

Article

Biofuel Production in Oleic Acid Hydrodeoxygenation Utilizing a Ni/Tire Rubber Carbon Catalyst and Predicting of n-Alkanes with Box–Behnken and Artificial Neural Networks

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Abstract: Oleic acid is a valuable molecule for biofuel production, as it is found in high proportions in vegetable oils. When used, oleic acid undergoes hydrodeoxygenation reactions and produces alkanes within the diesel range. These alkanes are free of oxygenated compounds and have molecular structures similar to petrodiesel. Our research introduces a novel approach incorporating oleic acid into the hydrodeoxygenation process of Ni/Tire Rubber Carbon (Ni/C_{TR}) catalysts. These catalysts produced renewable biofuels with properties similar to diesel, particularly a high concentration of n-C₁₇ alkanes. Moreover, our Ni/C_{TR} catalyst produces n-C₁₈ alkanes, but the generation of n-C₁₈ alkanes typically requires more complex catalysts. Our procedure achieved 74.74% of n-C₁₇ alkanes and 2.28% of n-C₁₈ alkanes. We used Box–Behnken and artificial neural networks (ANNs) to find the optimal configuration based on the predicted data. We developed a dataset with pressure, temperature, metal content, reaction time, and catalyst composition variables as inputs. The output variables are the n-C₁₇ and n-C₁₈ alkanes obtained. ANN602020 was our best model for obtaining the peak response; it accurately forecasted the n-C₁₇ and n-C₁₈ generation with R² scores of 0.9903 and 0.9525, respectively, resulting in an MSE of 0.0014, MAE of 0.02773, and MAPE of 2.03979%. The combined R² score for both alkanes was 0.97139.

Keywords: renewable biofuels; Ni/Tire Rubber Carbon; hydrodeoxygenation; artificial neural networks; Box–Behnken



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1. Introduction

Oleic acid is recognized as a representative molecule prevalent in used vegetable oils [1], making it a suitable model for evaluating catalytic efficiency in oil hydrodeoxygenation reactions. Derived from agro-industrial processes and food production in restaurant chains [2], vegetable oils serve as a source of this vital molecule. The hydrodeoxygenation of oleic acid and vegetable oils yields oxygen-free alkanes in the diesel range [3,4], commonly referred to as green diesel, with molecular properties akin to petrodiesel [5]. This eco-friendly fuel exhibits high cetane numbers [6], excellent ignition quality [7], and effectively mitigates cold flow associated with conventional biodiesel. Furthermore, its use in diesel engines significantly reduces NO_x, PM, HC, CO, and greenhouse gas emissions compared to petrodiesel [8,9].

Catalytic hydrodeoxygenation reactions involve using catalysts to remove oxygen from biomass at high pressures of up to 200 bar and temperatures reaching 400 °C [10]. This process eliminates oxygen from hydrocarbons through various catalytic reactions, including

hydrodeoxygenation, hydrodecarbonylation, and hydrodecarboxylation, as documented in [11,12]. Several studies have demonstrated that catalysts based on transition metals such as Ni, and noble metals such as Pt, Pd, Ru, and Rh, effectively promote and facilitate hydrodeoxygenation reactions [2]. The reaction rates are directly proportional to the hydrogen pressure within the reactor [13]. Additionally, the literature highlights the importance of the sufficient dispersion of the metallic active phase in the porous support. The support should offer a high surface area, adequate mechanical strength, and thermal stability to create the optimal catalytic material [14].

Porous carbon materials are a promising choice for catalytic support in hydrodeoxygenation reactions due to their favorable surface area and pore volume characteristics. These attributes allow them to expedite the conversion reactions of large molecules in both the petrochemical and pharmaceutical industries [15]. Moreover, there is significant interest in producing carbon from recycling processes, as evidenced by various studies [16,17]. For instance, approximately 5 million tons of waste tires are generated globally each year, and researchers have repurposed sulfonated carbon from these tires to produce biodiesel through transesterification, as demonstrated in 2016 [2].

Recently, catalysts containing noble metals such as Pt and Pd have demonstrated excellent stability and catalytic activity, driving the HDO hydrodeoxygenation [18,19]. However, their widespread industrial application has been limited due to their high cost. In contrast, catalysts based on transition metals such as Ni and Co have shown promising results in HDO hydrodeoxygenation, converting vegetable oils into renewable, eco-friendly fuels, making them more viable for large-scale industrial use [20]. Similarly, the literature shows promising outcomes for hydrodeoxygenation reactions under various conditions using Ni–Mo, Co–Mo, and Ni–W catalysts supported on γ -Al₂O₃ [21], activated carbon, SiO₂, and SBA-15 [19]. Oleic acid hydrodeoxygenation reactions using a 20% by weight catalyst of Pt/H₃PO₄@MIL-101 (Cr) achieved a 95% conversion rate [22], with a selectivity to paraffins of 75.5%. The reaction was carried out at 300 °C, under 2 MPa pressure, and lasted 2 h. The hydrodeoxygenation of oleic acid reaches 97% selectivity to paraffins using a 10 wt% La/HZSM5 catalyst at 400 °C, 5 MPa, and for 2 h [23]. On the other hand, in [24] they reached 100% conversion and selectivity to paraffin in hydrodeoxygenation experiments on palmitic acid. The experiments used catalysts containing 25% and 14% by weight of Ni supported on P-MIL-101 in a stainless-steel stirred batch reactor, with operating conditions of 3 h, 400 °C, and 3 MPa. The hydrodeoxygenation of methyl palmitate was studied using Ni catalysts on various supports (SiO₂, γ -Al₂O₃, SAPO-11, HZSM-5, and HY). The highest yield of 93% for n-C₁₅ alkanes was with the catalyst containing 7% Ni/SAPO-11 at 493 °K and 2 MPa [20]. A catalyst for the hydrodeoxygenation of oleic acid containing 7% by weight of Ni/ γ -Al₂O₃ achieved an 84.8% conversion in a four-blade reactor at 23 bar and a temperature range of 320 to 340 °C [2]. Under similar conditions, a different study reported a 98% conversion using a Pt/ γ -Al₂O₃ catalyst [1].

Based on previous studies, our research is focused on synthesizing n-C₁₇ and n-C₁₈ alkanes from oleic acid hydrodeoxygenation by utilizing Ni/C_{TR}. The catalyst preparation involves two methods: incipient wet impregnation for depositing Ni onto the support, followed by pyrolysis to create Ni catalytic powders supported on a carbonaceous structure. Additionally, we aim to enhance the efficiency of our approach by employing Box–Behnken and artificial neural network (ANN) models for experimental designs, response surface development, and predictive modeling. The Box–Behnken design is a response surface methodology used in engineering for experimental designs. This design involves three levels for each factor and utilizes a rotating pattern. When working with multiple factors, the method requires a specific number of experiments to be carried out. The data are then fitted to a polynomial model that predicts independent variables. In recent studies, the Box–Behnken method has shown promising results in analyzing the impact of operational variables, utilizing quadratic polynomials to predict responses, and identifying optimal factor combinations to enhance the performance of chemical hydrodeoxygenation processes [25,26]. On the other hand, artificial intelligence techniques, such as artificial

neural networks (ANNs) and other machine learning models, have been employed by researchers for modeling purposes [27,28]. ANNs have demonstrated significant efficacy in predicting independent variables for regression. For instance, in 2023 Adeyinka Sikiru Yusuff and colleagues predicted the performance of catalytic transesterification reactions of cooking oil using ANNs and determined the significance of input variables in the process. Additionally, Abdulrahman Sumayli and team in 2023 applied artificial intelligence methods, including multilayer perceptron (MLP), gradient boosting (GB), and Gaussian process regression (GPR), to model and predict biodiesel production from papaya oil.

In our proposal, we aim to synthesize Ni/C_{TR} catalysts of varying Ni content through incipient wet impregnation and pyrolysis methods. These catalysts will be employed in the hydrodeoxygenation of oleic acid to produce renewable biofuels with diesel-like properties, specifically targeting a high concentration of n-C₁₇ alkanes. Our catalyst also yields n-C₁₈ alkanes, albeit in lower quantities compared to more intricate catalysts. Furthermore, we utilize the Box–Behnken model and artificial neural networks (ANNs) for the prediction of n-C₁₇ and n-C₁₈ alkane production, enhancing our ability to model relationships and optimize performance. Our prediction models have achieved a peak performance of 74.74% for n-C₁₇ alkanes and 2.28% for n-C₁₈ alkanes in ANNs, in addition to R² 0.97139 and 0.80170 in the Box–Behnken model, respectively. Furthermore, we use the experimental data to compare Box–Behnken optimization models with artificial neural networks for analyzing the impact of H₂ pressure, weight percentage of Ni, temperature, and reaction time on the hydrodeoxygenation reaction. The study aims to identify the optimal combination of these factors for achieving the highest yield of n-C₁₇ and n-C₁₈ alkanes, which are renowned as renewable biofuels with diesel-range characteristics, high energy value, and significant potential to reduce atmospheric pollutant emissions when utilized in diesel engines [29,30]. The rest of this paper is organized as follows: Section 2 covers the definitions, general concepts, and the proposed methodology for carrying out hydrodeoxygenation of oleic acid using different variations of our Ni/C_{TR} catalyst. This section also includes the modeling techniques used to predict the generation of n-C₁₇ and n-C₁₈ alkanes, as well as the metrics employed for evaluation purposes. Section 3 details the results obtained and provides a comprehensive discussion of these results. Finally, in Section 4, we present our findings and outline the future work for our research.

2. Materials and Methods

Our novel approach for integrating oleic acid into the hydrodeoxygenation process of Ni/C_{TR} catalysts involves a multi-step methodology. We begin by establishing parameters for reaction time, hydrogen pressure, temperature, and % of metal in the catalyst by conducting several experiments to find different levels of production in alkanes. Then, to optimize the quantity of alkanes produced we run additional measurements to complete 345 tests, identifying alkane concentration using gas chromatography to build a dataset. Next, we develop Box–Behnken and ANN models and proceed to evaluate and compare them based on metrics such as Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE), and R-Squared coefficient (R²). Finally, we find the optimal values for maximizing alkane production based on those models. The experimental design is illustrated in Figure 1 for reference.

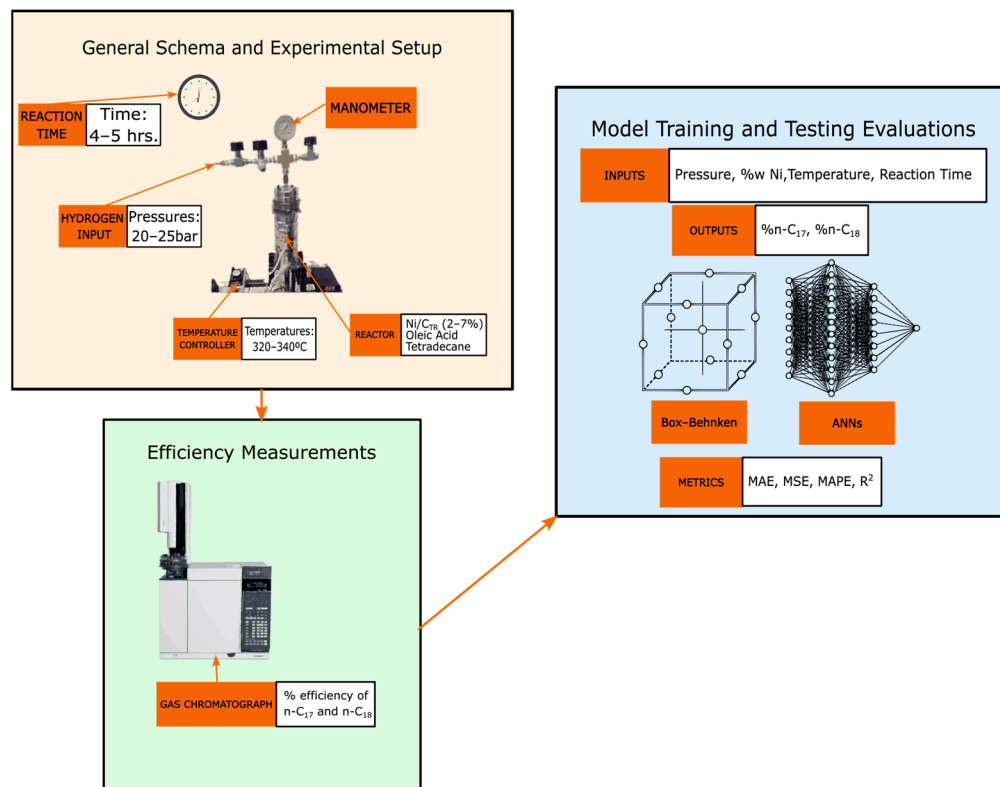


Figure 1. General experimental design.

2.1. Catalyst Preparation

Catalytic powders supported on C_{TR} with varying Ni weight percentages (from 2% to 7%) were fabricated using pyrolysis methods and incipient wet impregnation [2,13]. First, the incipient wet impregnation method was applied, in which the metal-free vulcanized from Neo Habitat was mixed with precise amounts of Nickel (II) acetate tetrahydrate Ni(OCOCH₃)₂•4H₂O (Sigma-Aldrich 99.99%, St. Louis, MO, USA). After obtaining a homogeneous mixture, a 1:16 solution of nitric acid HNO₃ (JT Baker, 67–70%, Phillipsburg, NJ, USA) was added dropwise to disperse and achieve the adsorption of the metallic active phase by regulating the acid-base balance on the surface of the support and forming a paste. The paste was dried and then ground finely. Subsequently, in the pyrolysis process, the ground paste was exposed to a temperature of 515 °C for 2 h in a stainless-steel tubular reactor with an N₂ flow of 35 mL/min. The Ni catalytic powders supported in a carbonaceous structure underwent washing with distilled water and subsequent drying at 60 °C in an electric oven; these powders then underwent a reduction process using a flow of H₂ at 400 °C for 3 h [31]. Recent studies have reported this temperature reduction, demonstrating TPR profiles for the reduction of Ni oxide species [32]. Additionally, this process has been explored in studies where nickel catalysts were prepared and utilized in hydrodeoxygenation reactions [31].

2.2. Characterization of Catalysts

To know the morphology of the catalysts, a JEOL (Tokyo, Japan) JSM-6300-S scanning electron microscope (SEM) equipped with a JSM-6300 basic unit consisting of an electronic column, control system, and sample visualization was used. The team has the advantage of having devices to perform energy-dispersive X-ray (EDX) elemental analysis.

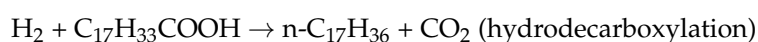
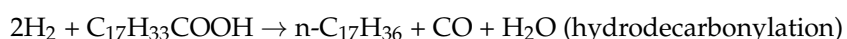
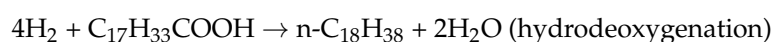
The surface area and pore size distribution were determined with a Quadrasorb SI instrument (Quantachrome Instruments, Beach, FL, USA). Each catalyst sample was subjected to degassing before nitrogen adsorption at 77.5 °K. To obtain the BET apparent surface area (SBET), the BET equation was applied for the N₂ adsorption isotherms. From the amount of N₂ adsorbed at P/P₀ = 0.95 (V_{0.95}) the total pore volume was obtained.

The X-ray diffractograms of the catalysts were obtained in a Bruker D8 Advance diffractometer. The equipment uses CuK α radiation ($\lambda = 0.154$ nm) and scans the samples in a 2θ interval of 10 – 100° with a speed of $0.02^\circ/\text{s}$, voltage of 40 kV, and current of 40 mA.

With a Mettler-Toledo analyzer mod. TGA/DSC1, thermogravimetry analysis was performed with an initial temperature of 35°C and a temperature increase rate of $10^\circ/\text{min}$ until reaching a maximum temperature of 950°C .

2.3. Hydrodeoxygenation of Oleic Acid

This procedure was carried out in a 500 mL stainless-steel autoclave equipped with an electromagnetic stirring system that allows alternating rotation of four fixed stirring paddles in the center of the base to achieve radial and axial stirring of 120 rpm. Through a feed pipe placed at the top, an amount of 0.9 g of Ni/C_{TR} catalyst was added with the percentages by weight of Ni defined in the experiment to be carried out (2% , 3% , 4% , 5% , 6% , or 7%). The feed duct was closed, and a hydrogen flow was passed at 25 bar and 310°C for 15 min to achieve complete chemical reduction of the Ni oxides resulting from the catalyst's contact with air [33]. It has been reported in the literature that this reduction temperature is sufficient to reduce the Ni oxides formed by exposure to air [2,33]. The reactor was cooled, and 0.032 moles of oleic acid and 0.2 moles of tetradecane (the solvent) were introduced. Tetradecane was chosen for this process because it is generated in negligible amounts during the hydrodeoxygenation reaction and has a boiling point that differs by more than 40°C from the main product. A distillation column was used to separate the n-alkanes n-C₁₇ and n-C₁₈ from the hydrodeoxygenation mixture using the following process: all reactor conduits are closed and a flow of N₂ is passed through to purge it. Then the required amount of hydrogen is injected so that when heated to the corresponding temperature (320 – 340°C) it reaches the pressure indicated in the experiment to be carried out (20 – 25 bar). In all reactions, stirring is kept constant during the defined reaction time (4.5 h). In an Agilent Technologies 7890 gas chromatograph (Santa Clara, CA, USA), the percentage of n-C₁₇ and n-C₁₈ alkanes generated as products of the reaction was analyzed, carbon disulfide was used as a calibration standard, and the alkane content was determined with the SIMDIS method based on the distribution of boiling points. The reactions of the conversion of oleic acid to alkanes are the following:



2.4. Development of Box–Behnken and Artificial Neural Networks Optimization Models to Predict n-Alkanes

A design of experiments (DOE) was used to measure the degree of correlation and determine the effect of pressure (P), weight % of Ni (W), temperature (T), and reaction time (t), considered as the main control factors and their interactions that influence the hydrodeoxygenation reaction of oleic acid for its conversion to n-C₁₇ and n-C₁₈ alkanes [2].

Table 1 shows the range of values of the variables and the coding requested by the DOE Box–Behnken design, which is a response surface methodology that, based on the number of factors and their levels, automatically used 27 best points of the data obtained experimentally to fit a polynomial model with the ability to predict the optimal values for the performance of n-C₁₇, the method also used 27 best points to obtain the polynomial model to optimize the performance of n-C₁₈. Two replicates were run for each experiment and the average was used to develop the theoretical models.

Table 1. Ranges and coded levels of the independent variables.

Independent Variable	Symbol	Coded Levels		
		−1	0	+1
Pressure (bar)	P	20	22.5	25
Weight % Ni	W	2	4.5	7
Temperature (°C)	T	320	330	340
Reaction time (h)	t	4	4.5	5

Therefore, the answer of quadratic polynomials is shown in Equation (1) [34].

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=i+1}^k \beta_{ij} X_i X_j \quad (1)$$

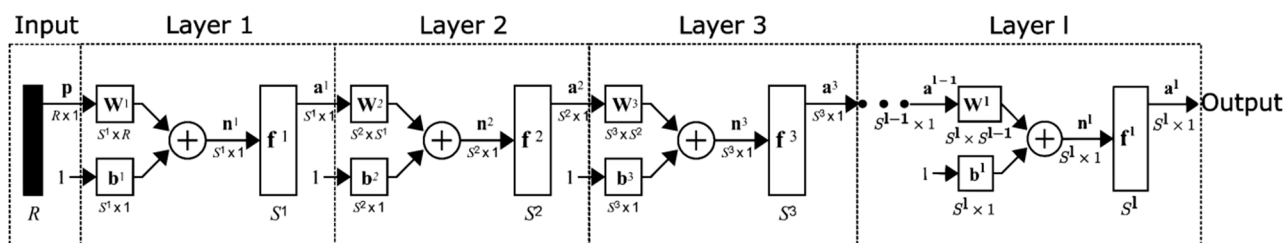
where Y is the predicted response value; β_0 , β_i , β_{ii} , β_{ij} are the regression coefficients (β_0 is the intercept coefficient; β_i is the linear effect term; β_{ii} is the quadratic effect term; and β_{ij} is the interaction effect). X_i and X_j are the independent variables and k is the total number of independent variables.

Statgraphics 16.1.03 software (Centurion XV, 2006, Stat Point Inc., (Warrenton, VA, USA)) was used to obtain regression models based on the response surface. The software performs an analysis of variance (ANOVA) that provides Fisher values (F) and the coefficient of determination (R^2).

2.5. Development of Artificial Neural Networks Models to Predict n-Alkanes

Prediction of n-alkanes involves preparing inputs and outputs for training an artificial neural network (ANN) model. The selected inputs are the same as those used in the Box–Behnken design, including pressure (bar), weight % Ni, temperature (°C), and reaction time (h). The outputs are the moles % of n-C₁₇ and n-C₁₈ alkanes.

The ANN utilized in this work is a feedforward architecture commonly employed in regression models. The feedforward neural networks consist of an input layer, hidden layers, and an output layer, with consistent activation functions and the capability for multiple neurons in each layer [35,36]. An example structure with l layers is shown in Figure 2, where $p^l \in R^{R \times 1}$ is the input vector, $W^l \in R^{S^l \times R}$ is the weights matrix, $b^l \in R^{S^l \times 1}$ is the bias vector, $n^l \in R^{S^l \times 1}$ is the logits vector, $f^l \in R^{S^l \times 1}$ is the activation function, $a^l \in R^{S^l \times 1}$ is the output of the neuron, l is the number of layers, S is the number of neurons per layer, and R is the number of inputs in that layer. Notice that $p^1 = p = a^0$, $p^2 = a^1$, $p^3 = a^2$, and $p^l = a^{l-1}$.

**Figure 2.** Three layers feedforward neural network.

In this work, we used an input vector $p \in R^{5 \times 1}$, having five features corresponding with the catalyst index, pressure (bar), weight % Ni, temperature (°C), and reaction time (h). Then, the input vector was connected to five layers in the ANN with activation functions $f^l = \tanh(n^l)$ for $l = 1, 3$, $f^l = \text{Relu}(n^l)$ for $l = 2, 4$, and $f^5 = \text{linear}(n^5)$, since these are activation functions with proven efficiency in regression problems [37]. These activation

functions are defined as in Equations (2)–(4). The final output of the ANN is $a^5 \in R^{2 \times 1}$ for the n-C₁₇ and n-C₁₈ alkanes predicted.

$$\tanh(x) = \frac{e^x - e^{-x}}{e^x + e^{-x}} \quad (2)$$

$$\text{Relu}(x) = \max(0, x) \quad (3)$$

$$\text{linear}(x) = x \quad (4)$$

An exhaustive search with 1350 configurations across various hyperparameters allowed us to find a suitable ANN configuration and the patience (Pa) required for test loss improvement. We tested $Pa = 10, 20, 30, 40, 50$ for patience; $S^1 = 5, 10, 15, 20, 25, 30$ for neurons in layer 1; $S^2 = 5, 10, 15, 20, 25, 30$ for layer 2; $S^3 = 1, 5, 10$ for layer 3; $S^4 = 1, 5, 10$ for layer 4; and the linear layer is always $S^5 = 2$ for obtaining n-C₁₇ and n-C₁₈ alkanes. Moreover, we tested two dataset distributions. The first used 27 samples for training and validation with 345 samples, having conditions similar to those in the Box–Behnken design. The second one splits the 372 samples in the dataset into 60% for training, 20% for validation, and 20% for testing.

2.6. Metrics of Comparison

The evaluation metrics employed for model assessment encompass MAE (Mean Absolute Error) in Equation (5), MSE (Mean Squared Error) in Equation (6), MAPE (Mean Absolute Percentage Error) in Equation (7), and R^2 (R-squared) in Equation (8). These metrics are frequently utilized in regression models to measure the discrepancy between the model and the target samples in the dataset [38].

$$\text{MAE}(\hat{y}, y) = \frac{1}{N} \sum_{i=1}^N |\hat{y}_i - y_i| \quad (5)$$

$$\text{MSE}(\hat{y}, y) = \frac{1}{N} \sum_{i=1}^N (\hat{y}_i - y_i)^2 \quad (6)$$

$$\text{MAPE}(\hat{y}, y) = \frac{1}{N} \sum_{i=1}^N \left| \frac{\hat{y}_i - y_i}{y_i} \right| \quad (7)$$

$$R^2(\hat{y}, y, \bar{y}) = \frac{\sum_{i=1}^N (y_i - \bar{y})^2 - \sum_{i=1}^N (y_i - \hat{y}_i)^2}{\sum_{i=1}^N (y_i - \bar{y})^2} \quad (8)$$

where y is the target, $\hat{y}$ is the obtained output, $\bar{y}$ is the mean of y , and N is the number of samples.

3. Results

3.1. Ni/C Catalyst Characterization

Using the EDS (Energy-Dispersive X-ray) technique, the elemental chemical composition of the Ni/C_{TR} catalysts prepared with the Ni loads determined in the experimental design was determined. The compositions obtained with the EDS equipment were: 1.91%, 2.86%, 4.21%, 5.14%, 6.11%, and 7.19%, which show compliance with the theoretical quantities calculated and used for the preparation by the combination of pyrolysis and incipient wet impregnation methods. The slight variations observed between the experimental quantities obtained by EDS and the expected calculated values (2%, 3%, 4%, 5%, 6%, and 7%) can be attributed to the fact that EDS is a technique that reports the elemental composition of the Ni/C_{TR} catalysts in a timely manner [39]. Figure 3 illustrates the morphology of C_{TR} and the changes in surface characteristics due to the deposition of Ni at varying weight percentages on the catalytic support. The Ni is uniformly deposited on the carbon surface

components. As the weight percentage of nickel increases, a greater surface area is covered by the metallic active phase.

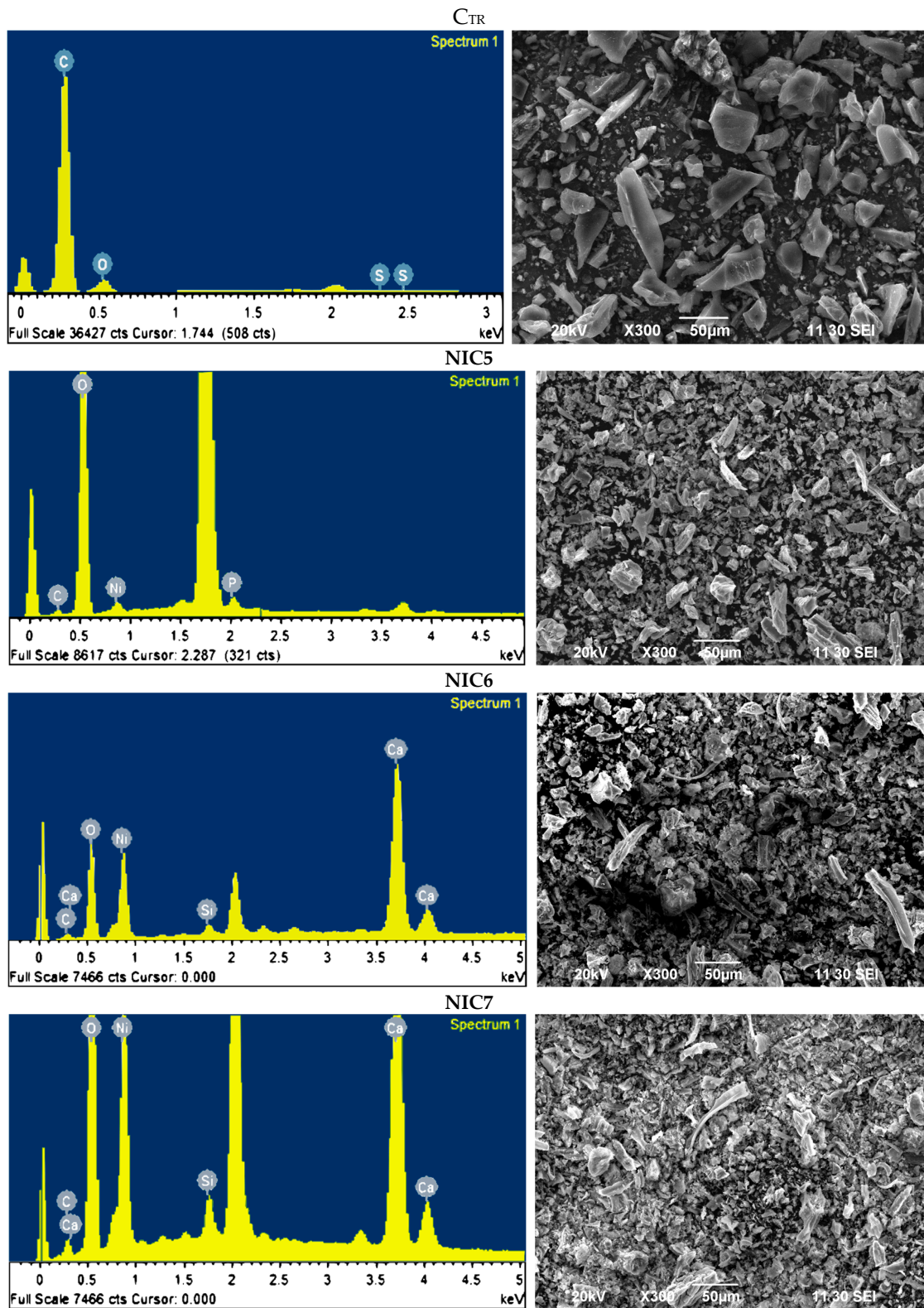


Figure 3. SEM and EDS characterization of Ni/C_{TR} catalysts and pure C_{TR}.

Table 2 presents the texture properties of the Ni catalysts supported on tire rubber carbon, by comparing the specific surface areas S_{BET} , the average pore volume V_p , and the

average pore diameter D_p of the rubber carbon support of C_{TR} tire with the catalysts with different weight percentages of Ni; it is observed that as the amount of Ni increases, the pores of the support are partially blocked [40,41].

Table 2. Textural properties of Ni/ C_{TR} catalysts.

Catalyst	Weight % Ni	Textural Properties		
		SBET (m^2/g)	V_p (cm^3/g)	D_p (nm)
CTR	0	114.21	0.39	12.27
NiC2	2	108.34	0.36	12.02
NiC3	3	104.32	0.341	11.77
NiC4	4	100.18	0.318	11.54
NiC5	5	95.01	0.31	11.28
NiC6	6	90.24	0.302	11.25
NiC7	7	87.75	0.287	10.99

Figure 4 presents the nitrogen adsorption–desorption isotherms for C_{TR} and the catalysts C_{TR} , NiC5, NiC6, and NiC7. In all instances, the isotherms display a characteristic type IV shape along with a well-defined type H3 hysteresis loop, which is typical of mesoporous materials [42].

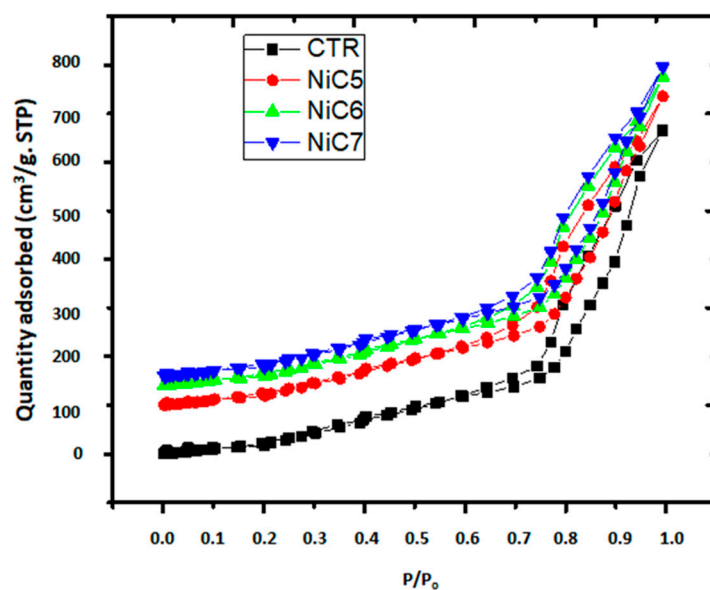


Figure 4. Nitrogen gas adsorption–desorption isotherms of Ni/ C_{TR} catalysts and pure C_{TR} .

Figure 5 shows the XRD diffractograms of the three catalysts that presented yields of $n-C_{17}$ and $n-C_{18}$ alkanes closest to the optimization zone. In the three catalysts, peaks attributed to the presence of NiO located at 37° , 43° , and 63° can be observed [43,44], and the intensity of the peaks increases with the weight percentage of NiO [45]. The peaks corresponding to the C_{TR} tire rubber carbon are not observed due to the overlap of the peaks of the NiO metallic active phase, however, a preparation of pure C_{TR} was carried out and subjected to the same processes and preparation conditions as the catalysts with deposition of NiO, which serves as a witness that the C_{TR} catalytic support is made up of disordered graphene characterized with the peak at 25.1° , as well as graphite according to the peak at 43.4° [2,46].

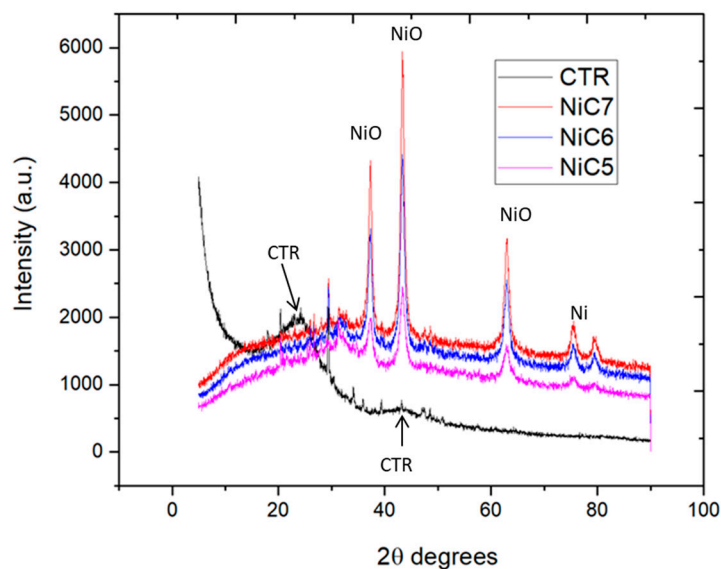


Figure 5. XRD diffractograms of the Ni/CTR catalysts and pure CTR.

Figure 6 shows the thermogravimetric (TG) measurements of the catalysts that favored yields close to the optimization zone. For the three samples NiC5, NiC6, and NiC7, the first transition zone is in the range of 200 to 350 °C, with mass losses less than 5% attributed to the loss of –OH groups [9]. The most important transition zone and with the greatest mass elimination occurs from 360 to 760 °C, attributed to the elimination of the acid group (COOH) and other functional groups that begin to be lost at 500 °C [40]. The greatest mass loss was observed for the NiC5 catalyst, followed by NiC6, and NiC7 was the one with the least mass loss, which could be related to the strong metal–support interaction: the greater the amount of active metal phase, the lower the mass loss [41].

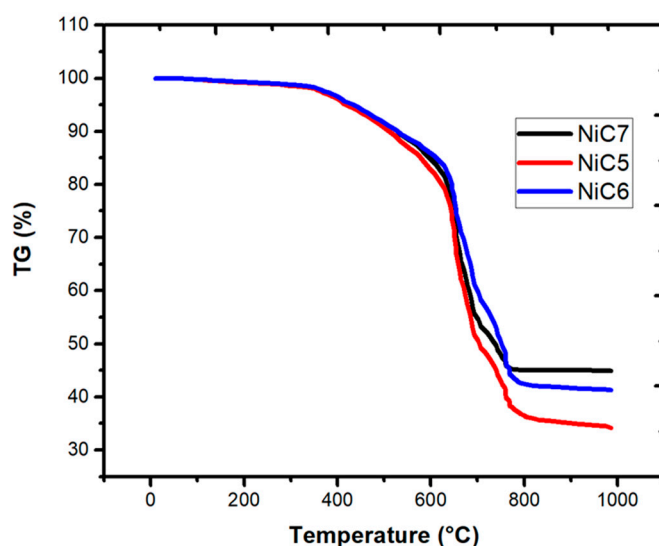


Figure 6. Thermogravimetric measurements (TG) of the Ni/CTR catalysts.

3.2. Conversion of Oleic Acid to n -C₁₇ and n -C₁₈ by Hydrodeoxygenation

Table 3 shows the yields of n -C₁₇ and n -C₁₈ obtained from the hydrodeoxygenation of oleic acid with different combinations of control factors. The highest yield obtained of n -C₁₇ was 70.74% with the NiC7 catalyst at 25 bar, 340 °C, and 4 h of reaction; however, a very close yield of 70.54% was obtained with the NiC6 catalyst at 25 bar, 340 °C, and 5 h. Other n -C₁₇ yields greater than 70% were obtained with NiC7 catalysts with different combinations of factors, but on the other hand, n -C₁₇ yields close to 65% were observed with NiC5,

NiC4.5 and NiC4 catalysts; this trend indicates that the optimization zone could be located in the range of 4% to 7% by weight of Ni. The lowest n-C₁₇ yields were obtained with the NiC2 catalyst, which, when applied with different combinations of pressure, temperature, and time, favored n-C₁₇ yields in a range of 40 to 45%. The range of n-C₁₇ yields of 40 to 45% obtained with the NiC2 catalyst were close and in some cases managed to improve the yields recently reported in which 5% Pd/C catalysts were used [46], 5%Pt/ γ -Al₂O₃ [33] and 5%Pt/SAPO-11 [47] for the hydrodeoxygenation of oleic acid. The 70.74% n-C₁₇ yield obtained with the NiC7 catalyst was lower when compared to the yields close to 75% of n-C₁₇ reported with a 1%Pt/ γ -Al₂O₃ catalyst at 340 °C [1] and a 20 wt% Pt/H₃PO₄@MIL-101 (Cr) catalyst used at 300 °C and 2 MPa [22] in the hydrodeoxygenation of oleic acid; however, when comparing the availability, costs, and ability of Ni to accelerate and direct hydrodeoxygenation reactions, it makes its application in this type of reaction promising. The yields obtained with the NiC5, NiC4.5, and NiC4 catalysts managed to improve what was reported by Srifa and his work team, in which they used CoAl, NiAl, and PtAl catalysts with 5% metal loading for the hydrodeoxygenation of oleic acid and obtain n-C₁₇ yields of 47%, 23.71%, and 47.82%, respectively at 330 °C, 5 MPa, LHSV of 2 h⁻¹, and H₂/fatty acid ratio of 1000 N (cm³/cm³) [48]. Table 3 shows that a higher weight % of Ni favors the performance of n-C₁₇, which can be demonstrated by comparing the best performance obtained with the NiC7 catalyst with a recent study, in which it was reported a yield of 81.3% of n-C₁₇ using Ni/ γ -Al₂O₃ with 10% Ni loading at 330 °C and 50 bar [49]. In the analysis of the effect of H₂ pressure in a range of 20 to 25 bar for all reactions, the common trend was that an increase in H₂ pressure favors greater production of n-C₁₇ and n-C₁₈ alkanes, which demonstrates that it is a key factor for the conversion and selectivity of the process to obtain renewable biofuels. For example, when comparing the behavior of the NiC3 and NiC7 catalysts at 340 °C and 5 h of reaction, there were increases in the yields of n-C₁₇ higher than 5% and 6%, respectively, when the H₂ pressure was raised from 20 to 25 bar. These results show agreement with recent studies in which Pd catalysts were used for the conversion of fatty acids to long-chain hydrocarbons, in which it was shown that at 3 bar of H₂ pressure only a poor conversion of 6% was promoted, and an increase of up to 25 bar of H₂ raises the conversion of fatty acids to 65% [50,51]; a similar performance of 66.46% for n-C₁₇ can be observed with the NiC5 catalyst at 25 bar. The yields shown in Table 3 indicate that increases in reaction temperatures favor greater production of n-C₁₇, in accordance with recent studies of the hydrodeoxygenation of oleic acid, in which they demonstrated that after 5 h and 275 °C they observed conversions of less than 5%; however, at 300 °C 50% of oleic acid was converted, and at temperatures above 320 °C conversions close to 100% were achieved [33]. The results shown in all the experimental runs indicate that the Ni/C_{TR} catalysts in the hydrodeoxygenation of oleic acid present a strong selectivity to the production of n-C₁₇ alkanes, which proves that there is a strong tendency towards decarboxylation and decarbonylation reactions [9,33].

Table 3. Yields of n-C₁₇ and n-C₁₈ of the hydrodeoxygenation reaction of oleic acid with Ni/carbon tire rubber (C_{TR}) catalysts at different combinations of pressure, % by weight of metal, temperature, and reaction time.

Catalyst	Pressure (bar)	wt% Metal	Temperature	Reaction Time (h)	Yield of n-C ₁₇ (% Mole)	Yield of n-C ₁₈ (% Mole)
NiC2	20	2	340	5	48.38	1.29
NiC2	20	2	340	4	44.82	1.17
NiC3	20	3	340	5	56.95	1.41
NiC3	20	3	340	4	52.92	1.49
NiC4	20	4	340	5	59.54	1.61
NiC4	20	4	340	4	55.48	1.52
NiC5	20	5	340	5	64.55	1.82
NiC5	20	5	340	4	61.86	1.75

Table 3. Cont.

Catalyst	Pressure (bar)	wt% Metal	Temperature	Reaction Time (h)	Yield of n-C ₁₇ (% Mole)	Yield of n-C ₁₈ (% Mole)
NiC6	20	6	340	5	65.44	1.83
NiC6	20	6	340	4	62.28	1.76
NiC7	20	7	340	5	68.94	1.95
NiC7	20	7	340	4	66.34	1.87
NiC2	20	2	320	5	46.87	1.27
NiC2	20	2	320	4	40.05	1.08
NiC3	20	3	320	5	53.33	1.5
NiC3	20	3	320	4	47.11	1.33
NiC4	20	4	320	5	56.37	1.56
NiC4	20	4	320	4	50.43	1.45
NiC5	20	5	320	5	61.7	1.74
NiC5	20	5	320	4	56.66	1.6
NiC6	20	6	320	5	63.67	1.75
NiC6	20	6	320	4	58.3	1.65
NiC7	20	7	320	5	66.17	1.87
NiC7	20	7	320	4	61.3	1.73
NiC4.5	22.5	4.5	330	4.5	60.31	1.72
NiC2	22.5	2	330	4	44.23	1.18
NiC4.5	22.5	4.5	340	5	64.42	1.83
NiC2	22.5	2	340	4.5	52.15	1.3
NiC4.5	25	4.5	330	5	64.71	1.91
NiC4.5	25	4.5	320	4.5	59.64	1.77
NiC4.5	20	4.5	320	4.5	56.29	1.58
NiC4.5	25	4.5	330	4	59.88	1.71
NiC2	20	2	330	4.5	45.03	1.2
NiC2	22.5	2	330	5	49.87	1.38
NiC7	20	7	330	4.5	65.68	1.85
NiC7	22.5	7	340	4.5	70.06	2.03
NiC4.5	25	4.5	340	4.5	64.95	1.85
NiC7	22.5	7	330	5	65.73	2.06
NiC4.5	20	4.5	330	4	48.82	1.36
NiC2	25	2	330	4.5	49.08	1.35
NiC4.5	22.5	4.5	320	5	60.83	1.76
NiC7	25	7	330	4.5	69.88	2.1
NiC7	22.5	7	330	4	65.69	1.9
NiC4.5	20	4.5	340	4.5	60.35	1.67
NiC4.5	22.5	4.5	340	4	60.89	1.7
NiC7	22.5	7	320	4.5	65.51	1.92
NiC4.5	20	4.5	330	5	62.36	1.73
NiC2	22.5	2	320	4.5	45.23	1.25
NiC4.5	22.5	4.5	340	5	64.42	1.83
NiC2	25	2	340	5	53.38	1.49
NiC2	25	2	340	4	48.92	1.28
NiC3	25	3	340	5	61.65	1.62
NiC3	25	3	340	4	57.12	1.61
NiC4	25	4	340	5	64.44	1.83
NiC4	25	4	340	4	59.78	1.65
NiC5	25	5	340	5	69.15	2.06
NiC5	25	5	340	4	66.46	1.89
NiC6	25	6	340	5	70.54	2.1
NiC6	25	6	340	4	66.98	1.93
NiC7	25	7	340	5	74.24	2.25
NiC7	25	7	340	4	70.74	2.07
NiC2	25	2	320	5	50.87	1.47
NiC2	25	2	320	4	43.15	1.19
NiC3	25	3	320	5	57.23	1.71
NiC3	25	3	320	4	50.01	1.45

Table 3. Cont.

Catalyst	Pressure (bar)	wt% Metal	Temperature	Reaction Time (h)	Yield of n-C ₁₇ (% Mole)	Yield of n-C ₁₈ (% Mole)
NiC4	25	4	320	5	60.07	1.78
NiC4	25	4	320	4	53.63	1.58
NiC5	25	5	320	5	65.2	1.98
NiC5	25	5	320	4	59.66	1.74
NiC6	25	6	320	5	67.37	2.02
NiC6	25	6	320	4	61.2	1.82
NiC7	25	7	320	5	70.17	2.17
NiC7	25	7	320	4	64.4	1.93

The results shown in all the experimental runs indicate that the Ni/C_{TR} catalysts in the hydrodeoxygenation of oleic acid present a strong selectivity to the production of n-C₁₇ alkanes, which proves that there is a strong tendency towards decarboxylation and decarbonylation reactions [9,33]. Table 4 presents the composition of the liquid product obtained with NiC₇, which achieved the highest yield of n-C₁₇.

Table 4. Composition of the liquid product obtained with the highest yield of n-C₁₇ from the hydrodeoxygenation reaction of oleic acid at 25 bar, 340 °C, and 5 h.

Catalyst	n-C ₁₈	n-C ₁₇	Yield (% Mole)		n-C ₁₄ –n-C ₈	Others
			n-C ₁₆	n-C ₁₅		
NiC7	2.25	74.24	4.5	1.2	0.9	16.91

3.3. Box–Behnken Results

The optimization of Box–Behnken was carried out on a computer running Microsoft Windows 11 Pro with a 10.0.22631-core 12th Gen Intel(R) Core (TM) i5-12400F processor, operating at 2500 Mhz. The system was equipped with 6 main cores, 12 logical cores, and 64.0 GB of RAM. The software Statgraphics (Centurion XV, 2006, Stat Point Inc., (Warrenton, VA, USA) for Box–Behnken computations.

Based on the experimental results in Table 3, the Box–Behnken method was applied to develop two polynomial regression models capable of predicting the yields of n-C₁₇ and n-C₁₈ based on pressure (P), temperature (T), reaction time (t) and weight % of Ni (W). An analysis of variance was carried out to measure the effect and interaction between the physical and operational variables of the oleic acid hydrodeoxygenation process for the production of n-C₁₇ and n-C₁₈ alkanes. The complete statistical study provides the statistical value (F) Fisher and the *p*-value that help measure the effect between the control factors; the effect is considered significant if the *p*-value (*p*-value) is less than 0.05 and the F-value is greater than the F-value (1, 5, 0.05). The Box–Behnken statistical model uses polynomial regression methodology to obtain response surface plots and also shows the combination of factors for higher yield of n-C₁₇ and n-C₁₈ alkanes. The results of the analysis of variance indicate that W is the factor that has the most significant effect on the performance of n-C₁₇ with a value of *p* = 0.0001; however, P, T and t are also significant with values of *p* = 0.007, 0.0409, and 0.022, respectively. It is also interesting that W is the factor that has the most significant effect on the yield of n-C₁₈ (Table 5).

Figure 7 shows the n-C₁₇ comparison between the target test in blue and the model response in orange for the trained Box–Behnken. The metrics that evaluate this comparison are shown in Table 6, including the Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and R².

Table 5. Statistical coefficients for the performance of n-C₁₇ and n-C₁₈ and their statistical significances.

Model 1 Regression Coefficients for the Yield of n-C ₁₇ and Its F-Ratio and <i>p</i> -Value Values.			
Factor	Coefficient	F-Ratio	<i>p</i> -Value
constant	60.31		
A:P	2.4675	10.53	0.0070
B:W	9.74667	164.33	0.0001
C:T	1.74167	5.25	0.0409
D:t	1.99917	6.91	0.0220
PP	−0.80875	0.50	0.4918
PW	0.0375	0.00	0.9778
PT	0.3125	0.06	0.8164
Pt	−2.1775	2.73	0.1241
WW	−3.125	7.51	0.0179
WT	−0.5925	0.20	0.6608
Wt	−1.4	1.13	0.3087
TT	1.45	1.62	0.2277
Tt	1.78	1.83	0.2014
tt	−0.16125	0.02	0.8899

Model 1

$$\text{Yield of n-C}_{17} (\% \text{ mole}) = 60.31 + 2.4675 \times P + 9.74667 \times W + 1.74167 \times T + 1.99917 \times t - 0.80875 \times P^2 + 0.0375 \times P \times W + 0.3125 \times P \times T - 2.1775 \times P \times t - 3.125 \times W^2 - 0.5925 \times W \times T - 1.4 \times W \times t + 1.45 \times T^2 + 1.78 \times T \times t - 0.16125 \times t^2$$

Model 2 Regression Coefficients for the Yield of n-C ₁₈ and Its F-Ratio and <i>p</i> -Value Values.			
Factor	Coefficient	F-Ratio	<i>p</i> -Value
constant	1.72		
A:P	0.108333	30.46	0.0001
B:W	0.35	317.98	0.0000
C:T	0.0225	1.31	0.2740
D:t	0.0825	17.67	0.0012
PP	−0.0258333	0.77	0.3975
PW	0.025	0.54	0.4762
PT	−0.0025	0.01	0.9426
Pt	−0.0425	1.56	0.2351
WW	−0.0958333	10.60	0.0069
WT	0.015	0.19	0.6669
Wt	−0.01	0.09	0.7737
TT	0.0254167	0.75	0.4049
Tt	0.05	2.16	0.1671
tt	0.00791667	0.07	0.7926

Model 2

$$\text{Yield of n-C}_{18} = 1.72 + 0.108333 \times P + 0.35 \times W + 0.0225 \times T + 0.0825 \times t - 0.0258333 \times P^2 + 0.025 \times P \times W - 0.0025 \times P \times T - 0.0425 \times P \times t - 0.0958333 \times W^2 + 0.015 \times W \times T - 0.01 \times W \times t + 0.0254167 \times T^2 + 0.05 \times T \times t + 0.00791667 \times t^2$$

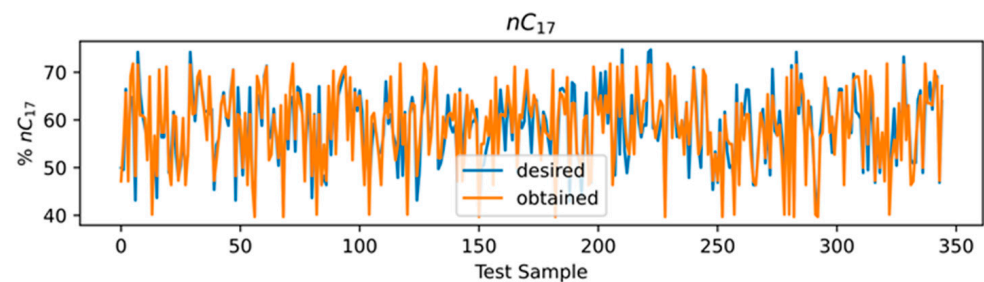
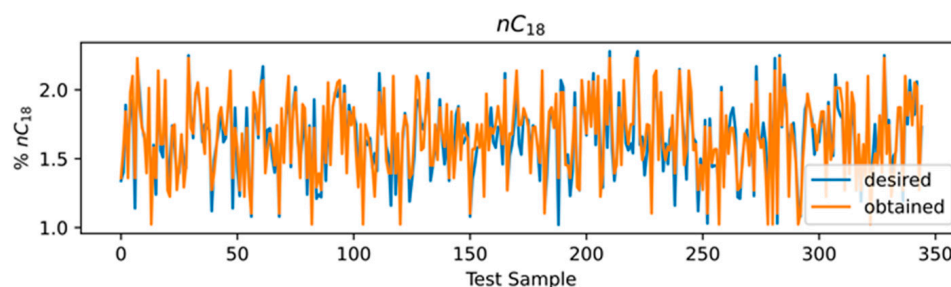
**Figure 7.** n-C₁₇ comparison between test and Box–Behnken model response.

Table 6. n-C₁₇ comparison metrics of test response and Box–Behnken model response.

Metric	Value
MAE	2.9109908579710146
MSE	13.448980818453808
MAPE	5.1193371481436586%
R ²	0.7880365513288001

Similarly, Figure 8 shows the n-C₁₈ comparison between the target test in blue and the best model response in orange for the trained Box–Behnken model. The metrics that evaluate this comparison are shown in Table 7, including the Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and R².

**Figure 8.** n-C₁₈ comparison between test and Box–Behnken model response.**Table 7.** n-C₁₈ comparison metrics of test response and Box–Behnken response.

Metric	Value
MAE	0.09526569939130435
MSE	0.014199636479194434
MAPE	6.0985543534315845%
R ²	0.8153592131544917

The metrics that evaluate this comparison between the target test in blue and the Box–Behnken model response in orange for both alkanes n-C₁₇ and n-C₁₈, trained using 27 samples, are shown in Table 8, including the Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and R².

Table 8. Metrics of n-C₁₇ and n-C₁₈ for comparison of the test response and Box–Behnken response.

Metric	Value
MAE	1.503128278681158
MSE	6.731590227466498
MAPE	5.6089457507876216%
R ²	0.8016978822416458

Moreover, we determined the Pearson correlation among the variables, the test data, and the Box–Behnken model response, as shown in Figure 9 and Table 9. The positive Pearson coefficients represent a direct correlation whereas the negative ones represent inverse correlation, expressed in ranges [0, 1]. The Pearson correlation is reliable when there is statistical significance, i.e., when the p -value is less than 5.0×10^{-1} , or there is an error below 5%. Based on Table 9, The Box–Behnken (BB) model has a high Pearson correlation of 0.901432 with a statistical significance of 9.3×10^{-127} for predicting n-C₁₇ alkanes. Similarly, the BB model has a high Pearson correlation of 0.860052 with statistical significance of 2.9×10^{-102} for predicting n-C₁₈ alkanes. Additionally, all inputs contribute to the BB model for alkane prediction with different levels of correlation, but there is

not enough statistical significance for supporting the contribution of temperature to the generation of n-C₁₈ alkanes, since the *p*-value is 0.149284.

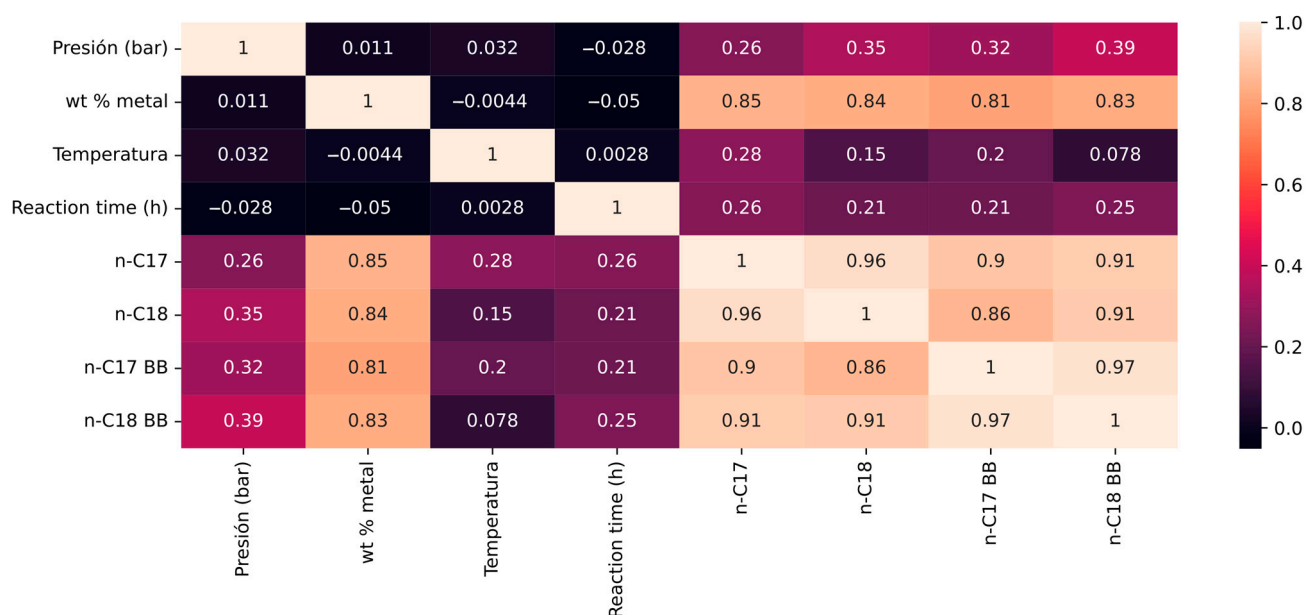


Figure 9. Heat map of correlations among the input variables, the target output, and Box–Behnken model response.

Table 9. Pearson correlation among the input variables, the target output, and Box–Behnken model with *p*-value.

Tested Correlation	Pearson Coefficient	<i>p</i> -Value
n-C ₁₇ to n-C ₁₈ BB	0.91473	4.8×10^{-137}
n-C ₁₈ to n-C ₁₈ BB	0.912676	2.4×10^{-135}
n-C ₁₇ to n-C ₁₇ BB	0.901432	9.3×10^{-127}
n-C ₁₈ to n-C ₁₇ BB	0.860052	2.9×10^{-102}
wt% metal to n-C ₁₈ BB	0.829173	1.19×10^{-88}
wt% metal to n-C ₁₇ BB	0.80735	1.4×10^{-80}
Pressure (bar) to n-C ₁₈ BB	0.388761	6.81×10^{-14}
Pressure (bar) to n-C ₁₇ BB	0.315907	1.96×10^{-9}
Reaction time (h) to n-C ₁₈ BB	0.247907	3.15×10^{-6}
Reaction time (h) to n-C ₁₇ BB	0.214262	6.02×10^{-5}
Temperature to n-C ₁₇ BB	0.198049	0.000214
Temperature to n-C ₁₈ BB	0.077803	0.149284

For the practical application of models 1 and 2 in predicting yields of n-C₁₇ and n-C₁₈, respectively, the values of the physical and operational variables are encoded and replaced in the models. An ANOVA was used to evaluate the goodness of fit of the models; the values of the determination coefficients of $R^2 = 88.079\%$ and $R^2 = 93.5001\%$ for models 1 and 2, respectively, demonstrate that the models describe the response surface in the ranges indicated for the variables analyzed and can predict with an acceptable level of statistical confidence the yields of n-C₁₇ and n-C₁₈. The combination of levels of physical and operating factors for maximum yields of n-C₁₇ = 71.5468 and n-C₁₈ = 2.22304 are presented in Table 10.

Table 10. Combination of factor levels for maximum yields of n-C₁₇ and n-C₁₈.

Maximum Yield of n-C ₁₇ (% Mole) = 71.5468	
Factor	Optimized Values
Pressure (bar)	24.98
wt% metal	6.94
Temperature (°C)	340
Reaction time (h)	4.74
Maximum Yield of n-C ₁₈ (% Mole) = 2.22304	
Factor	Optimized Values
Pressure	24.82
wt% metal	6.95
Temperature	340
Reaction time	5

3.4. ANN Results

The optimization of ANNs was carried out on a computer running Microsoft Windows 11 Pro with a 10.0.22631-core 12th Gen Intel(R) Core (TM) i5-12400F processor, operating at 2500 MHz. The system was equipped with 6 main cores, 12 logical cores, and 64.0 GB of RAM, and Python version 3.9.10 was used for all computations. Parallel computing and ANN computations were conducted on TensorFlow 2.10.

The parallel plot of the hyperparameter optimization with exhaustive search across the S^1 , S^2 , S^3 , S^4 , and Pa with the configuration described in Section 2.5 for the training distribution with 27 samples for training and 345 for testing is shown Figure 10, obtaining the best result with $R^2 = 0.91$, when $S^1 = 30$, $S^2 = 10$, $S^3 = 10$, $S^4 = 10$, and $Pa = 50$.

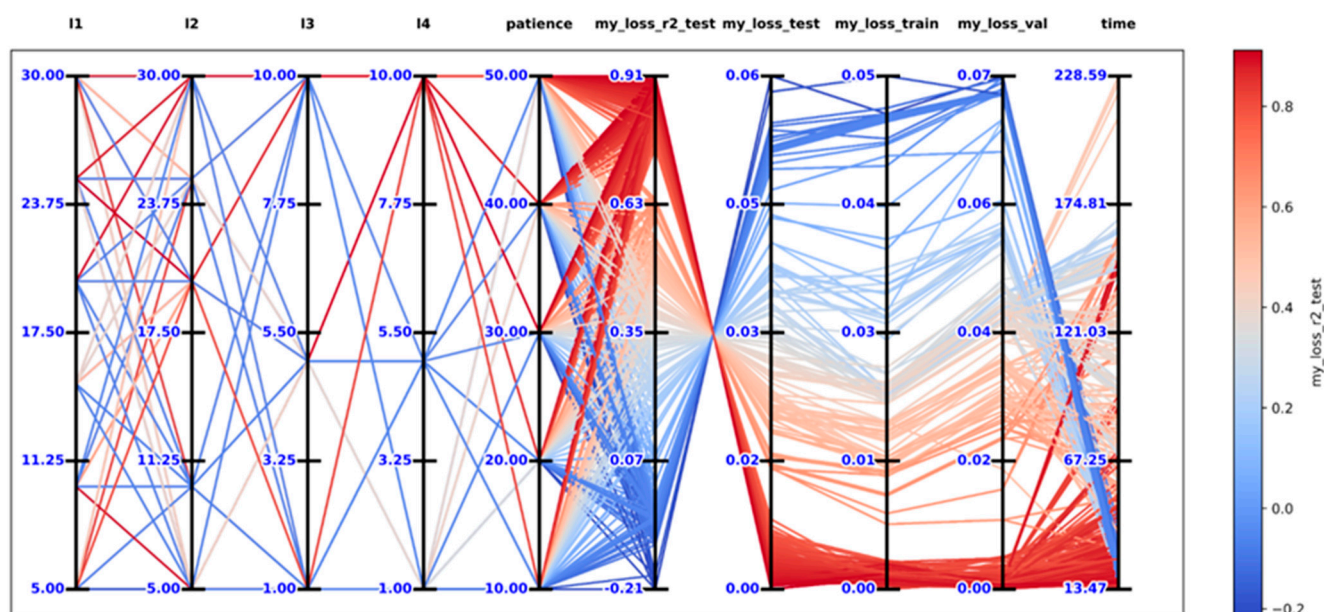
**Figure 10.** Parallel plot of hyperparameter optimization with 27 points for training and 345 points for testing.

Figure 11 shows the n-C₁₇ comparison between the target test in blue and the best model response in orange for the trained ANN using 27 samples (ANN27). The metrics that evaluate this comparison are shown in Table 11, including the Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and R^2 .

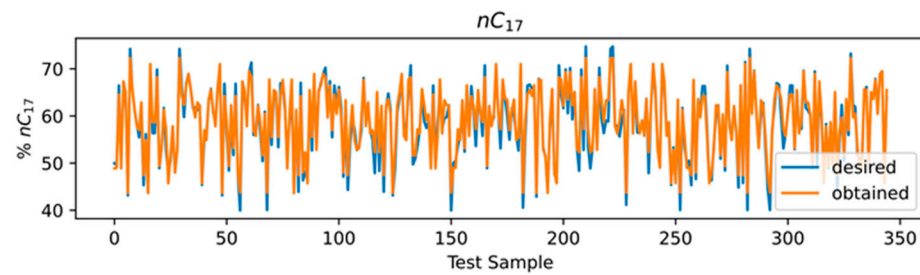


Figure 11. n-C₁₇ comparison between test and ANN27 model responses.

Table 11. n-C₁₇ comparison metrics of test and ANN27 responses.

Metric	Value
MAE	1.5393119812011713
MSE	3.7038989347370617
MAPE	2.7534556120058794%
R ²	0.9416244842390435

Similarly, Figure 12 shows the nC₁₈ comparison between the target test in blue and the ANN27 model response. The metrics that evaluate this comparison are shown in Table 12, including the Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and R².

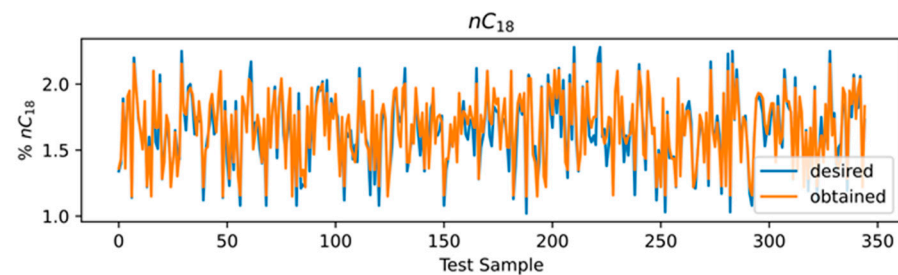


Figure 12. n-C₁₈ comparison between test and ANN27 model responses.

Table 12. n-C₁₈ comparison metrics of test and ANN27 model responses.

Metric	Value
MAE	0.0775767906575963
MSE	0.009133386009309954
MAPE	4.936592052944989%
R ²	0.8812367075879945

The metrics that evaluate the comparison between the target test in blue and the ANN27 model response in orange for both alkanes n-C₁₇ y n-C₁₈ are shown in Table 13, including the Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and R².

Table 13. Metrics of n-C₁₇ and n-C₁₈ for comparison of the test and ANN27 model responses.

Metric	Value
MAE	0.8084443859293845
MSE	1.8565161603731877
MAPE	3.8450238324754346%
R ²	0.911430595913519

Additionally, we determined the Pearson correlation among the variables (see Figure 13), the test data, and the ANN27 model response. Based on Table 14, the ANN27 model has a high Pearson correlation of 0.973276 with a statistical significance of 3×10^{-221} for predicting n-C₁₇ alkanes. Similarly, the ANN27 model has a high Pearson correlation of 0.941994 with statistical significance of 1.1×10^{-164} for predicting n-C₁₈ alkanes. Additionally, all inputs contribute to the ANN27 model for alkane prediction with different levels of correlation. Moreover, the ANN27 model has statistical significance for all the tested Pearson correlations. Table 15 shows the optimal configuration obtained for maximizing alkane production with pressure 25 bar, wt 7% metal, 340 °C of temperature, and 5 h of reaction time.

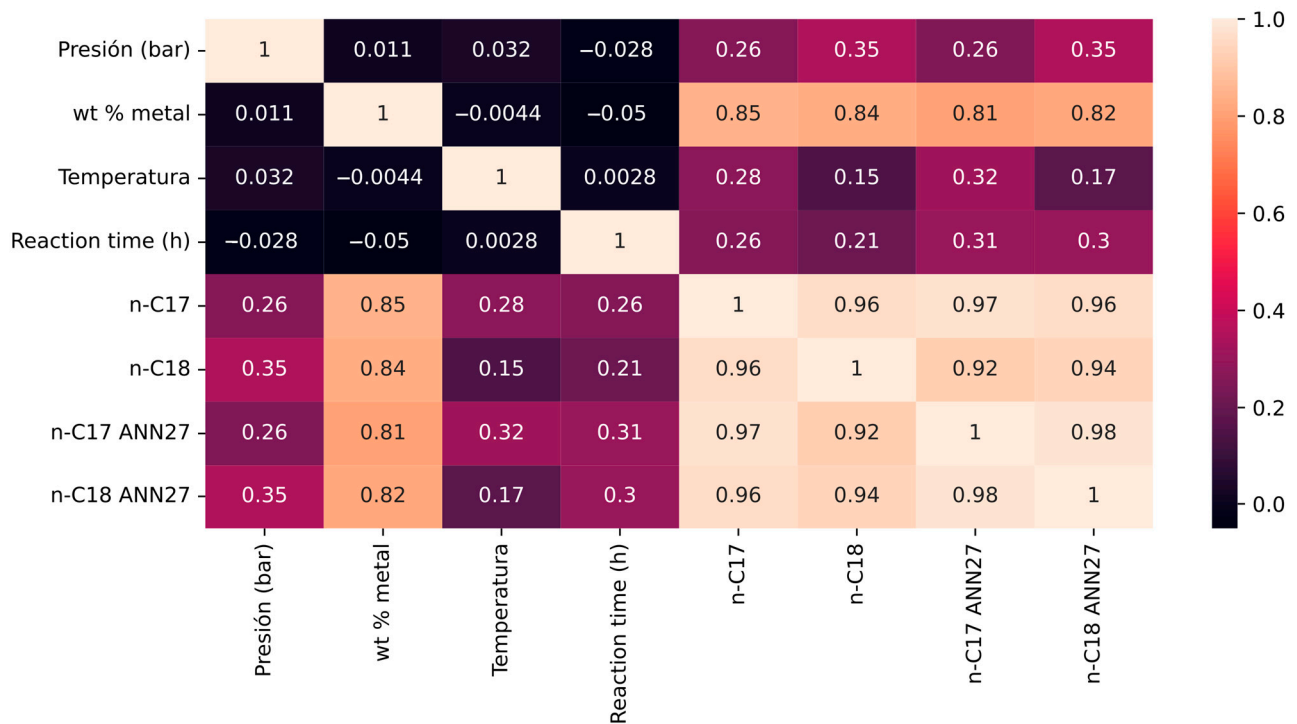


Figure 13. Heat map of correlations among the input variables, the target output, and ANN27 model response.

Table 14. Pearson correlation among the input variables, the target output, and ANN27 model with *p*-value.

Tested Correlation	Pearson Coefficient	<i>p</i> -Value
n-C ₁₇ to n-C ₁₇ ANN27	0.973276	3×10^{-221}
n-C ₁₇ to n-C ₁₈ ANN27	0.962993	2.2×10^{-197}
n-C ₁₈ to n-C ₁₈ ANN27	0.941994	1.1×10^{-164}
n-C ₁₈ to n-C ₁₇ ANN27	0.921942	2.4×10^{-143}
wt% metal to n-C ₁₈ ANN27	0.816651	6.9×10^{-84}
wt% metal to n-C ₁₇ ANN27	0.807074	1.75×10^{-80}
Pressure (bar) to n-C ₁₈ ANN27	0.351109	1.91×10^{-11}
Temperature to n-C ₁₇ ANN27	0.321232	1.01×10^{-9}
Reaction time (h) to n-C ₁₇ ANN27	0.306582	6.08×10^{-9}
Reaction time (h) to n-C ₁₈ ANN27	0.302872	9.44×10^{-9}
Pressure (bar) to n-C ₁₇ ANN27	0.256717	1.35×10^{-6}
Temperature to n-C ₁₈ ANN27	0.172889	0.001264

Table 15. Maximum yields predicted of n-C₁₇ and n-C₁₈ with ANN27 model response.

Maximum Yield of n-C ₁₇ (% Mole) = 72.2953	
Factor	Optimized Values
Pressure (bar)	25
wt% metal	7
Temperature (°C)	340
Reaction time (h)	5

Maximum Yield of n-C ₁₈ (% Mole) = 2.1534	
Factor	Optimized Values
Pressure	25
wt% metal	7
Temperature	340
Reaction time	5

Figure 14 shows the parallel plot of the hyperparameter optimization with exhaustive search across S^1 , S^2 , S^3 , S^4 , and Pa with the configuration described in Section 2.5 for the training distribution with 60% for training, 20% for validation, and 20% for testing of 372 samples in the dataset, obtaining the best result with $R^2 = 0.97$, when $S^1 = 20$, $S^2 = 30$, $S^3 = 10$, $S^4 = 10$, and $Pa = 50$.

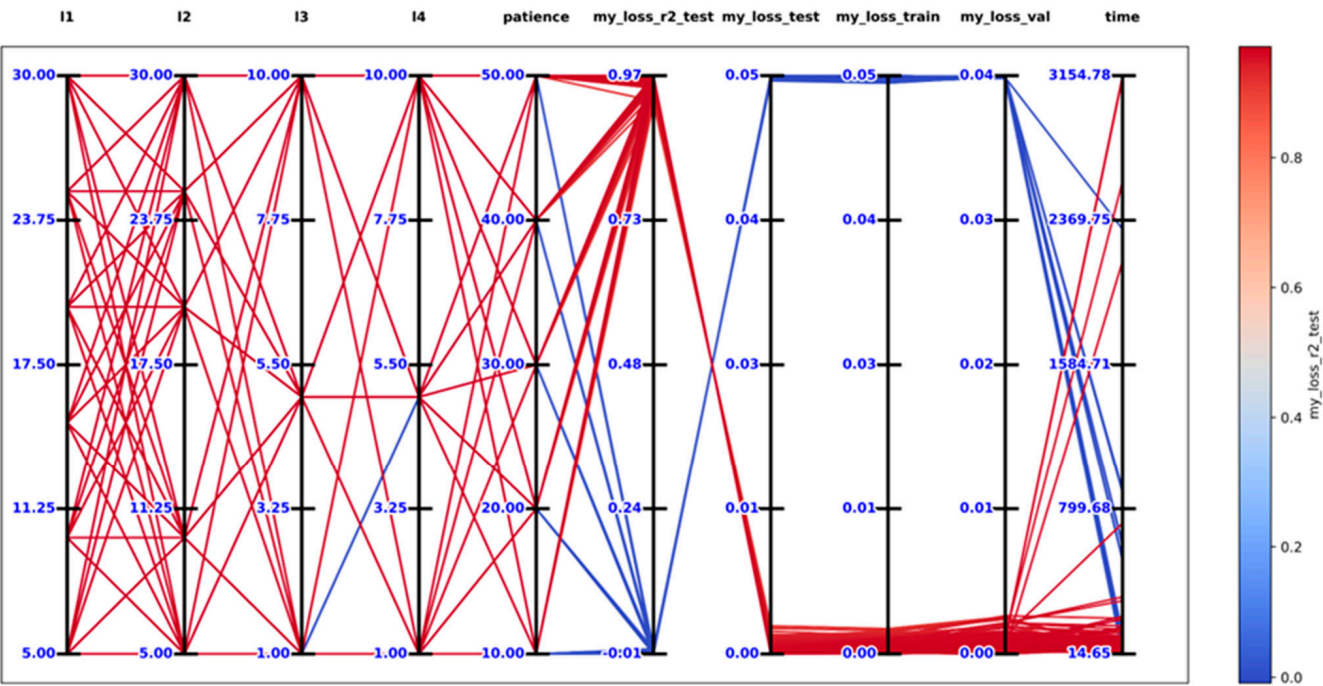


Figure 14. Parallel plot of hyperparameter optimization with 60%-20%-20% dataset distribution.

Figure 15 shows the n-C₁₇ comparison between the target test in blue and the best model response in orange for the trained ANN with 60%-20%-20% distribution of the dataset (ANN602020). The metrics that evaluate this comparison are shown in Table 16, including the Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and R^2 .

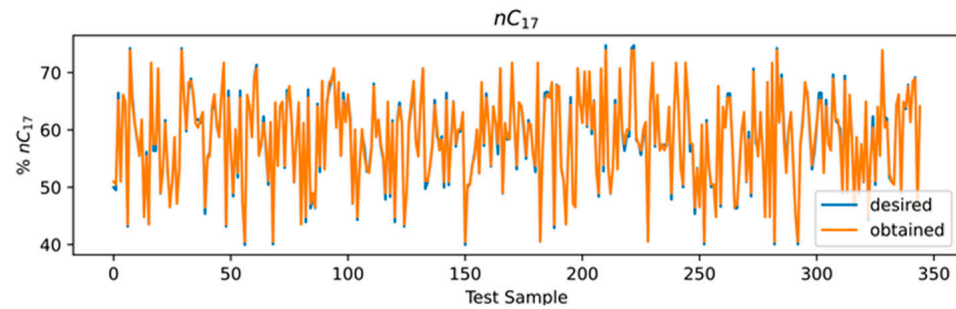


Figure 15. n-C₁₇ comparison between test and ANN602020 model responses.

Table 16. n-C₁₇ comparison metrics of test and ANN602020 model responses.

Metric	Value
MAE	0.6345773381772246
MSE	0.6185777595032578
MAPE	1.0887789453225924%
R ²	0.9902508690475856

Similarly, Figure 16 shows the n-C₁₈ comparison between the target test in blue and the ANN602020 model responses. The metrics that evaluate this comparison are shown in Table 17, including the Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and R².

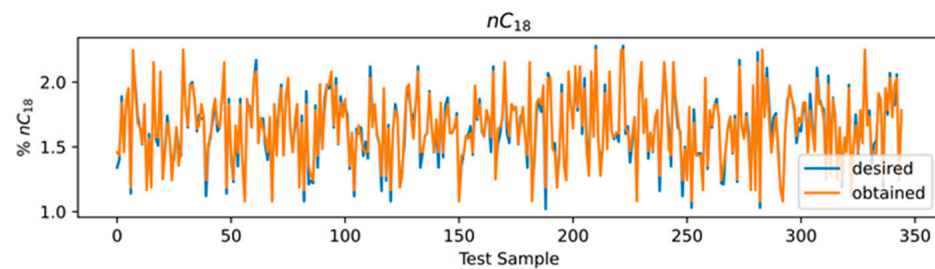


Figure 16. n-C₁₈ comparison between test and ANN602020 model responses.

Table 17. n-C₁₈ comparison metrics of test and ANN602020 model responses.

Metric	Value
MAE	0.046886737533237625
MSE	0.0036509875484390993
MAPE	2.9908108061085723%
R ²	0.952525459740136

The metrics that evaluate the comparison between the target test in blue and the ANN602020 model response in orange for both alkanes n-C₁₇ and n-C₁₈ are shown in Table 18, including the Mean Absolute Error (MAE), Mean Square Error (MSE), Mean Absolute Percentage Error (MAPE) and R².

Table 18. Metrics of n-C₁₇ and n-C₁₈ for comparison of the test and ANN602020 model responses.

Metric	Value
MAE	0.34073203785523093
MSE	0.31111437352584853
MAPE	2.0397948757155816%
R ²	0.9713881643938609

Additionally, we determined the Pearson correlation among the variables (Figure 17), the test data, and the ANN602020 model response. Based on Table 19, the ANN602020 model has a high Pearson correlation of 0.995199804 with a statistical significance of 0.0 for predicting n-C₁₇ alkanes. Similarly, the ANN602020 model has a high Pearson correlation of 0.976071019 with a statistical significance of 2.2912×10^{-229} for predicting n-C₁₈ alkanes. Additionally, all inputs contribute to the ANN602020 model for alkane prediction with different levels of correlation. Moreover, the ANN602020 model has the highest statistical significance for all the tested Pearson correlations. Table 20 shows the optimal configuration obtained for maximizing alkane production with pressure 25 bar, wt 7% metal, 340 °C of temperature, and 5 h of reaction time.

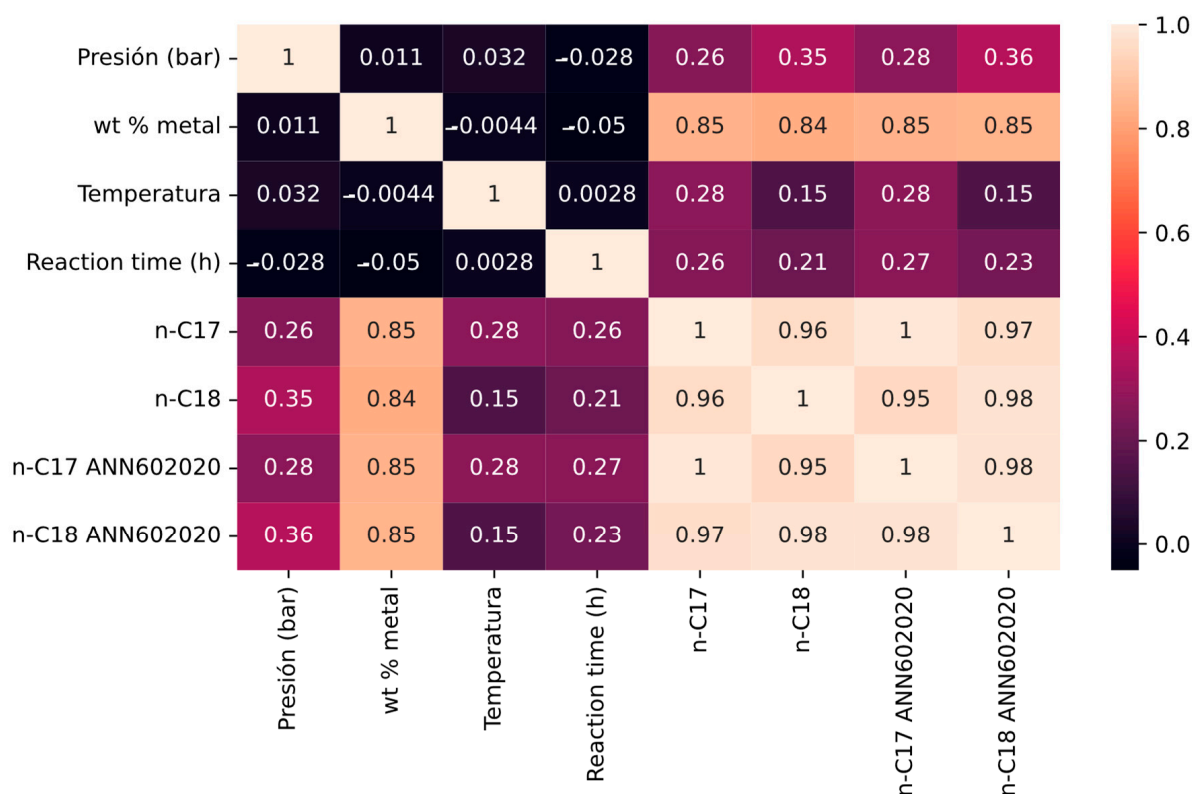


Figure 17. Heat map of correlations among the input variables, the target output, and ANN602020 model response.

Table 19. Pearson correlation among the input variables, the target output, and ANN602020 model with *p*-value.

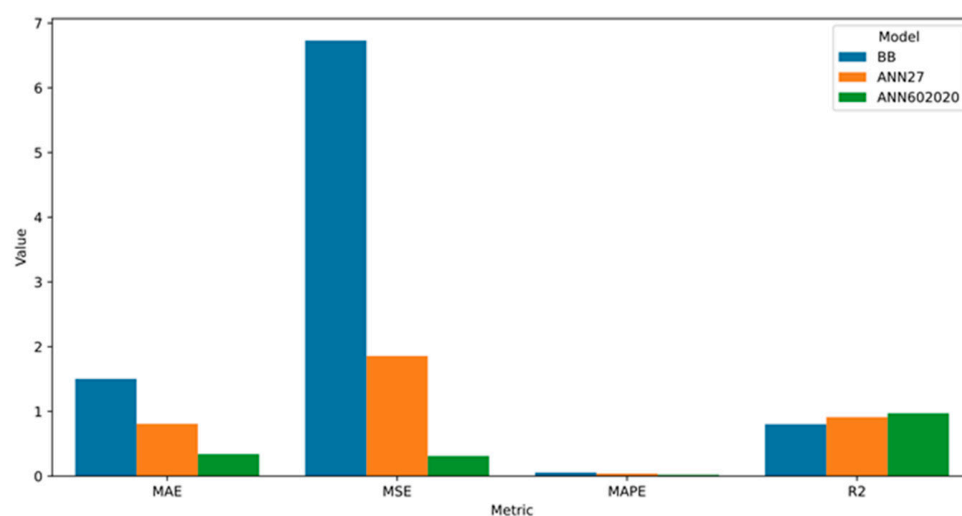
Tested Correlation	Pearson Coefficient	<i>p</i> -Value
n-C ₁₇ to n-C ₁₇ ANN602020	0.995199804	0
n-C ₁₈ to n-C ₁₈ ANN602020	0.976071019	2.2912×10^{-229}
n-C ₁₇ to n-C ₁₈ ANN602020	0.970654942	2.2636×10^{-214}
n-C ₁₈ to n-C ₁₇ ANN602020	0.952805659	1.1885×10^{-179}
wt% metal to n-C ₁₈ ANN602020	0.851587787	3.12006×10^{-98}
wt% metal to n-C ₁₇ ANN602020	0.84645346	6.65384×10^{-96}
Pressure (bar) to n-C ₁₈ ANN602020	0.364380744	2.84642×10^{-12}
Temperature to n-C ₁₇ ANN602020	0.27855838	1.44305×10^{-7}
Pressure (bar) to n-C ₁₇ ANN602020	0.276223795	1.85016×10^{-7}
Reaction time (h) to n-C ₁₇ ANN602020	0.269802864	3.62168×10^{-7}
Reaction time (h) to n-C ₁₈ ANN602020	0.22970418	1.64118×10^{-5}
Temperature to n-C ₁₈ ANN602020	0.152945617	0.004409192

Table 20. Maximum yields predicted of n-C₁₇ and n-C₁₈ with ANN602020 model response.

Maximum Yield of n-C ₁₇ (% Mole) = 73.8834	
Factor	Optimized Values
Pressure (bar)	25
wt% metal	7
Temperature (°C)	340
Reaction time (h)	5
Maximum Yield of n-C ₁₈ (% Mole) = 2.2503	
Factor	Optimized Values
Pressure	25
wt% metal	7
Temperature	340
Reaction time	5

3.5. Comparison of Models

In order to select the optimal model, we evaluated the MAE, MSE, MAPE, and R² metrics across both n-C₁₇ and n-C₁₈ alkanes. The comparison depicted in Figure 18 showcases the performance of the BB metrics in blue, ANN27 in orange, and ANN602020 in green. Upon visual inspection, it is evident that ANN602020 stands out as the most promising model. It is important to note that smaller values of MAE, MSE, and MAPE indicate superior performance, while an R² value approaching 1 signifies better accuracy.

**Figure 18.** Comparison of metrics evaluation among BB, ANN27, and ANN602020 models.

Despite the compelling visual evidence indicating that ANN602020 is the superior model, it is essential to normalize all metrics to a range of 0 to 1. This normalization allows for consistent scaling across all metrics, ensuring that they are directly comparable and enabling them to achieve their optimal value at 1 and worst value at 0. This normalization is particularly crucial since error-related metrics have varying scales and perform worse as their values increase, which is contrary to the behavior of the R² metric. After standardizing the metrics, we used a boxplot, shown in Figure 19, to compare the models; once again the best model is ANN602020. Additionally, we performed an ANOVA test, as presented in Table 21, to showcase that there are significant differences among the models with statistical significance since $F = 252.6423$ and $PR(>F) = 1.24 \times 10^{-8}$.

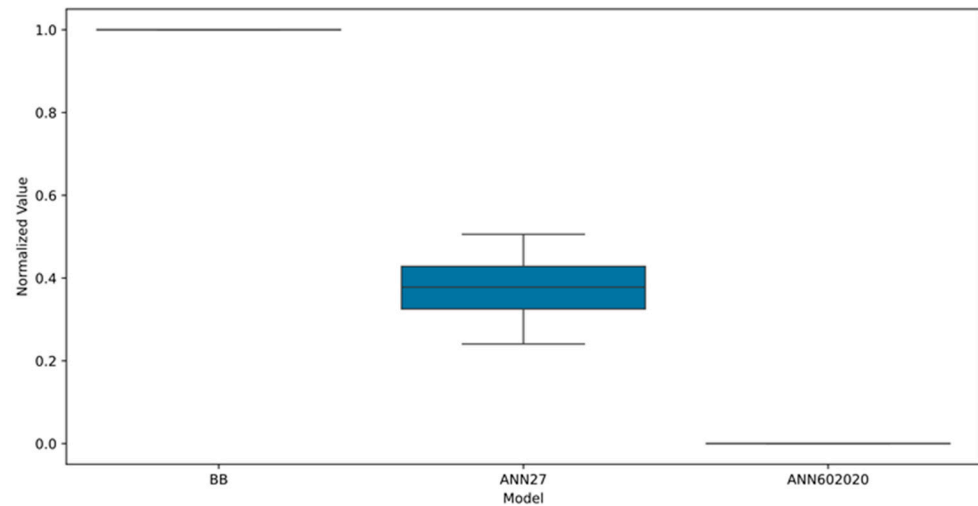


Figure 19. Comparison of models using normalized metrics.

Table 21. Comparison of significant difference among models using ANOVA test.

Source of Variation	sum_sq	df	F	PR (>F)
C (Model)	2.041302	2	252.6423	1.24×10^{-8}
Residual	0.036359	9		

4. Conclusions

In this work, a novel approach to integrating oleic acid into the hydrodeoxygenation process of Ni/Tire Rubber Carbon (Ni/C_{TR}) catalysts is presented. Catalysts with varying Ni loadings were synthesized using incipient wet impregnation and pyrolysis techniques. These catalysts were then utilized in oleic acid hydrodeoxygenation reactions to produce renewable biofuels with diesel-like properties, particularly a high concentration of n-C₁₇ alkanes and some production of n-C₁₈ with lower concentration. This is notable as the generation of n-C₁₈ typically requires more complex catalysts.

In our hydrodeoxygenation experiments, we employed oleic acid and conducted tests using different Ni/C_{TR} catalysts, while adjusting parameters such as pressure (P), tungsten content (W), temperature (T), and time (t). Our findings demonstrated the effectiveness of this approach in producing sustainable biofuels. Furthermore, we created a dataset with 372 different configurations for training models to predict the most efficient production of n-C₁₇ and n-C₁₈ alkanes.

After that, we developed and fine-tuned three models using our generated dataset. The first model utilized the Box–Behnken method and 27 training points to establish a prediction polynomial. The second model employed an artificial neural network trained with the same 27 training points. The final model utilized an artificial neural network with a training distribution of 60%, validation distribution of 20%, and testing distribution of 20%.

The Box–Behnken model accurately predicted the n-C₁₇ and n-C₁₈ generation, achieving R² scores of 0.7880 and 0.8154, respectively, for each alkane. It resulted in a mean squared error (MSE) of 6.73159, a mean absolute error (MAE) of 1.50313, and a mean absolute percentage error (MAPE) of 5.60895%. The combined R² score for both alkanes was 0.80170. The ANN27 model with 27 training points, under the same conditions as the Box–Behnken model, forecasted the n-C₁₇ and n-C₁₈ generation with R² scores of 0.9416 and 0.8812, resulting in an MSE of 0.00441, MAE of 0.05291, and MAPE of 3.84502%. The combined R² score for both alkanes was 0.91143. Additionally, we tested another model ANN602020 with 223 training points, corresponding to 60% of the data for training, and accurately forecasted the n-C₁₇ and n-C₁₈ generation with R² scores of 0.9903 and 0.9525,

resulting in an MSE of 0.0014, MAE of 0.02773, and MAPE of 2.03979%. The combined R^2 score for both alkanes was 0.97139.

After analyzing normalized metrics using a boxplot and conducting an ANOVA test, we have found that model ANN602020 is the top-performing model with statistical significance. The ANOVA test results ($F = 252.6423$, $PR(>F) = 1.24 \times 10^{-8}$) indicate significant differences among the models, reinforcing this conclusion. Moreover, both the ANN602020 model and ANN27 (second best model), validate that the optimal conditions for generating n-C₁₇ and n-C₁₈ alkanes involve a pressure of 25 bar, 7% wt% metal, 340 °C, and a reaction time of 5 h.

In addition, we conducted testing on this setup and determined the actual percentage of moles in the production of n-C₁₇ and n-C₁₈ alkanes, yielding 74.24% and 2.25% respectively. These values represent the highest level of efficiency achieved, closely matching the predicted values of 73.8834% and 2.2503% from the ANN602020 model.

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