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Determination of the Optimum Blend Ratio of Diesel, Waste Oil Derived Biodiesel and 1-Pentanol Using the Response Surface Method

Nadir Yilmaz [1,*], Alpaslan Atmanli [2,*], Matthew J. Hall [3] and Francisco M. Vigil [4]

[1] Department of Mechanical Engineering, Howard University, Washington, DC 20059, USA
[2] Department of Mechanical Engineering, National Defense University, Ankara 06654, Turkey
[3] Department of Mechanical Engineering, The University of Texas at Austin, Austin, TX 78712, USA; mjhall@mail.utexas.edu
[4] Los Alamos National Laboratory, Los Alamos, NM 87545, USA; franciscov@lanl.gov
* Correspondence: yilmaznadir@yahoo.com (N.Y.); aatmanli@hotmail.com (A.A.); Tel.: +1-202-806-6600 (N.Y.); +90-3124-175-190 (A.A.)

Abstract: Higher alcohols can be included as a third component in biodiesel-diesel mixtures to improve fuel properties and reduce emissions. Determining the optimum concentrations of these fuels according to the purpose of engine use is important both environmentally and economically. In this study, eight different concentrations of diesel (D), waste oil derived biodiesel (WOB), and 1-pentanol (P) ternary mixtures were determined by the design of experimental method (DOE). In order to determine the engine performance and exhaust emission parameters of these fuels, they were tested on a diesel engine with a constant load of 6 kW and a constant engine speed of 1800 rpm. Using the test results obtained, a full quadratic mathematical model with a 95% confidence level was created using the Response Surface Method (RSM) to predict five different output parameters (BSFC, BTE, CO, HC, and NO_x) according to the fuel mixture ratios. The R^2 accuracy values of the outputs were found at the reliability level. According to the criteria that BTE will be maximum and BSFC, CO, HC, and NO_x emissions will be minimum, the optimization determined that the fuel mixture 79.09% D-8.33% WOB-12.58% P concentration ($DWOBP_{opt}$) will produce the desired result. A low prediction error was obtained with the confirmation test. As a result, it is concluded that the optimized fuel can be an alternative to the commonly accepted B7 blend and can be used safely in diesel engines.

Keywords: waste oil biodiesel; 1-pentanol; response surface methodology; optimization; confirmation; diesel engine

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1. Introduction

Diesel engines will continue to be used in the electrical power generation and heavy-duty transport industry [1]. Carbon monoxide (CO), unburned hydrocarbon (HC), and nitrogen oxides (NO_x) released at the end of the diesel combustion process were determined as the main pollutants to be reduced [2,3]. Especially in the case of generator engines running for long durations at a constant speed, it is necessary to control these emissions due to environmental and human health concerns. Two common approaches to reduce emissions in diesel engines are the use of after-treatment systems and reducing fuel-based emissions that are a result of the fuel composition. Another driver toward the implementation of alternative fuels for application in diesel engines is the instability in oil prices and strict emission regulations [4]. In addition, it is inevitable to use alternative fuels in terms of sustainability at the point of protecting the environment [5].

Research investigating the types of biodiesel and alcohols that can be used in diesel engines as alternative fuels has been performed for many years [6]. The feedstocks for oil used in the production of biodiesel must be inedible so as to not affect food safety [7,8]. If biodiesel is used directly in a diesel engine at 100% concentration, it will cause malfunctions in the diesel fuel system. Therefore, biodiesel should be mixed with diesel fuel. In addition to mechanical issues, the raw material supply for biodiesel, insufficient production amount, high NO_x emissions, and phase separation problems at low temperatures cause the optimal mixing ratio to be low [9,10]. When diesel-biodiesel mixtures are used in diesel engines, it is stated in the literature that it can be mixed with up to 20% biodiesel (B20) depending on the fuel properties, while diesel engine manufacturers recommend mixing diesel with 7% biodiesel (B7) for the fuel sold at gas stations [11]. Currently, in order to increase the adoption of alternative fuels, diesel-biodiesel fuel properties must be improved.

Alcohols can be used in diesel engines with diesel fuel in certain proportions, but when used together, high-carbon alcohols should be selected [12]. Alcohols can also be used effectively, as an alternative to additives, to improve fuel parameters such as viscosity, density, and cold flow properties of diesel-biodiesel or vegetable oil blends [10,13]. When low carbon alcohols such as methanol (CH_3OH) and ethanol (C_2H_5OH) are used together with diesel fuel, phase separation occurs at low temperatures. In addition, the low cetane number, viscosity, and high latent heat of evaporation (LHE) of low carbon alcohols negatively affect engine performance and emissions [14–16]. 1-Pentanol ($C_5H_{11}OH$), one of the high-carbon alcohols that have come to the fore in recent years, is an alcohol type that can be produced from biomass and has fuel properties closer to diesel fuel than low-carbon alcohols. Thanks to its semi-polar nature, 1-pentanol can be mixed with diesel fuel in any proportion, and it has the potential to provide phase stability at low temperatures with its co-solubility in diesel-biodiesel mixtures [17]. There are a limited number of studies in the literature on diesel-biodiesel-1-pentanol mixtures. Huang et al. produced mixtures of 20% n-pentanol with diesel (80% and 64%), biodiesel (20% and 16%). The spray characteristics, engine performance, and emissions of these mixtures were tested [18]. Despite a slight decrease in engine performance, a decrease in pollutant emissions was observed. By using a 40% diesel, 30% biodiesel, and 30% pentanol blend, a significant reduction in NO_x emissions was obtained in the study conducted by Li et al. [19]. In a study by Manigan et al., the engine performance and emission parameters of diesel-biodiesel mixtures containing 10% and 20% pentanol were investigated [20]. Despite some increase in fuel consumption, a significant decrease was recorded in NO_x emissions from the 20% mixture. Combustion and emission characteristics of diesel-biodiesel mixtures containing 5% and 10% pentanol were investigated by Babu et al. [21]. It was emphasized that the mixture containing 10% pentanol showed the best performance in terms of emission reduction. In a study conducted by Yilmaz et al., despite the increase in HC and CO emissions between diesel-biodiesel mixtures to which 5%, 10%, and 20% 1-pentanol was added, a decrease in NO_x emissions was obtained depending on the 1-pentanol mixture ratio [22]. In the study conducted by Imdadul et al., 15% biodiesel-70% diesel and 20% biodiesel-60% diesel, 15% and 20% n-butanol or pentanol were mixed and it was stated that pentanol is a better alternative than n-butanol [23].

Although 1-pentanol has many advantages over other alcohols, a definite mixing ratio cannot be recommended in the current literature for its use as a co-solvent in diesel-biodiesel mixtures and for emission reduction purposes. Determination of optimum concentrations in a three-component mixture is a performance-requiring process both in terms of time and economy [24–28]. At this point, the response surface methodology, which is one of the statistical methods applied based on the experimental design, stands out as an effective method in determining the optimum concentration of the three components [28–32]. In addition, RSM is advantageous compared to other methods in terms of gaining maximum information from a small number of experiments, changing the effective parameters simultaneously, and optimizing [33–35]. According to the literature reviewed, most of the studies using RSM focus on optimizing the biodiesel production process and optimizing engine performance [35–38]. However, in the current literature, there are very limited studies on determining the optimum alternative mixture ratio. In the study conducted by How et al., the optimum biodiesel mixture ratio in the biodiesel-diesel mixture was determined by using RSM [39]. Krishnamoorthy et al. investigated the optimum engine performance comparison of waste oil (30%)-diesel (50%)-alcohol (20% n-propanol, n-butanol, n-pentanol) ternary mixtures [40]. It was emphasized that the n-pentanol mixture showed the best performance. Another study in which the optimum mixture ratio of diesel-vegetable oil and n-butanol was determined by RSM was carried out by Atmanli et al. [41]. The use of the RSM approach will contribute to the determination of the most suitable mixture ratios in the diesel engine and close the gap in the literature.

This study was carried out within the scope of designing an alternative biofuel mixture to be used in a diesel engine and was aimed at determining the optimum waste oil biodiesel-diesel and 1-pentanol ternary mixture. For this purpose, a reliable mathematical model has been developed considering the engine performance and emission outputs of eight different concentrations of fuels determined by the experimental design. The optimum mixing ratio was determined as a result of the RSM-based optimization according to the criteria that will be suitable for the purpose of the use of the test engine. After the validation test was carried out, the results of the physical experiment and the results obtained from the optimization were examined comparatively.

2. Materials and Methods

2.1. Test Fuels

Within the scope of this study, No. 2 diesel fuel was obtained from a local petroleum supplier. Biodiesel, which complies with ASTM D6751 standard, is produced from waste oils by the transesterification method. The Waste Oil Biodiesel (WOB) fatty acid composition was determined using an Agilent Technologies 6890 Network Gas Chromatograph (GC) System based on EN15779 testing standards [42]. A DB-225 column (30 m long, 0.25 mm diameter, and 0.2 μm film thickness) was used as the GC column. The measured fatty acid compositions are given in Table 1. Considering the ratio of saturated and monounsaturated fatty acids of WOB, the fuel will have good diesel combustion potential.

Table 1. Fatty acid composition of waste oil biodiesel.

Fatty Acid Ester	Structure	Formula	Mass	Composition (wt.%)
Methyl Palmitate	C16:0	$C_{17}H_{34}O_2$	270.45	9.35
Methyl Stearate	C18:0	$C_{19}H_{38}O_2$	298.50	3.45
Methyl Arachidate	C20:0	$C_{21}H_{42}O_2$	326.55	0.23
Methyl Behenate	C22:0	$C_{23}H_{46}O_2$	354.61	0.25
Saturation				*13.28*
Methyl Palmitoleate	C16:1	$C_{17}H_{32}O_2$	268.43	0.15
Methyl Oleate	C18:1	$C_{19}H_{36}O_2$	296.48	25.32
Methyl Linoleate	C18:2	$C_{19}H_{34}O_2$	294.47	49.65
Methyl Linolenate	C18:3	$C_{19}H_{32}O_2$	292.45	6.28
Unsaturation				*81.4*
Others				*5.32*

CAS No: 71-41-0 and 1-pentanol with 99.9% technical purity were used. By using diesel-biodiesel and 1-pentanol components, DWOBP mixtures were created with eight different concentrations to cover an orthogonal surface with the experimental design method. These mixtures were kept at room temperature (20 to 22 °C) for 72 h, phase stability was visually checked with a laser beam, and no phase separation occurred. The basic fuel properties of the fuel components and mixtures used in this study, measured according to ASTM standards, are given in Table 2. Despite the higher density and viscosity of the mixtures compared to diesel fuel, the calorific value and cetane numbers are at the desired level for the diesel combustion process. It can also be seen that fuel property values meet EN 14214 and ASTM D6751 standards.

Table 2. The basic properties of test fuels.

Test Fuels	ASTM Test Methods			
	D4052-91	D445	D240	D613
	Density (g/mL)	Kinematic Viscosity (mm^2/s)	Lower Heating Value (MJ/kg)	Cetane Number
Diesel fuel	0.818	2.95	44.81	54.5
WOB	0.855	4.57	40.50	52.2
1-Pentanol *	0.815	2.89	34.65	20
$D_{90}WOB_5P_5$	0.821	3.02	42.52	51.25
$D_{80}WOB_{15}P_5$	0.826	3.14	43.15	52.12
$D_{70}WOB_{10}P_{20}$	0.820	3.08	40.32	46.34
$D_{70}WOB_{20}P_{10}$	0.828	3.21	42.11	50.78
$D_{60}WOB_{20}P_{20}$	0.825	3.18	42.05	45.67
$D_{60}WOB_{30}P_{10}$	0.831	3.55	43.24	49.82
$D_{50}WOB_{25}P_{25}$	0.827	3.48	41.40	43.26
$D_{50}WOB_{35}P_{15}$	0.842	3.67	42.45	47.75

* Data taken from Refs. [17,24].

2.2. Experimental Procedure and Facility

The experiments were carried out using a four-cylinder, four-cycle, liquid-cooled, indirect-injection, ONAN DJC diesel engine. This engine currently makes up the majority of industrial-grade motors used for generator-type electricity generation in the USA. Detailed specifications of the test engine are listed in Table 3 and a schematic view of the engine test setup is given in Figure 1. Considering that the generator engine produces electricity for a long time under constant load, the tests were carried out at a maximum engine speed of 1800 rpm and a constant load of 6 kW in order to obtain engine performance and exhaust emission outputs.

Table 3. Test engine specifications.

Items	Onan DJC
Bore (mm)	82.55
Stroke (mm)	92.08
Displacement (mL)	1970
Max. power (kW)	9
Speed (rpm)	1800
Rated output	12 kW
Compression Ratio	19:1
Combustion chamber	Pre-chamber
Fuel injection system	Indirect
Injection pressure (bar)	131 (PSU pump)
Injection timing (BTDC)	18 °CA
Injection nozzle	Pintle type
Intake system	Natural aspirated
Cooling system	Air Cooled

The exhaust emissions profile of the generator from combustion of each of the test fuels was obtained using a gas analyzer (Emission Systems Inc., Whitby, ON, Canada, 5-Gas Analyzer, Model: EMS 5002-5). The analyzer provided a HC measurement range of 0–2000 ppm with a display resolution of 1 ppm, CO range of 0–10 vol.% with a display resolution of 0.01 vol.%, CO_2 range of 0–20 vol.% with a display resolution of 0.1 vol.%, O_2 range of 0–25 vol.% with a display resolution of 0.01 vol.%, and NO range of 0–5000 ppm with a display resolution of 1 ppm. The gas analyzer was calibrated using BAR97 low and BAR97 high calibration gases. The calibration process was repeated regularly for the engine tests. The accuracies of the measurements and the uncertainties of the calculated quantities have been given in Table 4.

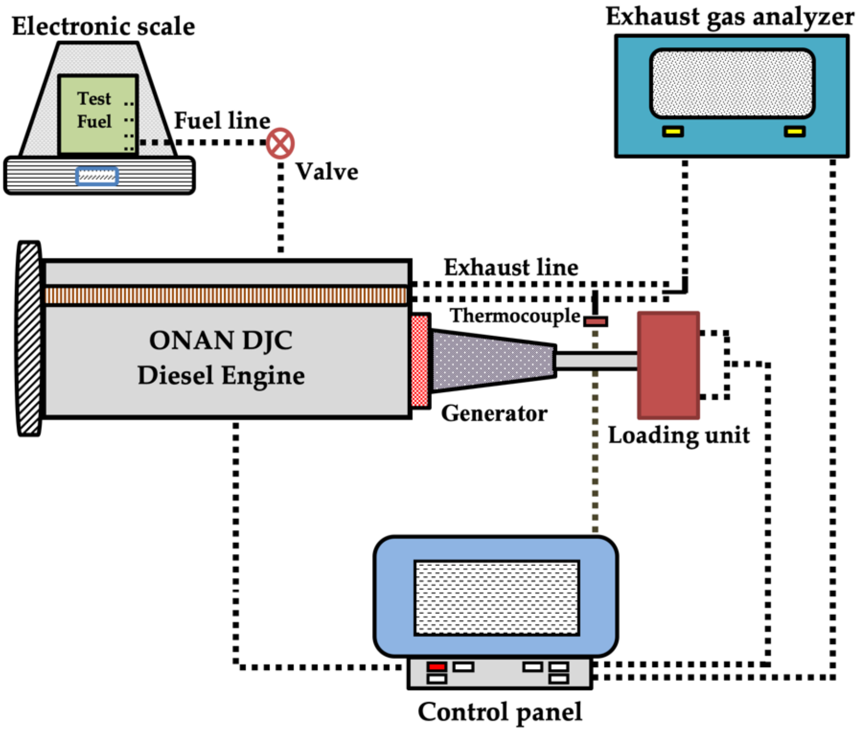


Figure 1. Schematic view of experimental facility.

Table 4. Accuracies of the measurements and the uncertainties of the calculated quantities.

Test Equipment	Measured Quantity	Measurement Range	Accuracy	Calculated Quantity	Uncertainty (%)
Electronic scale	Fuel consumption	0.5–3000 g	±0.5 g	BSFC	±1.01
Rotary encoder	Speed	0–6000 rpm	±1 rpm	BTE	±1.01
Loading unit (electrical resistance)	Load	1000/5000 W	±5 W		
Exhaust gas analyzer	NO HC CO	0–5000 ppm 0–2000 ppm 0–10 vol.%	±25 ppm ±4 ppm ±0.06 vol.%		

The propagation of errors methodology was used to determine the uncertainties for the engine performance parameters. The total percentage uncertainty (w_R) was calculated according to Equation (1),

$$w_R = \left[\left(\frac{\partial R}{\partial x_1} w_1 \right)^2 + \left(\frac{\partial R}{\partial x_2} w_2 \right)^2 + \ldots + \left(\frac{\partial R}{\partial x_n} w_n \right)^2 \right]^{\frac{1}{2}} \quad (1)$$

where R is a given function of the independent variables $x_1, x_2, \ldots, x_n$ and $w_1, w_2, \ldots, w_n$ are the uncertainties of the independent variables [43]. Table 4 shows the accuracies of the measurements and the uncertainties of the calculated quantities. In order to obtain engine performance and exhaust emission parameters, the engine operated with either diesel fuel or blended fuels for 10 min to warm up before tests were carried out. The experiments are possibly affected by atmospheric humidity and temperature variations. Each experiment was performed on the same day to limit day to day deviations in the experimental results. ISO 8178-6 test standards [44] were followed for exhaust emission tests. The engine performance and exhaust emissions tests were repeated three times for ternary blends and diesel fuel, in order to reduce experimental uncertainties and increase the reliability of the test results.

2.3. RSM Based Model

The mixing ratio of the two components selected with DOE were determined as the input factor. In a three-component mixture, the remaining ratio from the sum of the mixing ratios of the two components selected with DOE should be perceived as the mixing ratio of the third component. The actual test results obtained as a result of the engine tests were determined as the output factor (BTE, BSFC, CO, HC, and NO_x). DOE matrix and output results are shown in Table 5. The experiment matrix was analyzed using the RSM module in the Minitab 19 statistical package. In the experiment with RSM, the relationship between outputs and independent variables should be known and the model is created with the help of regression analysis. Therefore, the first step in RSM is to find the appropriate approach for the correct relationship between the output value and the independent variables.

Table 5. DOE matrix and factors.

Test Fuels	Input Factors (Blend Ratio)		Run Order	Output Factors (Engine Characteristics)				
	D (%)	WOB (%)		BTE (%)	BSFC (g/kWh)	CO (%)	HC (ppm)	NOx (ppm)
$D_{90}WOB_5P_5$	90	5	1	21.35	401.98	0.03	4.21	587.12
$D_{80}WOB_{15}P_5$	80	15	2	20.47	422.75	0.03	4.56	562.23
$D_{70}WOB_{10}P_{20}$	70	10	3	19.12	444.86	0.04	5.25	442.34
$D_{70}WOB_{20}P_{10}$	70	20	4	20.38	437.67	0.03	5.81	471.31
$D_{60}WOB_{20}P_{20}$	60	20	5	20.22	451.74	0.04	5.63	411.27
$D_{60}WOB_{30}P_{10}$	60	30	6	20.04	455.89	0.05	5.96	465.01
$D_{50}WOB_{25}P_{25}$	50	25	7	19.55	474.78	0.05	6.11	398.74
$D_{50}WOB_{35}P_{15}$	50	35	8	19.14	466.94	0.06	6.24	418.85

For this purpose, a full quadratic mathematical model was used, shown in Equation (2), that defines, separately. All outputs with the linear or non-linear function of independent variables.

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

where Y is the response, X_i are values of the factors (mixture ratios), terms β_0, β_i, β_{ii} and β_{ij} are the coefficients of the determined regression equation, and ε is the residual experimental error [45]. The model can be written in matrix notation as given Equation (3):

$$Y = \beta X + \varepsilon \quad (3)$$

where Y is the matrix that displays the response values while X is the matrix that displays the factor levels corresponding to the given response values, and ε is the residual matrix. The least square estimation of the β matrix that composes of coefficients of the regression equation is calculated by the formula in Equation (4) [45]:

$$\beta = (X^T X)^{-1} X^T Y \quad (4)$$

where the elements of β matrix are the parameters of mathematical model that represents the relationship between the factors and the responses in the same order represented in the X matrix, respectively. By using the experimental results in Table 5, the mathematical model of the function between the output and the input have been established with 95% confidence level as a second order polynomial shown in Equation (5). The lack of fit significance level is selected as 5% for the significance tests.

$$Outputs = \beta_0 + \beta_1 D + \beta_2 WOB + \beta_3 D^2 + \beta_4 WOB^2 + \beta_5 DWOB \quad (5)$$

where D = blend ratio of diesel fuel, WOB = blend ratio of waste oil biodiesel, β_0 = constant coefficient for each output value, β_1 = coefficient of diesel blend ratio for each output value, and β_2 = coefficient of WOB blend ratio for each output value. The accuracy of the mathematical model was calculated based on the comparison between the actual experimental results and the output values of the mathematical model constructed by the input values.

The coefficient and parameter values of the mathematical model created for all outputs in the order specified in Equation (5) are given in Table 6. The coefficient of determination (R^2) is a statistical measure that describes how close the data are to the appropriate regression function. The R^2 values of each output parameter are given in Table 7 and the values are in the reliable range at a satisfactory level.

Table 6. The mathematical equations of the outputs.

Coefficients	Input	Outputs				
	Blend Ratio (%)	**BTE (%)**	**BSFC (g/kWh)**	**CO (%)**	**HC (ppm)**	**NO_x (ppm)**
β_0	*Constant*	−47.1801	1536.33	0.112156	−26.4890	3891.75
β_1	D	1.3184	−22.74	−0.000669	0.7454	−84.74
β_2	WOB	2.2504	−29.40	−0.004288	0.9058	−97.59
β_3	D^2	−0.0063	0.11	−0.000002	−0.0045	0.53
β_4	WOB^2	−0.0193	0.21	0.000075	−0.0064	0.70
β_5	(D) (WOB)	−0.0221	0.32	0.000026	−0.0098	1.14

Table 7. Coefficient of determination (R^2) values of the mathematical model.

Coefficient of Determination	Outputs				
	BTE	**BSFC**	**CO**	**HC**	**NO_x**
R^2 (%)	86.31	99.77	98.63	94.18	99.80
Adjusted R^2 (%)	86.72	99.20	95.21	90.62	99.31
Predicted R^2 (%)	82.56	94.62	96.29	92.21	95.29

2.4. Optimization Approach

In the experiments designed considering the usage conditions of the test engine, determining the optimum mixing ratio for the engine is of great importance in terms of performance and emissions. With RSM, it is aimed to determine the optimum diesel fuel, WOB, and 1-pentanol ternary mixture concentration. For this reason, the last step after proving the accuracy of the mathematical model and obtaining R^2 values was the optimization study which helps find the ideal input values corresponding to the desired output values.

The optimization study, in which the mixing ratios of the three components were included as the input factors and BTE, BSFC, CO, HC, and NO_x were included as the output parameters, was carried out with the response optimizer module in the Minitab 19 statistical package. This module uses the gradient descent method to calculate the optimum factor levels using the determined mathematical Equations (2)–(5). In this method, the optimum solution is searched by using the gradient function that is calculated using partial differentiations. This method needs one initial starting point and defined restriction criterions for screening on the response surfaces determined by using the calculated mathematical equations. Response optimization bounds are given in Table 8. Since it is desired to reduce the emissions of pollutants emitted depending on fuel consumption, it is preferred that all emission outputs be minimum. As the starting point in the factor design, 50% diesel and 5% WOB were chosen, respectively, because they were the minimum mixture amounts of diesel fuel and WOB among the test fuels.

Table 8. Response optimization bounds.

Response	Unit	Goal	Lower	Target	Upper
BTE	%	Maximum	19.00	20.00	-
BSFC	g/kWh	Minimum	-	420.00	470.00
CO	%	Minimum	-	0.03	0.05
HC	ppm	Minimum	-	5.00	6.00
NO_x	ppm	Minimum	-	450.00	550.00

3. Results

3.1. Analysis and Evaluation of Model

Table 7 shows that the mathematical models can accurately predict outputs with low estimation error. If the *p*-value, which can be obtained from the Analysis of Variance (ANOVA) report of the Minitab 19 statistical package, is less than 0.05, it means that the model is significant [36,41]. Table 9 presents the ANOVA results showing the significance of the mathematical models given in Equation (5). The predictive reliability of the mathematical model established with the output values obtained according to the fuel mixture ratio contributed to determining the ideal fuel mixture for the test engine within the scope of this study.

Table 9. ANOVA for predicted mathematical model of the response.

Response	Source	Degrees of Freedom (DF)	*p*-Value (<0.05)	Result
BTE	Regression	5	0.030	Significant
BSFC			0.006	Significant
CO			0.034	Significant
HC			0.013	Significant
NO_x			0.005	Significant

3.2. Optimized Concentration and Validation Test

As a result of the optimization made according to the limitations specified in Table 8, the desired levels of the outputs and the triple mixing ratio are seen in Figure 2.

For the optimum blend ratio, valid factor settings are diesel blend ratio = 79.09, WOB blend ratio = 8.33, and 1-pentanol blend ratio = 12.58, and composite desirability is 0.89375. This determined optimum fuel mixture is named $DWOBP_{opt}$. The validation test of this mixture was carried out at 1800 rpm and 6 kW load conditions of the test engine. The results obtained are given in Table 10 with prediction errors (PE).

Table 10. Validation test for response.

Response	Predicted Response	Desirability	Experimental Response	PE (%)
BTE (%)	20.439	1.000000	20.684	1.18
BSFC (g/kWh)	420.023	0.999534	423.803	0.9
CO (%)	0.033	0.847821	0.033	1.02
HC (ppm)	4.999	1.000000	5.01	0.2
NO_x (ppm)	482.705	0.672947	485.78	0.63

The low level of PE (less than 1.18%) confirmed the effectiveness of the RSM algorithm, as designed. The fuel properties of the $DWOBP_{opt}$ mixture have been tested and found to meet ASTM D6751 and EN 14214 standards.

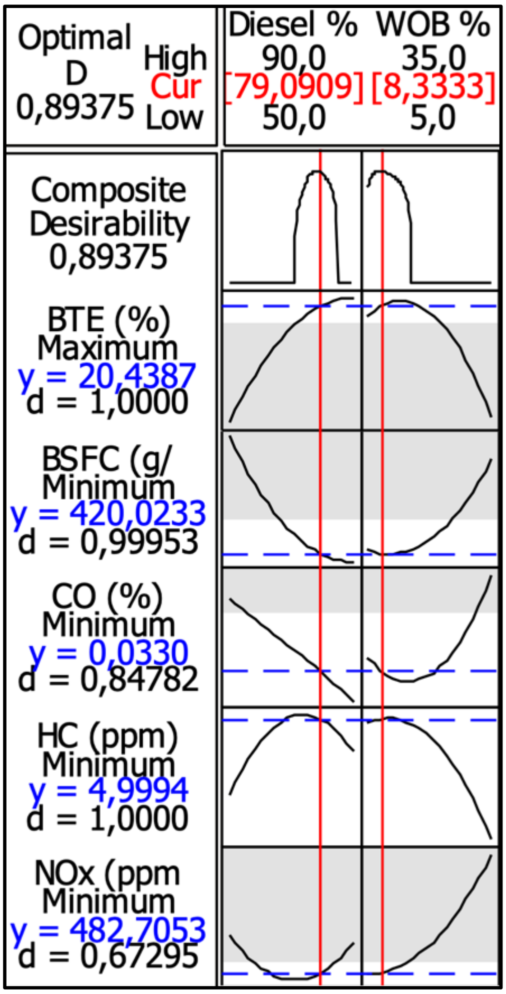
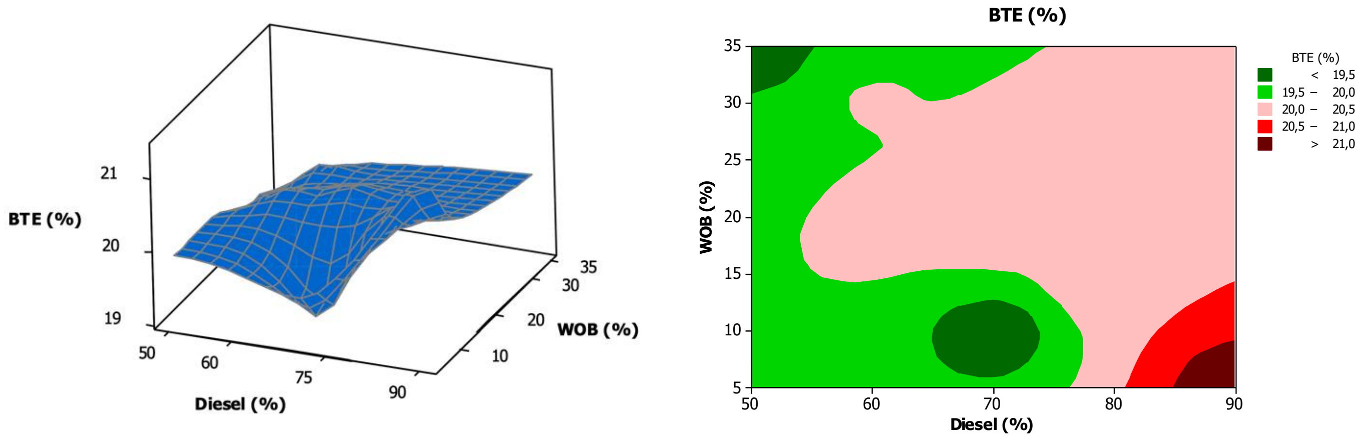


Figure 2. Optimized concentration and outputs.

4. Discussion

In this section, the changes in break thermal efficiency (BTE), break specific fuel consumption (BSFC), CO, HC, and NO_x parameters are discussed by using the surface and contour graphs created with the RSM-based mathematical model developed for the test engine. It should not be overlooked that the sum of the diesel and WOB mixture ratio will not exceed 100% in these graphs and that the third component, 1-pentanol, will be included in the mixture.

The BTE change depending on the fuel mixture ratio is seen in Figure 3. Thermal efficiency is a measure obtained by dividing the output work by the input energy in an internal combustion engine [46]. In this context, when the BTE figures are examined, an increase is observed depending on the calorific value of the diesel fuel as the ratio of diesel fuel in the mixture increases [47]. On the contrary, if the mixture ratio of WOB and 1-pentanol increases, there is a significant decrease in BTE. It is also emphasized in the studies in the literature that as the 1-pentanol ratio in the mixtures increases, the BTE will decrease [48]. Compared with diesel fuel, the maximum decrease in BTE was observed in the $D_{70}WOB_{10}P_{20}$ and $D_{50}WOB_{35}P_{15}$ mixtures 13.15% and 13.06%, respectively. The BTE value of $DWOBP_{opt}$ fuel decreased by 6.05% compared to diesel. The presence of 8.33% WOB and 12.58% 1-pentanol in the optimum mixture resulted in this reduction. However, when evaluated together with other output parameters, it meets the best value with 86.31% R^2 value and 1.18% PE.

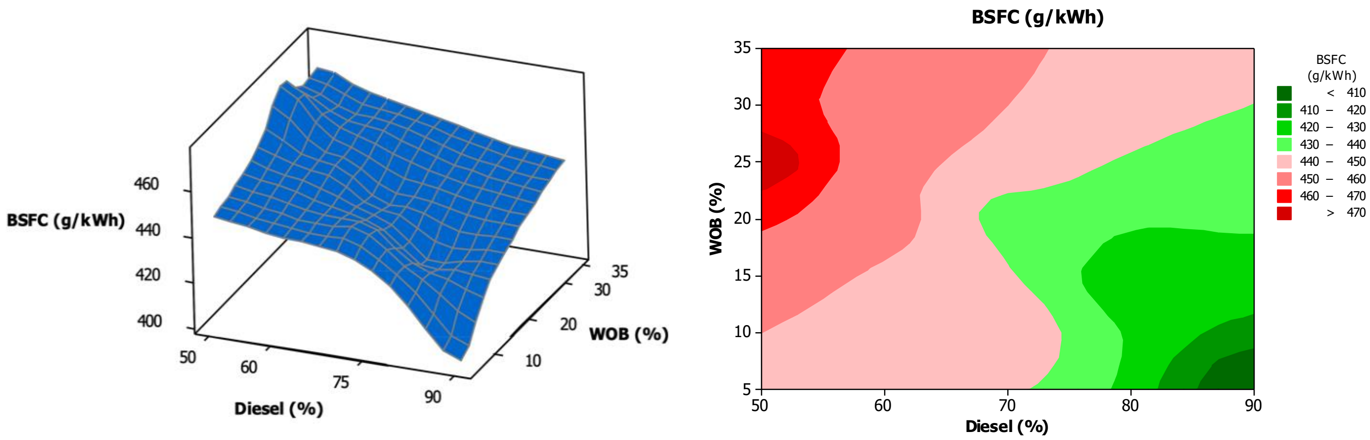


(**a**) (**b**)

Figure 3. (**a**) Surface plot; (**b**) Contour plot of BTE with input variables.

Low fuel consumption for a generator engine that will operate for a long time under constant speed and load conditions is essential for efficiency. BSFC as a function of blend ratio is shown in Figure 4. When the graphics have shown by the mathematical model that meets the 99.77% R^2 value are examined, the change of color range in both graphs is seen as the inverse of BTE. Due to the low calorific value and high viscosity of the ternary blends compared to diesel fuel, more fuel is consumed in order to obtain the same power [49,50]. As the ratio of 1-pentanol and WOB in the mixture increases, the BSFC value also increases. This increase is similar to the results obtained in the literature [25–28]. Compared to diesel fuel, DWOBPopt fuel increased by 7.21% and reached the optimum value with a PE of 0.9%.

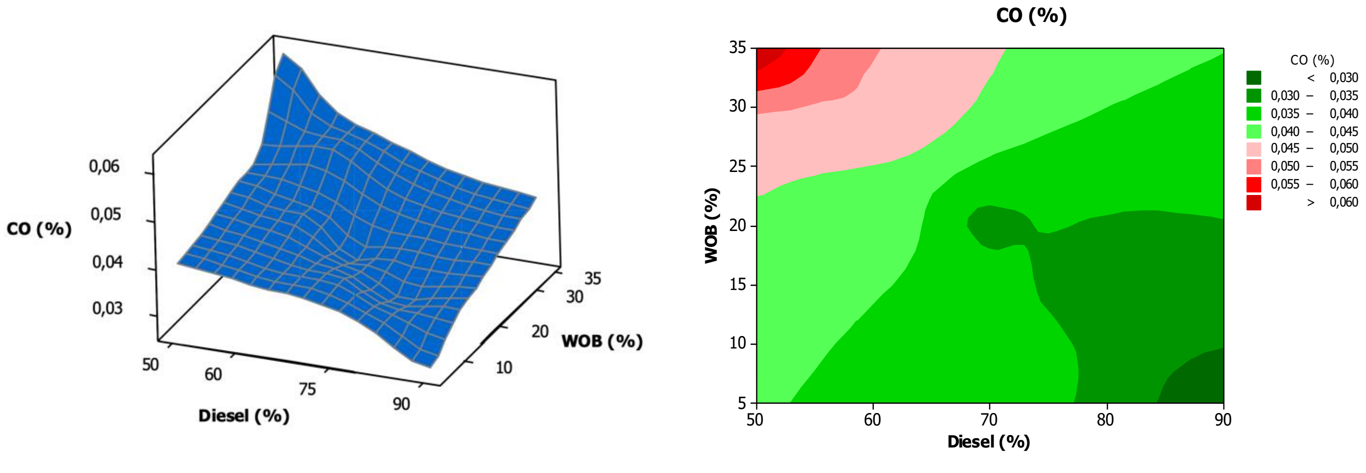
CO, HC, and NO_x have an important place among the main pollutant emissions emitted by diesel engines and regulations are being made to limit these emissions [8,14,15]. Since it is not economical to use after-treatment systems in generator engines, it is very important for the environment and human health to determine the conditions where engine-out pollutants will be at a minimum level during long-term operation.



(**a**) (**b**)

Figure 4. (**a**) Surface plot; (**b**) contour plot of BSFC with input variables.

CO emissions as a function of blend ratio of components are shown in Figure 5. The main cause of CO emissions is the low temperature and lack of sufficient oxygen concentration to provide CO_2 conversion [17,26,51]. Despite the oxygen content of WOB and 1-pentanol, the low cetane number of the mixtures increases the premixed combustion stage, creates timing problems in terms of combustion and expansion stages, and causes less oxidation of carbon and oxygen. Therefore, an increase in the CO emission of all the tested tripartite mixtures was recorded. The maximum increase in CO emissions was obtained with the fuel $D_{50}WOB_{35}P_{15}$ with 127.33%. This increase was smaller as the diesel fuel ratio in the mixtures increased. The mathematical model confirms the CO emission with an R^2 value of 98.63%. Thus, $DWOBP_{opt}$ was at the optimum level among all mixtures with an increase of 21% in CO emissions compared to diesel fuel. This increase is attributed to the high latent heat of evaporation (LHE) of 1-pentanol, which causes more heat to be absorbed from the combustion chamber, resulting in a cooling effect and lower combustion efficiency [29,48,52].



(**a**) (**b**)

Figure 5. (**a**) Surface plot; (**b**) contour plot of CO emission with input variables.

Figure 6 shows the variations of HC emissions depending on the blend ratios. HC emissions result from incomplete combustion or slower oxidation reactions due to too rich or poor fuel-air ratios in the cylinder, loss of heat to cold areas around the cylinders, and flame extinction in these areas [6,17]. When examined in both graphs, a decrease in HC emission is obtained as the diesel fuel ratio increases, similar to the CO emission. However, as the content of WOB and 1-pentanol increases, an increase in HC emission is observed. Compared to diesel fuel, the HC emissions of $DWOBP_{opt}$ fuel increased by 19.80%. When this increase is compared with the fuels used in the experimental design, it is seen that the HC emissions of $DWOBP_{opt}$ is at the optimum level with 94.18% R^2 and 0.2% PE values. The low in-cylinder temperature and flame quenching inhibited the combustion [14,38,47]. Thus, the weakness of fuel properties (cetane number, viscosity, and LHE) of ternary blends compared to diesel fuel is shown as the main reason for the increase in HC emissions.

The surface and contour graphics of the NO_x mathematical model established with an R^2 value of 99.80% depending on the mixing ratios are shown in Figure 7. Contrary to the CO and HC graphs, it is seen that there is a decrease in NO_x emissions as the alternative fuel ratio in the mixtures increases. In addition to the CO and HC emissions of the diesel engine, NO_X emissions, which must be reduced, are the main issue of using alternative fuels in diesel engines [53]. The formation of NO_x is affected by fuel activities in the engine, namely: thermal-related (Zeldovich), prompt in fuel rich condition (Fenimore), and fuel (nitrogen in fuel) mechanisms. The Zeldovich mechanism is responsible for the bulk of the NO_x production in diesel engines, which is stimulated by long residence times at high temperatures (~1800 K) inside the cylinder [54]. Compared with diesel fuel, a reduction in NO_X emissions was obtained for all ternary mixtures. When the NO_X emissions of the $DWOBP_{opt}$ blend is evaluated together with the other emissions, it is at the optimum level with a 17.92% reduction with 0.63% PE. These findings can be attributed to that 1-pentanol (308 kJ/kg) blended fuels have lower adiabatic flame temperatures due to higher LHE than diesel fuel (250 kJ/kg), and thus, their thermal NO_x emissions should be lower. The reduction of NO_x emissions by using alcohol in biodiesel-diesel mixtures was similar to the results obtained in this study [26,28,55]. This optimum reduction will enable the generator engine to work efficiently in energy production and to emit fewer pollutants in terms of the environment and human health.

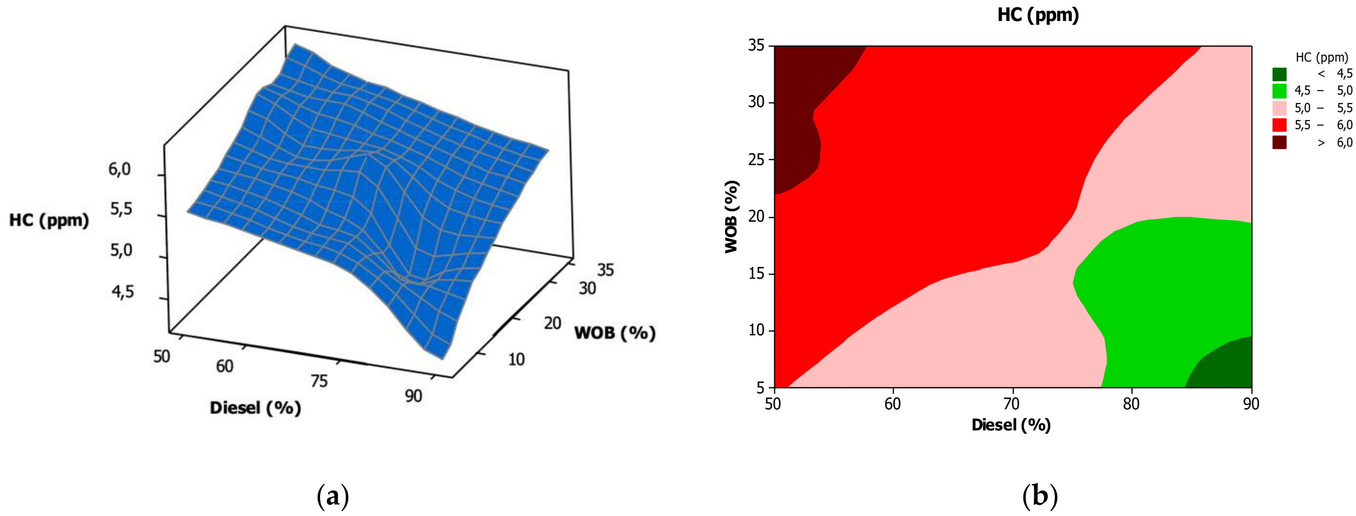


Figure 6. (**a**) Surface plot; (**b**) contour plot of HC emission with input variables.

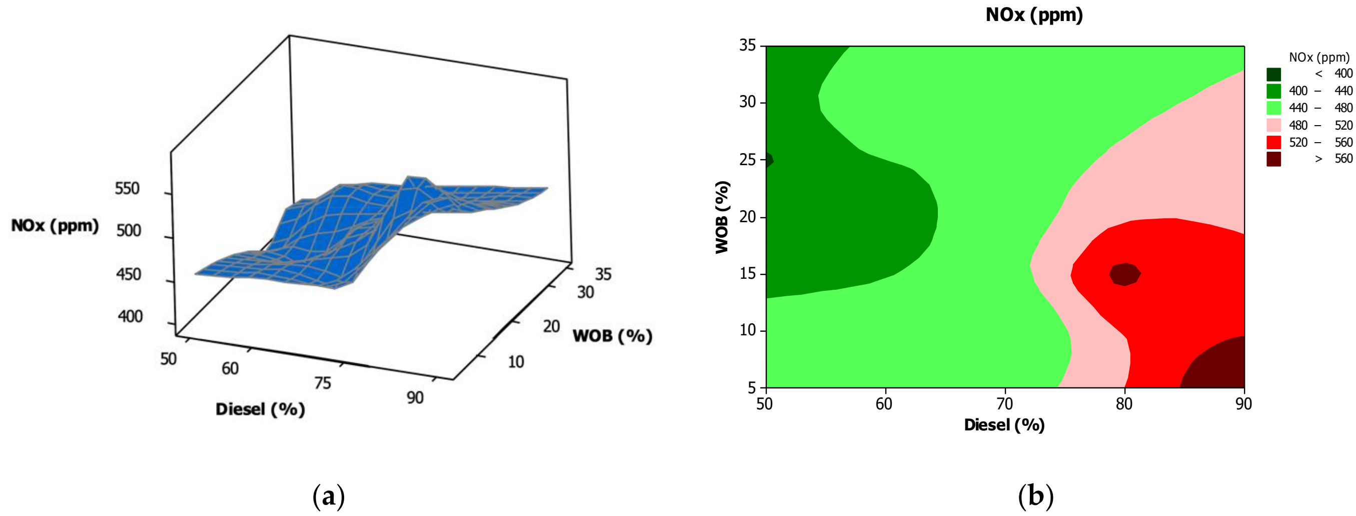


Figure 7. (**a**) Surface plot; (**b**) Contour plot of NO_x emission with input variables.

5. Conclusions

Biodiesel and high-carbon alcohols are suggested as the most suitable sources of alternative fuels for diesel engines. Producing biodiesel from waste oils will support food safety and adding 1-pentanol to the mixture will help increase the rate of alternative fuel use in diesel engines. The necessity of using these two important fuel sources together is still a research topic in the current literature in terms of both improving engine performance and reducing pollutant emissions. It is of great importance for the environment and economy to use a mixture formed with the most ideal ratios of a three-component fuel mixture based on the characteristics of the diesel engine. In order to determine the most ideal three-component alternative fuel mixture ratio to be used in a generator engine, extensive experiments are required. This is where the RSM approach can be used to estimate engine operating parameters and optimize the fuel mixture ratio in the range of values tested for the variables. This saves time and money while significantly reducing experimental work.

With this motivation in mind, this study aimed to use biodiesel produced from waste oils and 1-pentanol, which can be produced from biomass, with diesel fuel at the optimum mixing ratio for a generator engine used in electricity generation. For this purpose, mathematical models with a 95% confidence level have been established by using real test results of engine performance and emission parameters depending on eight different three-component mixing ratios. It has been determined that the R^2 values of the mathematical model established for each output are at the desired level. Based on the characteristics of the test engine and its intended use, the optimum three-component $DWOBP_{opt}$ fuel was found by using the ranges where the performance should be maximum, and the pollutant emissions should be minimum. As a result of the optimization made according to these criteria, composite desirability was obtained as 0.89375. Acceptable PE of the values determined as a result of the validation experiment revealed the reliability of the mathematical models. Thus, BSFC, CO, and HC emissions have increased due to the low cetane number, viscosity, and high LHE value of 1-pentanol. On the other hand, it has led to a significant reduction in NO_x emissions. Additionally, for a diesel engine used for a long time in electricity generation, the rate of alternative fuel usage has been increased and very harmful polluting components such as NO_x have been reduced.

It is suggested in the literature that up to 20% biodiesel (B20) can be safely mixed with diesel fuel in diesel engines, but this is reflected in gas stations as a maximum of 7% biodiesel (B7). Thus, increasing the rate of alternative fuel use in diesel-biodiesel mixtures will contribute positively to the environment and economy. In light of the results obtained from this study, the mixture ratio of 79.09% diesel, 8.33% WOB, and 12.58% 1-pentanol found with the RSM approach has the potential to be an alternative to B7. At this point, this study has brought a new approach to the literature in terms of determining the optimum ratio of ternary biodiesel-diesel and high-carbon alcohol mixture. In this context, determining the optimum mixing ratios of diesel-biodiesel and 1-pentanol using RSM for different engine types will greatly contribute to the environment and economy. In addition, the performance of different statistical techniques can be compared using different fuel types.

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Abbreviations

ANOVA	Analysis of Variance
ASTM	American Society for Testing and Materials
BSFC	Break Specific Fuel Consumption
BTE	Break Thermal Efficiency
B7	7 vol% Biodiesel + 93 vol% Diesel
B20	20 vol% Biodiesel + 80 vol% Diesel
CO	Carbon monoxide
CO_2	Carbon dioxide

D	Diesel
DOE	Design of Experimental
$D_{90}WOB_5P_5$	90 vol% Diesel + 5 vol% Waste Oil Biodiesel + 5 vol% 1-pentanol
$D_{80}WOB_{15}P_5$	80 vol% Diesel + 15 vol% Waste Oil Biodiesel + 5 vol% 1-pentanol
$D_{70}WOB_{10}P_{20}$	70 vol% Diesel + 10 vol% Waste Oil Biodiesel + 20 vol% 1-pentanol
$D_{70}WOB_{20}P_{10}$	70 vol% Diesel + 20 vol% Waste Oil Biodiesel + 10 vol% 1-pentanol
$D_{60}WOB_{20}P_{20}$	60 vol% Diesel + 20 vol% Waste Oil Biodiesel + 20 vol% 1-pentanol
$D_{60}WOB_{30}P_{10}$	60 vol% Diesel + 30 vol% Waste Oil Biodiesel + 10 vol% 1-pentanol
$D_{50}WOB_{25}P_{25}$	50 vol% Diesel + 25 vol% Waste Oil Biodiesel + 25 vol% 1-pentanol
$D_{50}WOB_{35}P_{15}$	50 vol% Diesel + 35 vol% Waste Oil Biodiesel + 15 vol% 1-pentanol
$DWOBP_{opt}$	79.09 vol% Diesel + 8.33 vol% Waste Oil Biodiesel + 12.58 vol% 1-pentanol
EN	European Standard
GC	Gas Chromatograph
HC	Hydrocarbon
LHE	Latent Heat of Evaporation
NO	Nitrogen oxide
NO_x	Nitrogen oxides
O_2	Oxygen
P	1-pentanol
RSM	Response Surface Method
WOB	Waste Oil Biodiesel

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