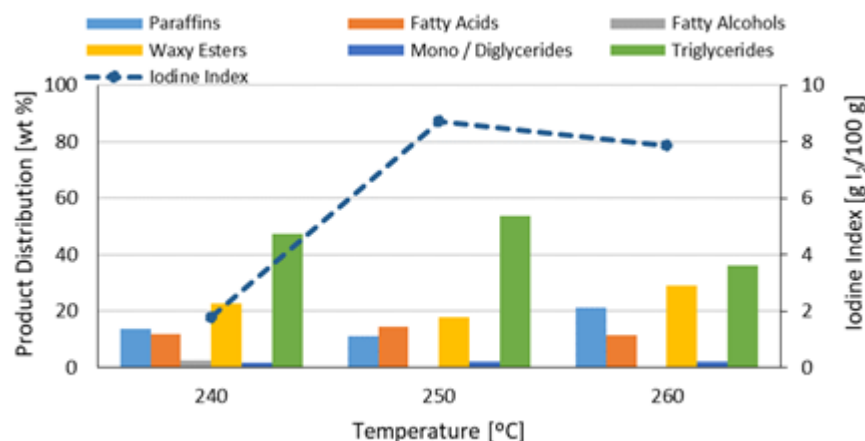


Figure 12. Composition of the reaction product(wax) at 55 bar and LHSV: 1.5 h^{−1} for catalyst, Reference 2, (NiMoB/Al₂O₃).

Table 7 shows the results obtained of the reaction gases based on the possible deoxygenation routes that can occur to produce paraffin (DCO, DCO₂, and HDO) and waxy esters. As observed in Table 7, the increase in temperature favors the decarboxylation route to produce paraffin and, to a minor extent, the decarboxylation of fatty acids.

Table 7. Oxygen byproducts as a function of reaction temperature—Reference 2 (NiMoB/Al₂O₃).

Temperature [°C]	CO ₂ [Vol. Molar%]	CO [Vol. Molar%]
240	13.80	1.38
250	18.62	1.55
260	34.00	1.55

The increase in the iodine number from 1.8 to 8 g of I₂/100 g; between the product obtained at 240 °C and that obtained at 260 °C agrees with what was observed with the Reference 1 catalyst. Additionally, it confirms that the increase in the reaction temperature in this range reduces the hydrogenation and hydrodeoxygenation reactions because it increases the content of unsaturated compounds in the final product [37].

The distribution of chemical families does not get affected in the Reference 2 catalyst due to the increase in the reaction temperature; this is also verified by the minor variation in the selectivity towards waxy esters.

4. Conclusions

We performed some hydrogenation tests to produce waxes from refined palm oil to evaluate the effect of the process variables, temperature, pressure, and space velocity, on TAG conversion and the distribution of the chemical families of the waxes obtained. In decreasing order, the operating variables with the greatest impact on conversion are Temperature > LHSV > Pressure. Temperature is almost directly proportional to triglyceride conversion as it favors the kinetics of the reactions (Table 1). The total pressure, which determines the partial pressure of hydrogen, has a positive impact on conversion as there is greater availability of hydrogen for triglyceride hydrogenation/hydrogenolysis reactions to occur, which triggers the mechanism of conversion of palm oil into fatty acids, fatty alcohols, waxy esters, and paraffins. On the other hand, the LHSV has an inverse effect; by reducing the value of this variable, it increases the residence time of the feedstock in the reactor, allowing high vegetable oil conversions. These results allow us to establish a set of conditions in which TAG conversion was higher than 50% and, at the same time, to have a distribution of different chemical compounds, such as waxy esters and paraffins, mainly, but also fatty acids and, in smaller proportions, fatty alcohols. This set of variables was tested with two different catalysts, the first a NiMo/Al₂O₃ catalyst and the second a

NiMoB/Al₂O₃ catalyst having similar results with both of them. The results of this study are interesting because they allow exploring applications for vegetable waxes other than candles or food wrapping, which are the common uses for waxes with high paraffin content, for example, in the cosmetic industry.

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