

# Central Composite Design Method for the Preparation, Stability and Properties of Water-in-Diesel Nano Emulsions

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## Abstract

Water in diesel nano-emulsion (WiDNE) due to their nano size, kinetically stable gives its beneficial in commercial and environmental aspects. However, the capability of this fuel strongly depends on the method of preparation, stability and their physic-chemical properties. Central composite design (CCD) method was used to optimize variable interactions in order to obtain maximum stability. Methodology RSM method with six independent variables was selected in order to understand the impacts on droplet size. The response surface and 3D plots of the quadratic polynomial model were created for studying the combination effect on response. Dynamic light scattering DLS technique was used for measuring of droplet sizes. The analysis result by ANOVA was with 95% confidence displaying F value model was 52.82. The results displayed model was fulfilled with the assumptions of ANOVA. This study has relied on Design Expert software to locate the optimum droplet size situations. The measured diameter is 26 nm, with 0.0297 errors between actual conditions and measured value. The optimum blend properties of prepared WiDNE fuel were compared with conventional diesel. Improvements in physical properties were observed in presence of water in WiDNE.

## Keywords

Water in Diesel, Optimization, Central Composite Design, Stability

## 1. Introduction

Emulsions consist of two immiscible liquids which one as small droplets in the dispersed liquid, and can be classified as oil-in-water or water-in-oil relying on which phase is constituting the disperse phase [1] [2] [3].

Nano-emulsion is a class of high stability emulsions with extremely small droplets in the range of 20 - 200 nm with no apparent flocculation or coalescence [4], and this makes them a useful applications for example in the pharmaceutical, cosmetics, agrochemicals, and in the chemical industries [5] [6] [7] [8] [9].

The most common process in the preparation of nanoemulsions is high energy method [10]. Recently also a neat low-energy method [11] has been developed, by taking advantage of phase behavior and properties, to promote the formation of ultra-small droplets. These low energy techniques include self-emulsification [12] [13], phase transition [1] [14] [15] and Phase Inversion Temperature methods (PIT) [16] [17].

In this study, WiDNE fuel preparation by using high shearing method. The emulsification process includes simulating droplet model for the optimum condition based on the Central Composite Design (CCD) [18] [19]. Consequently, CCD method is the best for illustration of these influences [20]. Both of the droplets size and distributions inside the WiDNE fuel were measured through DLS technique.

The path for implementing experimental design was evaluated for two purposes. The first is to identify a subset of the original processes factors that have substantial main and interaction impacts on the final WiDNE fuel properties achieved. Second, factors have to be significant optimized statistically to determine the best WiDNE properties, according to the assumed Response Surface Method (RSM) model.

## 2. Materials and Methods

### 2.1. Materials

#### 2.1.1. Diesel Fuel

Conventional diesel fuel produced from local Daura Refinery was used as continuous phase of WiDNE fuel. The characterization of diesel fuel is shown in **Table 1**.

**Table 1.** Characterization of diesel fuel.

No.	Properties	Value
1	Density at 15%. (Kg/ liter)	0.8932
2	Total sulfur (%wt)	2.88
3	Total Nitrogen (ppm wt)	320
4	Acidity (mg KOH g)	0.1
5	Viscosity at 60%. (cSt)	25.15
6	Pour point (°C)	6
7	Cloud point (°C)	8
8	Aniline point (°C)	71.8

### 2.1.2. Emulsifying Agent

The important step for forming stable emulsion was to select the suitable surfactant blend, Span80 and Tween80 that were used in the present work. The Specifications of the surfactants are shown in **Table 2**.

## 2.2. Experimental Methods

### 2.2.1. Process of Emulsification

WiDNE were generated by dispersing water content into diesel fuel according to **Table 3**. The formation was done in three steps:

- 1) Surfactants Tween80 (HLB = 15) and Span80 (HLB = 4.3) were blended to get the desired Tween80/Span80 ratio (HLB = 8).
- 2) The prepared blend was added into the diesel fuel, and homogenized at 15,000 rpm for 10 min.
- 3) Distilled water was added gradually, into the mixture of diesel and surfactants, and mixed according to **Table 3**.

### 2.2.2. CCD Experimental Design

Consequently CCD is a combination of both mathematical and statistical technique used to design experiments; evaluate the factors of process; obtaining the model; interaction between variables and find optimum condition to analyze the problem [21] [22]. Response Surface Methodology RSM was applied to study the impacts of the independent factors: applied water percent (w%), Tween80/Span80 ratio (TS%), mixing time (min), homogenizer speed rpm, alkalinity (pH) and HLB of WiDNE. The experiments were designed using a 54 factorial with five central points as shown in **Table 3**. The individual experiments were carried out in random order

## 3. Results and Discussion

### 3.1. Analysis of Variance

The sum of square sequential model was used to compare different models. It showed the statistical significance of adding new terms step by step in increasing order. It provided accounts of variation and associated P-values (Prob > F). The model was selected based on the highest order that was significant (P-value small) and not aliased, on lack of fit (P-value > 0.10) and reasonable agreement between adjusted R-squared and predicted R-squared (within 0.2 of each other). The summary table of the sequential model sum of square is shown on **Table 4**.

**Table 2.** Properties of the surfactants.

	Span 80	Tween 80
symbol	S	T
Appearance	Brown viscous	Amber sticky
Mwt	428.61	1310
Density (g/ml)@20°C	0.99	1.08
HLB	4.3	15

**Table 3.** The experiments design trial used for WiDNE fuel preparation.

NO.	W%	HLB	TS%	TIME(min)	rpm	pH	D (nm)
1	18	5.7	2.6	40	17,000	9.8	30
2	18	5.7	2.6	30	17,000	11.2	29.2
3	12	5.7	3.4	40	17,000	9.8	21
4	12	5.3	3.4	30	13,000	9.8	27.3
5	12	5.7	3.4	30	17,000	11.2	22
6	18	5.3	2.6	30	13,000	9.8	31.3
7	18	5.3	3.4	30	17,000	11.2	27
8	18	5.3	2.6	40	13,000	11.2	33
9	12	5.3	2.6	40	17,000	9.8	25
10	12	5.3	2.6	30	17,000	11.2	24.3
11	15	5.5	3	35	15,000	10.5	27
12	12	5.7	2.6	40	13,000	11.2	29
13	18	5.7	3.4	30	13,000	9.8	29
14	18	5.3	3.4	40	17,000	9.8	26.5
15	18	5.7	3.4	40	13,000	11.2	27
16	12	5.7	2.6	30	13,000	9.8	26.1
17	15	5.5	3	35	15,000	10.5	27.5
18	15	5.5	3	35	15,000	10.5	27
19	12	5.3	3.4	40	13,000	11.2	24.2
20	15	5.5	3	35	15,000	10.5	28
21	12	5.3	2.6	40	13,000	9.8	24.1
22	18	5.3	3.4	30	13,000	11.2	32
23	18	5.7	3.4	30	17,000	9.8	27.3
24	12	5.3	2.6	30	13,000	11.2	30
25	12	5.7	3.4	30	13,000	11.2	27
26	18	5.7	3.4	40	17,000	11.2	22.3
27	12	5.3	3.4	30	17,000	9.8	25
28	12	5.7	3.4	40	13,000	9.8	23.5
29	18	5.7	2.6	30	13,000	11.2	32.3
30	15	5.5	3	35	15,000	10.5	28
31	15	5.5	3	35	15,000	10.5	27.9
32	12	5.7	2.6	30	17,000	9.8	26
33	18	5.3	2.6	30	17,000	9.8	33
34	15	5.5	3	35	15,000	10.5	28
35	18	5.3	2.6	40	17,000	11.2	30.2
36	12	5.7	2.6	40	17,000	11.2	25.04

## Continued

37	18	5.3	3.4	40	13,000	9.8	30
38	18	5.7	2.6	40	13,000	9.8	29
39	15	5.5	3	35	15,000	10.5	27
40	12	5.3	3.4	40	17,000	11.2	21
41	15	6.5	3	35	15,000	10.5	25
42	15	5.5	3	35	25,000	10.5	21.7
43	15	5.5	3	35	15,000	7.5	30
44	15	5.5	3	35	15,000	13.5	28
45	15	5.5	5	35	15,000	10.5	29.5
46	0	5.5	3	35	15,000	10.5	2
47	15	4.5	3	35	15,000	10.5	30
48	15	5.5	3	35	5000	10.5	35
49	15	5.5	3	35	15,000	10.5	30.1
50	15	5.5	3	35	15,000	10.5	28
51	30	5.5	3	35	15,000	10.5	29
52	15	5.5	1.5	35	15,000	10.5	36.5
53	15	5.5	3	60	15,000	10.5	29.5
54	15	5.5	3	10	15,000	10.5	42

**Table 4.** Analysis of variance of the regression coefficients of the quadratic equation for the droplets size.

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Model Significant
Block	12.88	2	6.44			
Model	1401.79	27	51.92	52.82	<0.0001	Significant
A-w%	505.33	1	505.33	514.07	<0.0001	
B-HLB	22.72	1	22.72	23.11	<0.0001	
C-TS%	99.21	1	99.21	100.93	<0.0001	
D-TIME	99.79	1	99.79	101.52	<0.0001	
E-RPM	138.22	1	138.22	140.61	<0.0001	
F-pH	0.74	1	0.74	0.75	0.3942	
AB	7.64	1	7.64	7.78	0.0102	
AC	2.18	1	2.18	2.22	0.1491	
AD	0.097	1	0.097	0.098	0.7564	
AE	0.44	1	0.44	0.45	0.509	
AF	1.82	1	1.82	1.86	0.1858	
BC	2.9	1	2.9	2.95	0.0985	
BD	0.46	1	0.46	0.47	0.5001	

## Continued

BE	8.00E-04	1	8.00E-04	8.14E-04	0.9775	
BF	0.19	1	0.19	0.19	0.6674	
CD	6.34	1	6.34	6.45	0.018	
CE	7.84	1	7.84	7.98	0.0094	
CF	7.64	1	7.64	7.78	0.0102	
DE	0.19	1	0.19	0.19	0.6674	
DF	0.46	1	0.46	0.47	0.5001	
EF	22.71	1	22.71	23.11	<0.0001	
A2	212.62	1	212.62	216.3	<0.0001	
B2	2.98	1	2.98	3.03	0.0947	
C2	27.26	1	27.26	27.73	<0.0001	
D2	50.61	1	50.61	51.48	<0.0001	
E2	0.66	1	0.66	0.67	0.4195	
F2	0.017	1	0.017	0.017	0.8962	
Residual	23.59	24	0.98			
Lack of Fit	19.99	17	1.18	2.29	0.1348	Not Significant
Pure Error	3.6	7	0.51			
Total Corrected for the means	1438.26	53				

The lack of fit tests was included because extra design points beyond what was needed for the model were involved to provide estimation of pure error. Since it was not desirable, so a small F value and probability greater than 0.1 were desired.

Data obtained in **Table 5** was analyzed using the CCD. The analysis result by ANOVA was with 95% confidence displaying F value model was 52.82 and if the value of P lower than 0.05, that means the predicted model was substantial.

The appropriate of the models relied on the value of  $R^2$  coefficient, the model recording  $R^2 = 98.34\%$ . Furthermore, a suitable agreement with the adjusted coefficient of determination was discovered.

In this study, the Adj- $R^2$  value of 96.48% and Pred.  $R^2$  84.40% were obtained. Both values of Adj- $R^2$  and  $R^2$  very adjacent to 1.0 were high and supported a high closing between the predicted and the observed values.

The Pred- $R^2$  of 84.40% was in rational agreement with the Adj.  $R^2$  of 96.48%; the difference was less than 0.2. Value of lake of fit was 0.1348 > 0.05 (not significant) showing that the hypothesis of significance of fitting was rejected for RSM method. The model with p-value of 0.0001 means that there was only 0.01% chance that the F-value of the model. Response surface model equation for regression was in actual units to optimum diameter size by using Design Expert software as illustrated in the Equation (1).

**Table 5.** ANOVA model adequacy.

Statistical analysis	Values
R-Squared	0.9834
Adj. R-Squared	0.9648
Pred. R-Squared	0.8440
Adeq. Precision	51.660

$$\begin{aligned}
 D(\text{nm}) = & 27.93 + 2.48 \times A - 0.53 \times B - 1.25 \times C - 1.10 \times D \\
 & - 1.29 \times E - 0.10 \times F - 0.48 \times AB - 0.2 \times AC + 0.05 \times AD \\
 & + 0.11 \times AE - 0.23 \times AF - 0.30 \times BC + 0.12 \times BD - 0.005 \times BE \\
 & + 0.07 \times BF - 0.44 \times CD - 0.49 \times CE - 0.48 \times CF + 0.07 \times DE \\
 & + 0.12 \times DF - 0.84 \times EF - 0.54 \times A^2 - 0.06 \times B^2 + 0.24 \times C^2 \\
 & + 0.26 \times D^2 - 0.03 \times E^2 - 0.006 \times F^2
 \end{aligned} \quad (1)$$

Equation (1) is in terms of coded variables that can be used for making expectations toward the responses to each factor at given levels. Negative value for individual factor in equation means in reducing droplets size. By default, the low levels of the factors were coded as  $-1$  and the high levels of the factors interaction were coded as  $+1$ . The coded equation was useful for evaluating the relative effluent of the variables by comparing to the coefficients factor, where water W% (A), HLB (B), TS% (C), mixing time (min) (D), mixing speed rpm (E), and pH (F).

It was observed from **Figure 1** that the extent of proximity of the results with the expected values, through which we concluded that the mathematical relationship between the factors affecting the size of droplets already corresponds to reality and confirmed the compatibility of the results of the process and arithmetic.

The results displayed fulfilled with the model assumptions of ANOVA. It indicates no sign presented that the error terms were correlated with each other.

### 3.2. Effect of Emulsification Variables

The most significant step in the preparation of WiDNE is selection of an appropriate variables and the effect of each one on the response. In this study, RSM method with six variables was selected in order to understand the impacts on droplet size. Each of these variables had a different effluent and limited impact except W%, all other factors were associated to reduce droplet size.

**Figure 2** shows the effect and interaction of factors on the droplets size starting from the most influential factor and ending with the least impact. It has been found that the rpm has a direct impact on the size of droplets.

Therefore, the 3D plots are the best method for illustrating the interaction between variables and effect of each others as can be shown in **Figure 3**.

In order to clarify the impact of the independent variables according to the results, response surface and 3D plots of the quadratic polynomial model were

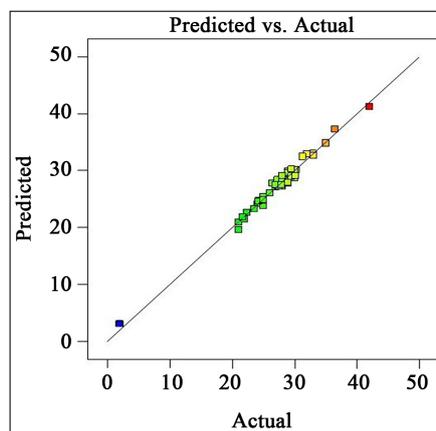


Figure 1. Predicted vs. actual result of droplet sizes.

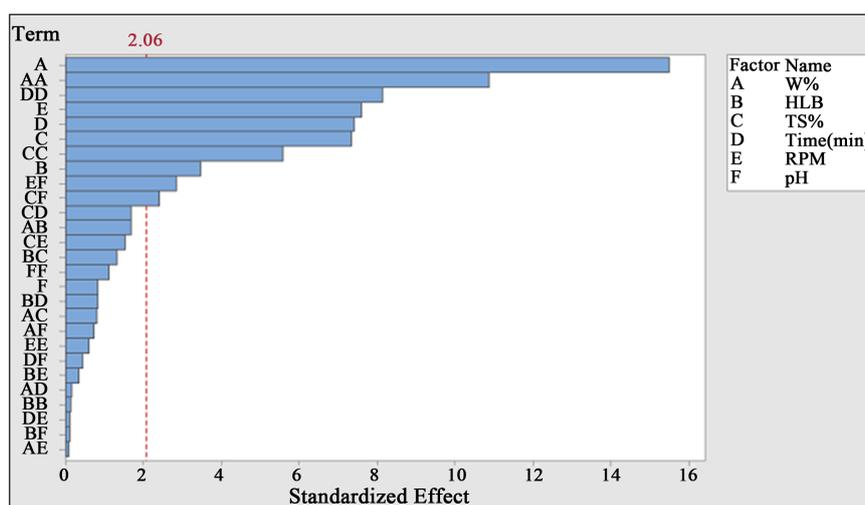


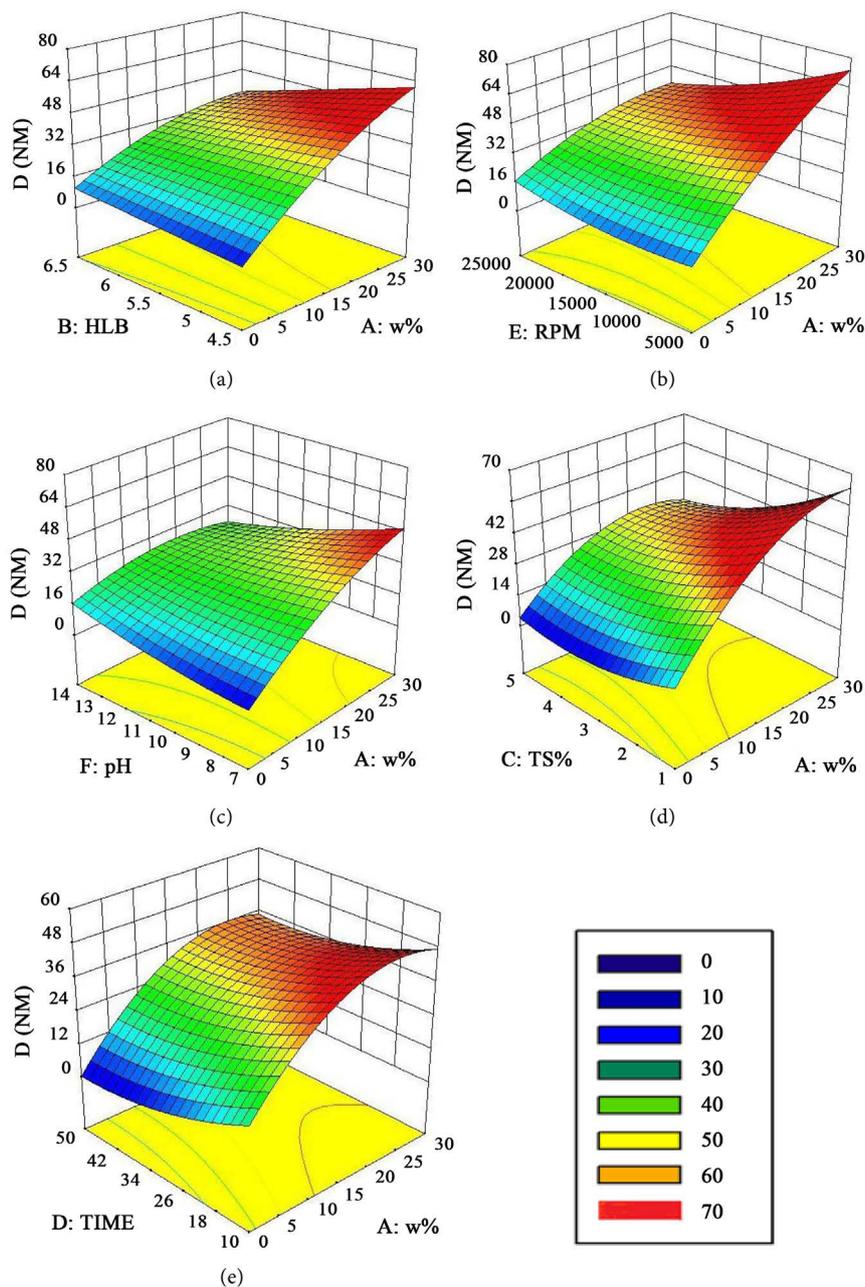
Figure 2. Pareto chart of the standardized effects.

created by varying two of independent variables (within the experimental range) for studying the combination effect on response.

Thus the Figures were generated by varying two variables in x and y axis while holding the other variables at optimum values. In this research, WiDNE fuels were prepared by two steps, the first step was prepared of a WiDNE at low rotating speed. Then, high energy homogenizer process was used to additionally decrease in the droplet size. The resistance of droplets to deformation was determined by the surface tension [23] [24].

The coalescence rate of droplets is specified by the ability of emulsifiers that are adsorbed on the surface of droplets, which is ruled by the concentration of surfactants and surface activity **Figure 3(a)** was plotted by varying the water ratio and surfactants HLB while maintaining the other variables constant.

According to Equation (1), the coefficient value of HLB was  $-0.53$  for WiDNE preparation. The higher value means this variable is significant. The negative value means that HLB leads to decrease the droplet size but in less effect than positive.



**Figure 3.** Interaction of factors with water percent with respect to droplet diameter.

**Figure 3(a)** illustrates the relationship between HLB and W% ( $-0.48$ ), the changes in droplet size are in very narrow and that can be confirmed by Equation (1). The lower interaction coefficient found between HLB and W%. The rpm are directly effect on reducing droplet size. It can be shown according to Equation (1)  $-0.1$  decreasing, while its interaction can more impact on response, as shown in **Figure 3(b)** and by Equation (1)  $+0.11$  rpm. pH of dispersed water into diesel fuel is shown in **Figure 3(c)** that limited to effect on droplets size.

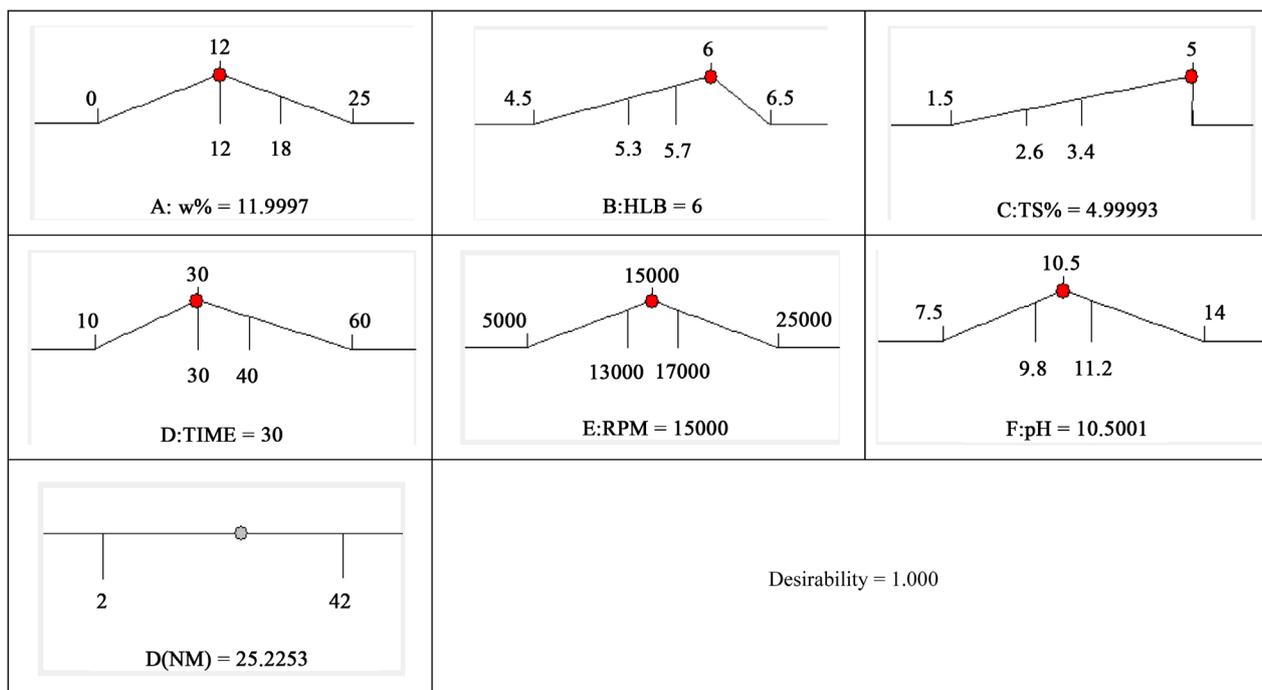
The surfactants role is very central in WiDNE system. It implements two functions. First, it will increase the interaction between the two immiscible sys-

tems; diesel fuel and water by decreasing interfacial tension. Second, it can be improved to stabilize the WiDNE system. Stability behavior of emulsions is highly reliant on concentration of surfactant and its nature.

Surfactant molecules organize themselves near interfacial film between water dispersed phase and diesel fuel a continuous phase, in order to stabilize the water dispersed droplets into the diesel phase. High concentration of surfactants avoids the integration of water droplets [16] [25] [26] [27]. It is observed from **Figure 3(d)** how readily surfactant stabilizing dispersed phase in diesel fuel. According to Equation (1) the impact of mixed surfactant is  $-1.25$ . More increasing the time of splitting droplets to mixing, much less size of droplets will be obtained, but this factor will effect to specific limit and more than it would be useless or don't have benefit economically. The effluents of mixing time are investigated through **Figure 3(e)** combined with W% on droplets size.

### 3.3. Optimum Stability Condition Specifications

Obtaining the best conditions for the WiDNE fuel preparation process is one of the advantages of using this study. As shown in **Figure 4**, the optimum conditions of prepared WiDNE according to response surface method (RSM) were water content 11.9997%, surfactant concentration 4.9993%, HLB 6, RPM 15,000, mixing time 30 min and pH 10.5001. This study has relied on Design Expert Software to locate the optimal situations by composite desirability, from which 25.2253 nm chosen to be the optimum droplet size which exhibited good stability without phase separation during two weeks. The stability in the WiDNE is determined by the water droplet size inside the diesel phase.



**Figure 4.** The best conditions for stability of prepared WiDNE fuel.

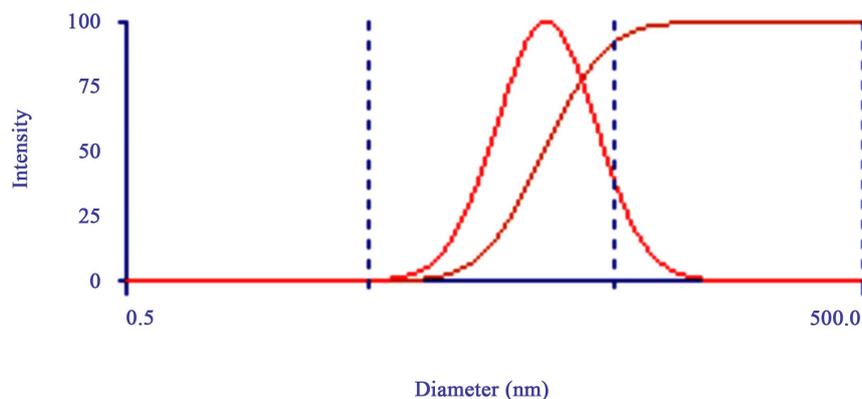
**Figure 5** shows the measured water effective diameter dispersed inside the WiDNE fuel. The measured diameter is 26 nm, with 0.0297 errors between actual conditions and measured by the Design Expert Software.

Optimum blend of prepared WiDNE fuel are compared with conventional diesel, as shown in **Table 6**.

The optimum water ratio was 12%, based on weight percent. The proportion of water inside the emulsified fuel must be kept within the specified limits, because the increase in the proportion of water quantity leads to a decrease in heat of combustion and affect the properties of fuel ignition.

Surfactant plays an important role in the stability of the WiDNE. This role lies in the ability of the surfaces to reduce the interfacial tension between the two liquids and facilitate the process of emulsification and protect droplets from adhesion, aggregations and thus protection from separation.

The exposure time of water droplet within the WiDNE fuel has a direct relationship to the conditions and the rotation speed. Increasing the time led drops to homogeneity and uniform distribution within the emulsion, but this will be limited if exceeded the optimum time, where considered consumed in energy and time. The optimum time was chosen to be 30 min. The rpm leads to the rupture of the droplets to smallest size. Therefore, it is the main factor affecting the size of droplets; the best speed is chosen to be 15,000 rpm. Alkalinity pH does not have a strong effect on droplets size but has interaction with other factors; it is optimized to be 10.5.



**Figure 5.** Measured effective diameter for WiDNE fuel at the best conditions.

**Table 6.** Properties of conventional diesel fuel and the optimum prepared WiDNE.

Properties	Diesel fuel	WiDNE fuel
Calorific value (kJ/kg)	44,800	38,850
Flash point (°C)	54	61
Viscosity at 40°C (cSt)	3.268	4.56
Pour point (°C)	9	7
Density g/cm <sup>3</sup>	0.87	0.882

### 3.4. WiDNE Fuel Properties

#### 3.4.1. Calorific Value

The variation in the calorific value of WiDNE fuel is shown in **Table 6**. The calorific value was reduced from 44,800 to 38,850 kJ/kg. The less calorific value observed due to the content of 12% water in WiDNE fuel. Water reduces the calorific value and then decreases the heat of reactions that produce high toxicity gases. The improvement in calorific value of WiDNE fuel could be observed with the addition of specific nanocatalyst [28].

#### 3.4.2. Flash Point

Flash point is an indication of the fuel's volatility. For safe handling of liquid fuel, it should always have high value. The influence of water content on flash point of WiDNE fuel is shown in **Table 6** determined using Pensky Martin Apparatus. It was observed that flash point of WiDNE fuel increased from 54°C to 61°C with respect to water percent.

#### 3.4.3. Viscosity

The effect of the presence of water on the viscosity of WiDNE fuel is shown in **Table 5**. It was observed that viscosity increases from 3.268 to 4.56 cSt. The increasing in viscosity leads to more power requirement for pumping of fuel and poor atomization.

#### 3.4.4. Density

The impact of water on density of WiDNE fuel is shown in **Table 5**. Density was increased from 0.87 g/cm<sup>3</sup> to 0.882 g/cm<sup>3</sup> for WiDNE. It is known that the water is heavier than diesel fuel. The impact of water is obvious in increases the density when blending with diesel. However, more fuel density means less volume will be taken for storing purpose.

#### 3.4.5. Pour Point

Pour point of WiDNE fuel +7°C were less compared with net diesel +9°C. Increasing water content on WiDNE fuel caused reduction in pour point as shown in **Table 6**. With formation of WiDNE fuel, this pour point can be lowered significantly in order to confirm safe transportation of these types of oils.

## 4. Conclusions

- 1) Response surface methodology (RSM) was used to enhance process variables for preparation of WiDNE fuel.
- 2) Surfactant concentration has very positive effect on emulsion stability.
- 3) Increasing in water content decreased the emulsion stability.
- 4) Mixing and time have enhanced the stability significantly up to a certain limit beyond which it remains the same.

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