J. Innovative Eng. Nat. Sci., vol. 6, no. 2, pp. 308-321, 2026.
http://doi.org/10.61112/jiens.1907318

JIENS
Journal of Innovative Engineering and Natural Science
(Yenilikçi Mühendislik ve Doğa Bilimleri Dergisi)
https://dergipark.org.tr/en/pub/jiens
Original Paper

Digital twin of waste cooking oil biodiesel: optimizing n-Butanol blends via mixture-process design

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ARTICLE INFO

Article history:
Received March 11, 2026
Received in revised form May 8, 2026
Accepted June 6, 2026

Available online

Keywords:
Digital Twin
Waste Cooking Oil Biodiesel
n-Butanol Blends
Mixture-Process Design
Multiple Response Optimization

ABSTRACT

Although waste cooking oil (WCO)-based biodiesel represents a sustainable alternative within the context of the circular economy, its direct application remains constrained by drawbacks such as high density, high kinematic viscosity, and elevated surface tension. This study aims to improve the weak thermophysical properties of WCO biodiesel through the addition of n-butanol, while simultaneously tailoring its density and kinematic viscosity to fall within the EN 590 diesel standard limits. To this end, rather than relying on costly and time-consuming trial-and-error approaches, this research introduces an innovative methodology based on the integration of the DWSIM process simulator and Mixture-Process Design. The chemical structure of the WCO biodiesel was defined as a surrogate model in the DWSIM environment using the mass fractions of its primary Fatty Acid Methyl Ester (FAME) components (methyl oleate, methyl linoleate, methyl palmitate, and methyl stearate). The fundamental thermophysical properties of the model were then validated against reference experimental data. To statistically model the constrained mixture space, a 15-run experimental matrix was generated utilizing the D-Optimal Extreme Vertices algorithm. The developed regression models accounted for the variations in kinematic viscosity, density, and surface tension with high statistical accuracy ($R^2 > 96.5\%$, $p < 0.05$). In the final stage, Multiple Response Optimization was performed using Derringer's Desirability Function to reconcile the conflicting targets of density and viscosity into a unified metric. The analysis indicated a maximum desirability score ($D = 0.835$) for a blend comprising 72.8 wt.% WCO and 27.2 wt.% n-butanol (WCO72.8/NB27.2) at an operating temperature of 30 °C. At this global optimum point, the density and kinematic viscosity of the fuel were determined as 840.0 kg/m^3 and 2.72 mm^2/s, respectively. Overall, the findings suggest that n-butanol acts as a highly effective solvent in reducing the internal friction and surface tension of waste oil biodiesels characterized by heavy ester profiles. Furthermore, the results indicate that the DWSIM-RSM digital integration can be utilized with high reliability in alternative fuel blending optimizations.

I. INTRODUCTION

Rising global energy demand and the environmental degradation caused by fossil fuels have directed researchers toward the search for sustainable and renewable alternative fuels. In this context, biodiesel derived from waste cooking oil (WCO) demonstrates a strong alignment with circular economy principles, offering strategic advantages from both environmental and economic perspectives. From an economic standpoint, WCO-based biodiesel production presents significant commercial potential because it requires considerably lower feedstock and production costs compared to edible or non-edible vegetable oils [1, 2]. From an environmental perspective, literature indicates that WCO biodiesel can be utilized in blends of up to 20% without requiring engine modifications [3]. Furthermore, studies have shown that it substantially improves air quality, yielding reductions of up to 85% in hydrocarbon, sulfur dioxide (SO_2), carbon monoxide (CO), and smoke emissions [4, 5]. Moreover, utilizing waste oils for biodiesel production addresses waste disposal challenges, thereby contributing directly to sustainability scenarios [6].

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Despite these environmental and economic benefits, the direct application of pure WCO biodiesel in diesel engines entails significant technical limitations due to its adverse physicochemical properties. Pure WCO biodiesel exhibits fundamental challenges, including high viscosity, a high pour point, and low volatility [7]. In particular, high viscosity and surface tension severely degrade atomization quality during fuel injection into the cylinder. This degradation leads to issues such as longer spray penetration, narrower spray angles, and reduced gas entrainment compared to standard diesel [8]. In addition to this deterioration in atomization, the high density of WCO biodiesel tends to increase direct fuel consumption and NOx emissions [9]. Indeed, existing studies quantitatively demonstrate that utilizing WCO blends ranging from B10 to B50 in engines increases brake specific fuel consumption (BSFC) by 1.61% to 18% [10].

One of the most effective methods to mitigate these combustion and performance losses stemming from the physical properties of WCO biodiesel is the introduction of high-energy, low-viscosity short-chain alcohols into the blend. Specifically, n-butanol serves as a highly successful additive in reducing the kinematic viscosity and density of both diesel and biodiesel blends. Literature indicates that diesel blends containing 5 to 15 vol.% n-butanol successfully meet the density and viscosity requirements outlined in the EN 590 standards [11, 12]. The density behaviors of WCO and 1-butanol blends across wide temperature and pressure ranges have been investigated using thermodynamic models (e.g., PC-SAFT) [13, 14]; however, researchers note that increasing the butanol addition beyond 20% may lead to performance declines [15].

Although the literature explores the properties of WCO biodiesel and n-butanol blends, determining the "optimum" mixing ratio and temperature conditions that simultaneously satisfy international standards (EN 590) still largely relies on trial-and-error methods and costly laboratory testing. Conversely, Response Surface Methodology (RSM) serves as an exceptionally robust statistical tool for understanding inter-parameter interactions and optimizing biodiesel processes [16, 17]. In recent years, integrating chemical process simulators like DWSIM with RSM has enabled high-accuracy optimization in complex processes, such as hydrogen production [18]; nevertheless, the direct application of this digital integration to predict and optimize the thermophysical properties of biodiesel blends represents a significant gap in the literature [19]. Recent studies have increasingly utilized sophisticated machine learning algorithms, such as Gaussian Process Regression (GPR), Artificial Neural Networks (ANN), and Support Vector Regression, to predict the density and viscosity of biodiesel-alcohol blends with high precision [20, 21]. While these advanced computational models and established thermodynamic frameworks like PC-SAFT offer excellent predictive capabilities, they are primarily designed for property estimation rather than multi-objective process optimization. There remains a notable lack of integrated frameworks that can simultaneously navigate conflicting thermophysical targets within a constrained mixture-process space. To address this literature gap, the present study introduces an innovative methodology that couples a digital twin of WCO biodiesel, developed in the DWSIM process simulator, with Mixture-Process Design-based Multiple Response Optimization. The primary objective of this research is to mathematically model the synergistic effects of n-butanol concentration and temperature on the kinematic viscosity, density, and surface tension of WCO biodiesel. Ultimately, this approach aims to determine, with high precision, the global optimum operating conditions that align the key fluidity properties (density and kinematic viscosity) with EN 590 diesel standards.

II. MATERIALS AND METHODS

2.1. Development of the WCO Biodiesel Surrogate Model in DWSIM

In simulation-based optimization studies, establishing surrogate fuel models represents a critical step for accurately modeling fuels with multi-component and complex thermophysical structures, such as waste cooking oil (WCO)-based biodiesel. The literature indicates that chemical process simulators (e.g., Aspen HYSYS, DWSIM) can be utilized with high efficiency in modeling WCO-based processes [22]. To accurately predict the thermophysical properties and combustion dynamics of these fuels, it is necessary to employ surrogate models composed of Fatty Acid Methyl Ester (FAME) components that represent actual biodiesel blends [23]. In this study, digital twin modeling was conducted in the open-source DWSIM process simulator (Version 9.0.5) to investigate the thermophysical behaviors of n-butanol/WCO blends.

To represent the chemical composition of WCO biodiesel with high accuracy, the FAME mass fractions experimentally characterized by [24] were utilized as a basis. Accordingly, to optimize computational cost and solve thermodynamic equations stably, four primary FAME components representing 94.95% of the actual WCO main skeleton were defined in the system. The WCO surrogate model used in the simulation was constructed using the mass fractions of 46.96% methyl oleate (C18:1), 31.72% methyl linoleate (C18:2), 12.77% methyl palmitate (C16:0), and 3.50% methyl stearate (C18:0). For the calculation of the physical properties (density, kinematic viscosity) of the blends, thermodynamic models, group contribution methods, and mixing rules, which have been demonstrated to provide high prediction accuracy for organic FAME systems and WCO-butanol blends in the literature, were employed [25]. In the simulation flowsheet, the total mass flow rate was fixed such that the sum of the mass fractions equaled 1.0, adhering to mixture design rules, and the blends were mass-controlled via an integrated mixer module. A validation study was conducted to verify the accuracy of the developed WCO biodiesel surrogate model and the simulation framework. For this purpose, the surface tension, liquid phase density, and kinematic viscosity values calculated for pure WCO biodiesel at 30 °C in the simulation environment were compared with the actual laboratory measurements from the reference study [24].

2.2. Mixture-Process Experimental Design

A Mixture-Process Design was formulated to mathematically model the synergistic interactions of biodiesel and n-butanol blends on their thermophysical properties. The independent factors (mixture and process variables) evaluated in this study, along with the targeted dependent response variables and their boundaries, are summarized in Table 1.

Table 1. Independent factors, levels, and targeted response variables used in the Mixture-Process design

Parameter	Variable Name	Role	Lower	Upper	Target
Factor (X_1)	WCO Biodiesel	Mass Fraction	0.7	1	-
Factor (X_2)	n-Butanol	Mass Fraction	0	0.3	-
Factor (Z)	Temperature	Process Factor (°C)	30	90	-
Response (Y_1)	Kinematic Viscosity	Physical Property (mm²/s)	-	-	Target: 3.25
Response (Y_2)	Density	Physical Property (kg/m³)	-	-	Target: 840.0
Response (Y_3)	Surface Tension	Physical Property (N/m)	-	-	Minimize

In mixture designs, the sum of the mass fractions of the components must always equal 100% (1.0) ($X_1 + X_2 = 1.0$). Due to this mandatory fundamental constraint, a specific regression model encompassing the interaction between the mixture components (X_1, X_2) and the process factor (Z) that alters the physical state of the system was employed instead of standard factorial designs. The mathematical framework utilized for predicting the response variables is expressed by Eq. 1:

$$Y = \sum_{i=1}^{2} \beta_i X_i + \sum_{i=1}^{2} \alpha_i X_i Z \quad (1)$$

Here, Y represents the measured response variable (Y_1, Y_2, Y_3), X_i denotes the constrained mixture mass fractions, and Z signifies the process factor (temperature). The β_i coefficients in the equation define the linear blending effects of the pure mixture components, while the α_i coefficients describe the interaction between the mixture components and the process factor.

Studies in the literature indicate that the D-Optimal Extreme Vertices design is the most effective method for modeling irregular experimental spaces constrained by upper and lower component limits [26]. This algorithm minimizes the variance of the model coefficients by maximizing the determinant of the variance-covariance matrix of the design matrix. Accordingly, utilizing a backward selection algorithm, the 15 most representative experimental points in the constrained mixture space were determined, and the DWSIM simulations were executed based on this optimum matrix (Table 2). Certain experimental points in the design matrix (e.g., runs 1 and 4, or runs 3 and 5) are replicated at specific intervals. The primary statistical rationale for intentionally incorporating these replicated runs into the algorithm is to calculate the pure error of the developed regression model, free from experimental errors and noise. This approach allowed the Lack-of-Fit tests, which verify the extent to which the model represents the data, to be performed with high statistical reliability.

2.3. Multiple Response Optimization

Following the statistical modeling of the blend properties within the constrained experimental space (see Section 2.2), Multiple Response Optimization was applied to determine the global optimum blending ratio and temperature that would simultaneously satisfy EN 590 diesel fuel standards. Derringer's Desirability Function [27] was utilized to combine dependent variables with distinct and often conflicting objectives into a single dimensionless metric [28, 29]. In this method, depending on the optimization objective (reaching a specific target or minimizing), individual desirability values (d_i) ranging from 0 (completely undesirable) to 1 (completely desirable) are calculated for each response variable. For response variables where achieving a specific target value is intended, such as density and kinematic viscosity, the individual desirability was calculated using Eq. 2:

$$d_i = \left[\frac{Y_i - Y_{min}}{Y_{target} - Y_{min}}\right]^{w_i} \quad (2)$$

For the surface tension variable, where minimization is targeted to enhance atomization quality, the individual desirability was formulated using Eq. 3:

$$d_j = \left[\frac{Y_{max} - Y_j}{Y_{max} - Y_{min}}\right]^{w_j} \tag{3}$$

Here, Y_i and Y_j represent the predicted response values, Y_{min} and Y_{max} denote the lower and upper limits of the system, Y_{target} signifies the precise goal to be achieved, and w indicates the shape/importance weight coefficient of the respective target. Following the calculation of individual desirabilities, all parameters were combined into a single global desirability score (D) via the geometric mean method, as shown in Eq. 4:

$$D = \left(\prod_{i=1}^{n} d_i\right)^{\frac{1}{n}} = (d_1 \times d_2 \times d_3)^{\frac{1}{3}} \tag{4}$$

In this study, the optimization criteria were defined in accordance with the targets specified in Table 1 based on international EN 590 standards. Because strict compliance with the standards was the primary objective, the optimization weights (w_i) for the kinematic viscosity and density variables were assigned as "High (3)". Conversely, the weight (w_j) for surface tension, which was minimized to decrease droplet diameter and improve in-cylinder atomization characteristics, was left as "Normal (1)". Under these mathematical constraints and weights, the optimization algorithm calculated the ideal mixture and process conditions that maximize the global desirability score (D).

III. RESULTS AND DISCUSSION

3.1 Validation of Surrogate Model

The surface tension (30.55 mN/m), liquid phase density (915.72 kg/m^3), and kinematic viscosity (3.73 mm^2/s) values calculated for pure WCO biodiesel at 30 °C in the simulation environment were compared with the actual laboratory measurements (30.21 mN/m, 871.2 kg/m^3 , and 5.57 mm^2/s , respectively) from the reference study [24]. The evaluation indicated that the simulation estimated the surface tension (1.1% error) and density (5.1% error) values with a margin of error exceptionally close to the experimental data.

The deviation observed in the kinematic viscosity prediction tends to stem from the surrogate model generation strategy and the chemical nature of WCO. While the four main components, representing 94.95% of the actual WCO composition in total, were included in the model, the remaining minor fraction of approximately 5% was neglected, and the ratios were normalized to 100%. However, waste cooking oils (WCO) contain heavy polymeric chains and complex oxidation products in varying proportions depending on the feedstock source and high-temperature frying history.

Kinematic viscosity, which represents the internal friction of the fluid, is highly sensitive to such heavy macromolecules compared to density and surface tension. Therefore, the simulation model's reliance solely on pure and unpolymerized primary FAME molecules led to a relatively lower viscosity prediction compared to the degraded WCO sample in the laboratory. Nevertheless, the model's success in capturing general thermodynamic trends (particularly responses to butanol addition and temperature) suggests that the simulation infrastructure is highly reliable and valid for blend optimization processes.

3.2. Evaluation of Statistical Analysis and Model Fit

The statistical validity of the data obtained from the Mixture-Process Design was evaluated using Analysis of Variance (ANOVA). The 15-run data matrix derived from the DWSIM simulations, which forms the basis for the multiple response optimization, is presented in Table 2.

Table 2. Dependent variable (response) values obtained from the mixture-process experimental design

Run	Temperature °C	WCO M. Fraction	n-Butanol M. Fraction	K. Viscosity (mm²/s)	Density (kg/m³)	S. Tension (N/m)
1	30	0.7	0.3	2.741	836.53	0.02395
2	30	1	0	3.731	915.72	0.03055
3	30	0.85	0.15	3.095	864.3	0.02762
4	30	0.7	0.3	2.741	836.53	0.02395
5	30	0.85	0.15	3.095	864.3	0.02762
6	60	1	0	2.219	892.55	0.02826
7	60	0.85	0.15	1.837	840.25	0.02529
8	60	0.7	0.3	1.613	812.03	0.02147
9	60	0.85	0.15	1.837	840.25	0.02529
10	90	1	0	1.467	868.8	0.02599
11	90	0.7	0.3	1.051	785.98	0.02113
12	90	1	0	1.467	868.8	0.02599
13	90	0.85	0.15	1.209	814.97	0.02293
14	90	0.7	0.3	1.051	785.98	0.02113
15	90	0.85	0.15	1.209	814.97	0.02293

Following the analysis, predictive regression models defining the interaction of the constrained mixture components (WCO, NB) and the process factor (T) were developed for each response variable. The equations for kinematic viscosity (KV), density (DEN), and surface tension (ST), obtained by calculating the actual coefficients, are given in Eq. 5, Eq. 6, and Eq. 7, respectively:

$$KV = 4.5760 \cdot WCO - 0.0357 \cdot WCO \cdot T + 0.9104 \cdot NB - 0.0100 \cdot NB \cdot T \quad (5)$$

$$DEN = 930.91 \cdot WCO - 0.737 \cdot WCO \cdot T + 689.50 \cdot NB - 1.132 \cdot NB \cdot T \quad (6)$$

$$ST = 0.03330 \cdot WCO - 0.000083 \cdot WCO \cdot T + 0.00710 \cdot NB + 0.000020 \cdot NB \cdot T \quad (7)$$

The statistical significance and explanatory power of these developed models were verified by the ANOVA results summarized in Table 3. The statistical significance of the models was found to be $p < 0.05$ for all response variables, demonstrating that the models are highly significant within a 95% confidence interval.

Table 3. ANOVA statistical summary of the developed regression models

Response Variable	P-value	R^2 (%)	Adj. R^2 (%)	Standard Error
Kinematic Viscosity (KV)	0	96.59	95.66	0.1791
Density (DEN)	0	97.31	96.58	6.831
Surface Tension (ST)	0	98.6	98.21	0.0003

Furthermore, the agreement between the developed models and the observed (simulated) data is visualized in Figure 1. An examination of Figures 1a, 1b, and 1c reveals that the predicted points for all three thermophysical properties exhibit an excellent distribution along the diagonal reference line. The high R^2 values in Table 3 (96.59% - 98.60%) and the robust visual fit in Figure 1 indicate that variations in the WCO biodiesel, n-butanol, and temperature parameters explain the changes in fuel properties with exceptional precision.

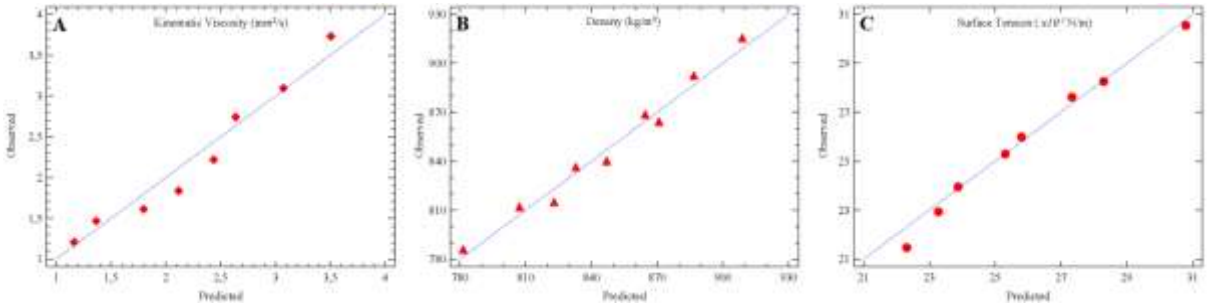

Figure 1. Agreement between observed and predicted values of the developed mixture-process models: (a) Kinematic Viscosity, (b) Density, (c) Surface Tension

3.3. Physical Mechanisms of Viscosity and Density Reduction

The behaviors of the independent factors on the fluidity properties of the fuel were analyzed using Main Effects and Trace Plots (Figure 2). The main effects plots in Figures 2a and 2c illustrate that the inherently high kinematic viscosity and density of pure WCO biodiesel experience a simultaneous and pronounced decline with the addition of n-butanol and the increase in temperature. Presenting the independent factors concurrently on a shared visual plane in these Main Effects plots is a deliberate approach; it allows for an immediate comparative assessment of their relative impacts. For instance, comparing the slopes of the variables directly reveals which factor exerts a more dominant physical influence on the fluid.

The sensitivity of the models to deviations from the reference point was examined through the Trace Plots in Figures 2b and 2d. In these plots, the center point of the experimental design space serves as the reference (coded as 0.0), and the x-axis represents the standardized displacement of each factor along its allowable range (from -1.0 to +1.0). This coded scaling allows for a direct visual comparison of how sensitive the response is to each independent variable. In the kinematic viscosity Trace Plot (Figure 2b), the steep negative slopes of the temperature and n-butanol curves indicate that viscosity is highly sensitive to increases in these two factors. The literature notes that adding n-butanol to biodiesel blends in proportions up to 30 wt.% can reduce kinematic viscosity by as much as 39.3%.

This dramatic decrease in viscosity cannot be solely explained by a simple dilution effect; it is also a consequence of alterations in intermolecular forces [14] identified negative binary interaction parameters when modeling the viscosity behavior of n-butanol and diesel/biodiesel blends. This negative parameter indicates that the short-chain,

branched structure of n-butanol intercalates between the long fatty acid methyl ester (FAME) chains in WCO biodiesel, weakening the intermolecular Van der Waals forces and thereby reducing internal friction (viscosity). Additionally, the synergistic effect created by increasing temperature alongside n-butanol enhances molecular kinetic energy, further improving fluidity. Although [30] stated that the impact of butanol might be limited in certain biodiesel blends, the statistical surface model generated in this study (Figure 2b) corroborates that n-butanol exerts a highly potent solvent effect on the heavy ester profile of WCO biodiesel.

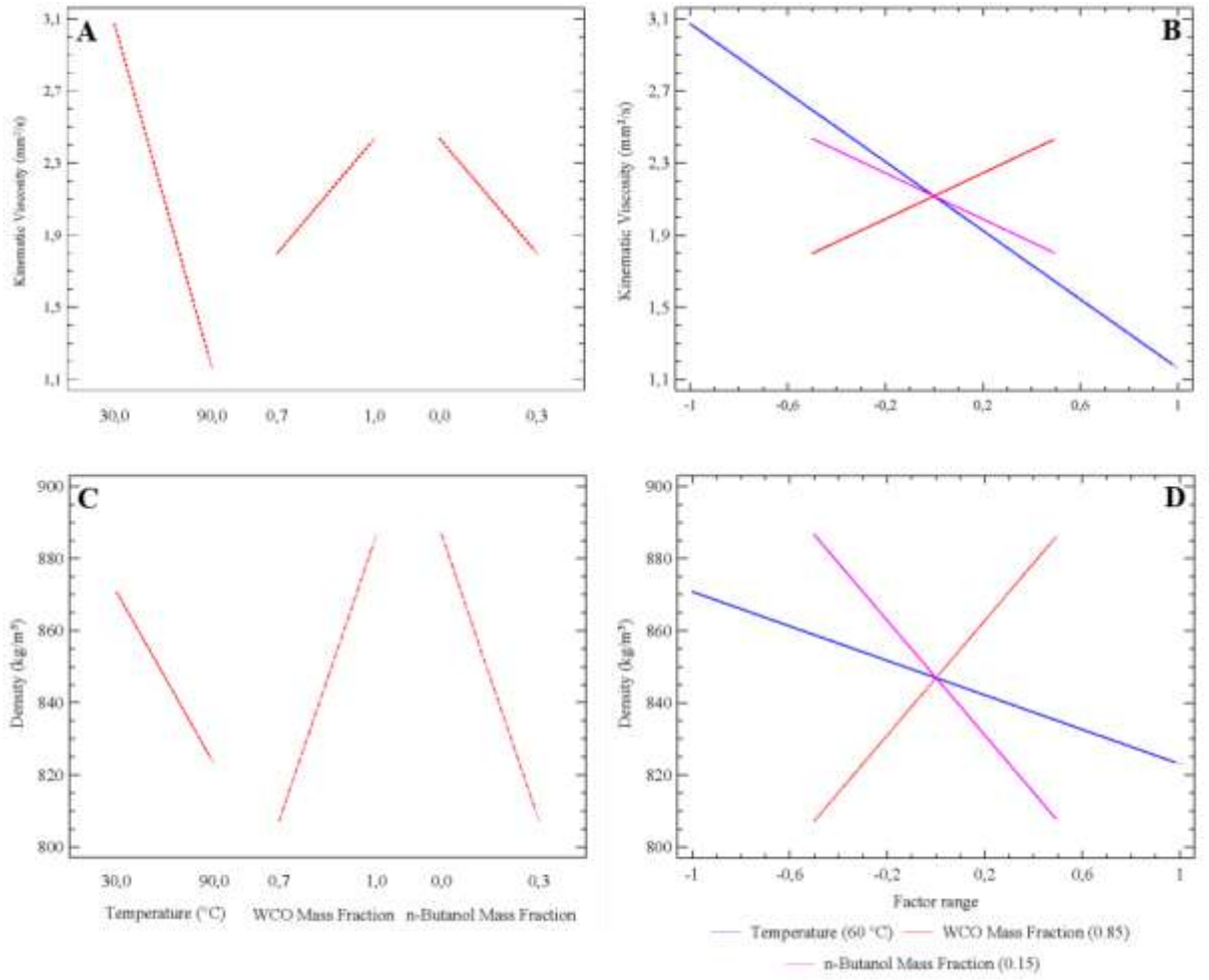

Figure 2. Effects of mixture and process variables on fuel properties: (a) Main Effects Plot and (b) Trace Plot for Kinematic Viscosity; (c) Main Effects Plot and (d) Trace Plot for Density. The concurrent presentation of independent factors on shared horizontal axes facilitates a direct visual comparison of their relative magnitudes and effect slopes.

3.4. Surface Tension and Atomization Characteristics

In the conducted analyses, surface tension exhibited a linear decreasing trend in response to increasing temperature and n-butanol ratios (Figure 3a). An analysis of the Trace Plot (Figure 3b), which illustrates the sensitivity of surface tension to independent variables, clearly reveals that an increase in the WCO ratio rapidly elevates surface tension (indicated by a steep positive slope). Conversely, the addition of n-butanol and the elevation of temperature symmetrically counterbalance and suppress this effect.

Reducing surface tension is of vital importance for droplet formation and atomization quality during fuel injection into the engine cylinder. Studies in the literature clearly reveal that a reduction in surface tension directly decreases the Sauter Mean Diameter (SMD), enabling the blend to break down into finer droplets. It has been established that the standalone use of biodiesel exhibits a poor atomization profile due to high surface tension; however, incorporating short-chain alcohols (such as ethanol or butanol) into the blend widens spray cone angles and significantly improves atomization morphology. The low surface tension values achieved for WCO/n-butanol blends in this study (Figure 3) confirm that optimum physical conditions are satisfied for enhancing in-cylinder combustion efficiency and mitigating soot emissions.

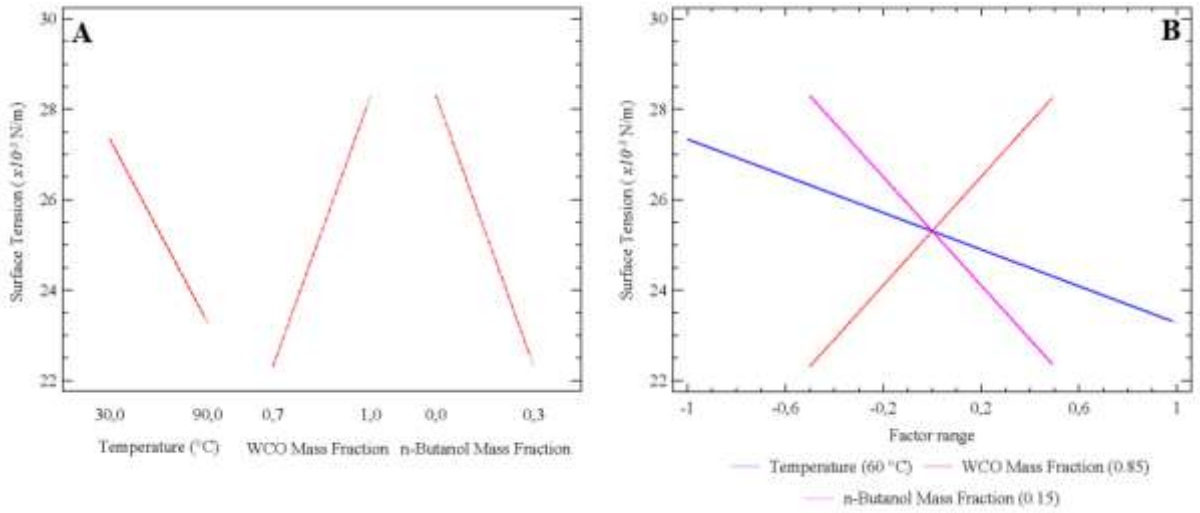

Figure 3. Surface tension behavior: (a) Main Effects Plot and (b) Trace Plot. The use of shared axes in the Main Effects Plot allows for a concurrent evaluation of the counterbalancing impacts of temperature and component mass fractions

3.5. Multiple Response Optimization and Identification of the Ideal Blend

Regarding engine performance and emission standards, fuel parameters frequently present conflicting objectives. For instance, while excessively lowering viscosity can cause wear in fuel pumps, maintaining density within the standard range (820 - 845 kg/m^3) requires a specific mass blending ratio. In this study, to align the blend's density and kinematic viscosity with the EN 590 diesel standard ranges, viscosity (target: 3.25 mm^2/s) and density (target: 840.0 kg/m^3) were targeted, while surface tension was minimized.

In the literature, numerous studies have demonstrated that Desirability functions are highly robust tools for simultaneously resolving such conflicting thermophysical and emission parameters in the optimization of biodiesel blends. Consequently, the Multiple Response Optimization, executed via the mathematical framework designed in Section 2.3, integrated all constraints and targets to achieve a high global desirability score of 83.5% ($D = 0.835$).

To thoroughly examine the performance of the developed regression models and identify the most ideal points within the experimental space, both observed and predicted thermophysical properties—along with their corresponding desirability scores (D)—for the 15 executed runs and the Global Optimum point predicted by the algorithm are presented in Table 4. To facilitate a comparative analysis of the data, the table is sorted in descending order based on the predicted desirability score (D_{pred}).

Table 4. Global optimum point and experimental runs sorted by their predicted desirability scores

Run	KV		DEN		ST		D	
	observed	predicted	observed	predicted	observed	predicted	observed	predicted
Optimum	NA	2.72	NA	840	NA	0.0245	NA	0.835
1	2.741	2.637	836.5	832.8	0.024	0.0239	0.828	0.784
4	2.741	2.637	836.5	832.8	0.024	0.0239	0.828	0.784
3	3.095	3.071	864.3	870.8	0.0276	0.0273	0.697	0.663
5	3.095	3.071	864.3	870.8	0.0276	0.0273	0.697	0.663
7	1.837	2.117	840.3	846.9	0.0253	0.0253	0.608	0.657
9	1.837	2.117	840.3	846.9	0.0253	0.0253	0.608	0.657
6	2.219	2.436	892.5	886.7	0.0283	0.0283	0.383	0.45
8	1.613	1.798	812	807.2	0.0215	0.0223	0.438	0.446
10	1.467	1.366	868.8	864.6	0.026	0.0258	0.385	0.365
12	1.467	1.366	868.8	864.6	0.026	0.0258	0.385	0.365
13	1.209	1.162	815	823	0.0229	0.0233	0.294	0.294
15	1.209	1.162	815	823	0.0229	0.0233	0.294	0.294
2	3.731	3.506	915.7	908.8	0.0305	0.0308	0	0
11	1.051	0.958	786	781.5	0.0211	0.0207	0.084	0
14	1.051	0.958	786	781.5	0.0211	0.0207	0.084	0

(KV: Kinematic Viscosity, DEN: Density, ST: Surface Tension, D: Desirability)

An examination of Table 4 reveals that the Multiple Response Optimization algorithm, based on the mathematical constraints established in Section 2.3, simultaneously scanned the continuous design space and discovered the highest global desirability score (Optimum Point) at 83.5% ($D_{pred} = 0.835$). This maximum score calculated by the algorithm was achieved using a blend of 72.8 wt.% WCO and 27.2 wt.% n-Butanol at an operating temperature of 30 °C. At this theoretical optimum point, the regression models predicted the blend's density as exactly 840.0 kg/m^3 and its kinematic viscosity as 2.72 mm^2/s. This computationally determined optimum n-butanol concentration (27.2 wt.%) is in strong agreement with the experimental "sweet spots" reported in the literature. Experimental investigations on biodiesel-butanol mixtures generally recommend an upper limit of approximately 20-25% for alcohol addition; blending up to this threshold significantly improves kinematic viscosity and atomization characteristics, whereas higher concentrations tend to deteriorate engine performance [15]. Moreover, experimental spray analyses have demonstrated that optimal atomization (indicated by the minimum average droplet size and directly correlated with surface tension reduction) is achieved at around 25% n-butanol fraction [14]. While some experimental works on WCO-butanol blends have primarily focused on density and thermodynamic interactions without full multi-property profiling [13], the concurrent reduction of surface tension and viscosity predicted by our 27.2% n-butanol model theoretically corroborates these experimental observations.

Among the 15 executed physical experiments (runs), the points with the highest desirability score were Runs 1 and 4 (70% WCO / 30% n-Butanol), which were closest to the Global Optimum ratio ($D_{obs} = 0.828$, $D_{pred} = 0.784$). Conversely, in Run 2, located at the bottom of the table, the system's desirability score was evaluated as "0" because the high density and viscosity values of pure WCO biodiesel (100% WCO) fell entirely outside the standard limits.

The ability of the developed models to extend beyond the tested physical matrix to discover a novel and superior optimum point (D = 0.835) demonstrates the efficacy of the utilized Desirability Function. These outcomes indicate that n-butanol acts as an excellent balancing additive for bringing waste cooking oil biodiesel up to international diesel standards (EN 590), and that digital simulation-supported optimization processes can be employed with high reliability.

IV. CONCLUSION

In this study, an innovative methodology based on the integration of digital twin modeling and statistical optimization is presented to improve the weak thermophysical properties (high viscosity and density) of waste cooking oil (WCO)-based biodiesel via n-butanol addition, and to tailor it to international diesel standards (EN 590). The WCO surrogate model, developed in the DWSIM process simulator utilizing Fatty Acid Methyl Ester (FAME) mass fractions, predicted the fundamental thermophysical properties with high precision. The primary findings derived from the Mixture-Process Design and Multiple Response Optimization conducted on the simulation data are as follows:

- *Model Performance:* The developed linear blending and interaction models accounted for the variations in kinematic viscosity ($R^2 = 96.59\%$), density ($R^2 = 97.31\%$), and surface tension ($R^2 = 98.60\%$) with excellent statistical accuracy ($p < 0.05$).
- *Synergistic Interaction:* The results demonstrate that the addition of n-butanol does not merely create a simple dilution effect; rather, coupled with an increase in temperature, it dramatically reduces the internal friction (viscosity) and surface tension among the long-chain ester molecules of WCO biodiesel, thereby enhancing atomization quality.
- *Global Optimum:* Derringer's Desirability Function was utilized to simultaneously align the conflicting density and viscosity targets with the standards. A maximum desirability score ($D = 0.835$) was achieved with a blend formulation comprising 72.8 wt.% WCO and 27.2 wt.% n-Butanol at an operating temperature of 30 °C.
- *Compliance with Standards:* Under these identified optimum conditions (WCO72.8/NB27.2), the density and kinematic viscosity of the fuel were calculated as precisely 840.0 kg/m^3 and 2.72 mm^2/s, respectively, indicating that the optimized blend satisfies the EN 590 requirements specifically for density and kinematic viscosity. It is crucial to note that full certification according to EN 590 necessitates the experimental assessment of other mandatory parameters such as cetane number, flash point, and oxidation stability, which were not within the technical scope of this simulation study.

In conclusion, the findings suggest that this digital integration based on DWSIM and RSM serves as a highly robust and reliable tool that eliminates the time and laboratory costs associated with trial-and-error approaches in alternative fuel blending processes.

V. LIMITATIONS AND FUTURE WORK

Although this study presents high-accuracy results in the optimization of the thermophysical properties of WCO biodiesel and n-butanol blends, it inherently contains certain limitations. First, the research is built upon DWSIM-based digital surrogate modeling and thermodynamic equations. While the model was validated against reference experimental studies, actual combustion dynamics and practical engineering performance indicators (such as Brake Thermal Efficiency (BTE), Brake Specific Fuel Consumption (BSFC), and exhaust emissions (NOx, CO, PM)) were not directly incorporated into the optimization loop. The present optimization focuses primarily on thermophysical properties, and the absence of engine-based performance data is acknowledged as a limitation for

direct industrial application. A second limitation stems from the assumption of a fixed FAME profile [24]. The chemical composition of actual waste cooking oils is highly variable, depending heavily on the feedstock origin, frying temperature, and duration of use. Extended frying cycles lead to the formation of heavy polymeric chains and complex oxidation products. Because the current surrogate model relies strictly on pure and unpolymerized primary FAME molecules, it may slightly underestimate the viscosity of highly degraded WCO samples. Therefore, assuming a constant chemical composition represents a boundary condition of this study, and future models should ideally incorporate dynamic variables accounting for oxidation and polymerization levels.

In light of these limitations, the following steps are recommended for future research:

- Testing the identified "WCO72.8/NB27.2" optimum fuel formulation in an actual diesel engine to experimentally validate performance parameters such as Brake Thermal Efficiency (BTE) and Brake Specific Fuel Consumption (BSFC).
- Integrating the varying FAME profiles (e.g., oxidation levels) of WCO samples obtained from different geographical regions into the simulation model as a dynamic variable.
- Conducting a Techno-Economic Analysis (TEA) and a Life Cycle Assessment (LCA) to evaluate the commercial potential that would arise if this optimum blend were produced on an industrial scale.

Author contributions: CRediT

Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Software, Validation, Visualization, Writing – original draft, Writing – review and editing: Mehmet Selman GÖKMEN

Conflict of Interest

The author has declared that there is no conflict of interest.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process:

During the preparation of this work the author used extensive AI-assisted technologies [Gemini] in order to improve the language, readability, and formatting of the manuscript. After using this tool/service, the author reviewed and edited the content as needed and takes full responsibility for the content of the published article.

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