Cetane Number Improvement of Distilled Diesel from Tawke Wells

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Abstract-The current research aims to improve the cetane number of diesel extracted from the crude oil of Tawke region in Iraqi Kurdistan. A specific mixture of chemical compounds was prepared which included m-nitrophenol, 4-nitro toluene, and nitrobenzene. The components' effects were investigated with regard to the cetane number, flash point, viscosity, and refractive index of diesel. The quantity of each compound mixed with diesel was prepared based on the statistical analysis of the experiment device (Box–Behnken Designs-BBDs). The tested mixture showed a good agreement and improvement of cetane and flash point and a very low effect on viscosity and refractive index. According to the statistical analysis, the main influence on cetane number and the flashpoint was from m-nitrophenol. The investigation showed that the best results were acquired from the samples of 25PPM 4-nitro toluene and 50PPM m-nitrophenol with a cetane number of 65.3. The correlation and the interaction of the regression equation were linear with all cases. It is worth mentioning that all additives positively influenced the cetane number in the regression equation. The sulfur content was measured as well, and the obtained weight percentage of sulfur was 0.8404%.

Keywords-diesel improvers; cetane number; flash point; viscosity

I. INTRODUCTION

Additives are mixed with fuel to improve its quality and to enhance its efficiency. This process is termed as mixing with fuel of the trace elements. Fuel in various forms like diesel and benzine does not perform well or reach the required international standards without improvers [1]. Therefore, the search for new improvers is in great demand. The utilizing of influential improvers is very essential in order to reach the requested mechanical and environmental standards [2]. In the past, attempts have been made to ignite fuel readily and thus upgrade ignition quality. Nitro compounds are commonly used as cetane number additives and such chemicals make the delay time of fuel ignition shorter and as a result the rate of knocking decreases [2]. Such additives can be utilized with bio-diesel, which commonly has low cetane number [3]. The cetane number is affected by physical and chemical properties of fuel such as density, viscosity, surface tension, and vaporization. The cetane number is also influenced by the molecular structure of fuel and additives [4].

The octane number is a parameter that determines the quality of a fuel. Fuels with high octane numbers, close to 100, knock less. Oxygenated compounds, aromatic hydrocarbons, aromatic amines, and organometallic compounds have been exploited for this purpose as octane number modificators [4-6]. Flash point temperature is another important factor to improve the valid ability of fuel in car engines [8], where lower flash point temperature means lower ignition temperature (piloted temperature) for the fuel oil ranging from 60 to 93^{0}C. However, this research article mainly considers cetane number improvement. The influence on the cetane number of adding dicyclopentadiene to diesel has been examined in [9]. The authors proposed a novel additive of hydrocarbon-based, dicyclopentadiene (DCPD) for diesel fuel which leads to minimized particulate emissions and also enhances cetane

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number. The improvement of diesel properties like viscosity, flash point, density, cloud point, water content, and sulfur content were investigated in [10]. The Design of Experiment (DOE) to study any oil sample represents a significant part of chemo measurements (effects of chemicals on the yield). The universal benefit of DOE is to ensure that the conditions between any test parameters and their yield of the reactions can be evaluated dependably with low cost and exertion with an insignificant number of trials and less amount of chemicals. DOE can be isolated into a few subtopics, for example, confirming factors from an enormous arrangement of factors which is called screening structures, finding the impact of a blend organization on the reaction factors tended to blend plans, and discovering wellsprings of error in estimation frameworks. This leads to concocting ideal conditions inconsistent procedures (evolutionary operation), batch process (response surface methodology), or planning tests for ideal parameter estimation in numerical models (optimal design or optimization) [11]. Different statistical DOE models have been utilized to smooth out factors in the exploratory plan. Accordingly, this helps to select the impact of exploratory factors by conventional methodologies. Tests have been conducted with conscious changes of the specific boundaries. These assessments should be repeated to each boundary effect achieving a reliable number of runs [12].

Numerous studies have been carried out to study the extracted crude oil from the wells of Tawke region in Iraqi Kurdistan [13], but the investigation in crude oil and its components from the specific wells requires more investigations to reach the desired characteristics and to improve its properties. The tests described in the current paper were performed using a sample consisting of diesel mixed with a measured amount of m-nitrophenol, 4-nitro toluene, and nitrobenzene to aggregate the effect of those components on the diesel.

II. EXPERIMENTAL SETUP AND METHODS

The portable analyzer instrument SHATOX SX-100M was used as the main device to analyze the octane/cetane numbers and to determine cetane and octane number, while a device NCL 120 - CLEVELAND OPEN CUP FLASH POINT TESTER MANUAL120 ASTM D 92, IP 36, ISO 2592 was utilized for flash point temperature determination as shown in Figure. 1.

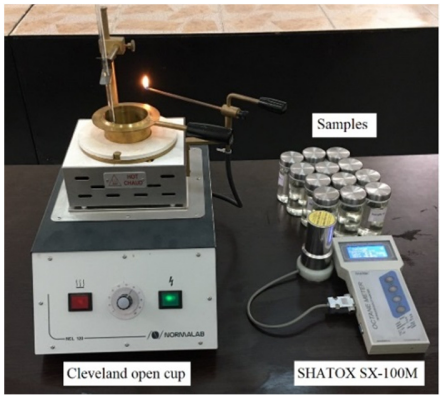
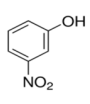
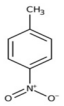
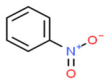


Fig. 1. The experimental devices.

TABLE I. LEVELS OF THE PARAMETERS STUDIED IN THE CCD STATISTICAL EXPERIMENT.

Chemical compound	Unit	Levels		
		-1 (low)	0 (middle)	+1 (high)
m-nitrophenol	PPM	0	25	50
4-nitro toluene	PPM	0	25	50
nitro benzene	PPM	0	25	50

TABLE II. PHYSICAL AND CHEMICAL PROPERTIES

Chemical compound	m-nitrophenol	4-nitro toluene	nitro benzene
IUPAC name	3-Hydroxynitrobenzene	1-methyl-4-nitrobenzene	Nitro benzene
Chemical structure			
Formula	$C_6H_5NO_3$	$C_7H_7NO_2$	$C_6H_5NO_2$
Appearance	Colorless to yellow crystals	Yellowish crystals	Yellowish, oily, aromatic nitro-compound
Molecular weight	139.11g/mol	137.14g/mol	123.11g/mol
Solubility	Soluble in hot and dilute acids and in caustic solutions. Insoluble in petroleum ether. Very soluble in ethanol, ether, and acetone. In water, 13.550mg/L at 25°C	Soluble in alcohol, benzene, ether, chloroform, acetone. In water, 442mg/L at 30°C	Slightly soluble in carbon tetrachloride. Very soluble in ethanol, diethyl ether, acetone, benzene. In water, $2.09\times10^{+3}$mg/L at 25°C
Boiling point	194°C/70mmHg	238.3°C	210.8°C
Melting point	96-98°C	51.6°C	5.7°C
Density	1.485g/cm³ at 20°C	1.29g/cm³	1.2037g/cm³
Vapour pressure	1.5×10^{-4} mm Hg at 25°C	0.0157mm Hg at 25°C	0.245mm Hg at 25°C
Toxicity	LD50=328mg/kg (Rat)	LD50=2250mg/kg body weight	LD50=640mg/kg (Rat)

M-nitro phenol, 4-nitro toluene, and nitrobenzene supplied from Germany were used as received. Solutions of m-nitrophenol, 4-nitro toluene, and nitrobenzene 50mL/L (PPM) were prepared in diesel and then were diluted to solutions according to Table I. The prepared solutions were covered by aluminum foil and kept in dark to avoid the photodegradation of the 13 samples. Diesel was brought from Tawke oil well distillery and was used as received. Different concentrations of improvers were prepared according to the needs of the experiments as shown in Table I. Table II shows the physic-chemical properties of the additives.

It is essential to fit a logical model in order to depict the response directly in the test field by choosing the DOE. Generally, this model is suitable for illustrating a plane surface, as indicated by:

$$R = \beta o + \sum \beta i Xi + \varepsilon \quad (1)$$

where R is the response, βo is the constant term, βi represents the coefficients of the linear parameters, Xi represents the parameters, and ε is the irregular error or commotion to the response. On specific events, it is called the essential impacts model since it incorporates just the principle impacts of the

factors as explained intensively in [14]. If the interaction between the parameters is contained, then the first-order model becomes:

$$R = \beta o + \sum \beta iXi + \sum \beta ijXiXj + \sum \beta iiX^2 i + \varepsilon \quad (2)$$

where βii indicates the quadratic coefficients of the variables and $i < j$.

Response Surface Methodology (RSM) was applied to identify the positive and negative effects of each factor. The experimental Box Behnken Design (BBD) was also utilized to select the number of required experiments for the present research as represented in [14, 15]. The effect of cetane number was studied. All tests were carried out based on the experimental design that is derived from the Minitab16 program (version 2018) as in Table III, where the estimated exact cetane number and the quantities of the mixed additives are stated. Flash point, viscosity, and the refractive index were measured. The solutions were taken for each run according to the run order and levels as illustrated in Table III and Table I. The mixtures were then put aside for 24 hours in order to assure solubility. In each run, before testing, the mixtures were shaken well for total miscibility. The readings were taken from the octane meter and flash point temperature meter. All runs were performed at ambient temperature and on the same day to avoid any environmental effect on the outcome.

TABLE III. CENTRAL COMPOSITE DESIGN MATRIX -BBD.

No. of run order	Nitro benzene (PPM)	4-nitro toluene (PPM)	M-nitro phenol (PPM)
1	25	0	0
2	25	0	50
3	25	50	0
4	25	50	50
5	0	25	0
6	0	25	50
7	50	25	0
8	50	25	50
9	0	0	25
10	0	50	25
11	50	0	25
12	50	50	25
13	0	0	0

III. RESULTS AND DISCUSSION

Statistical analysis was employed to determine the effect of each additive and their interactions in order to indicate the best model. All models were studied. During the present study, the linear model showed the best agreement among other models and regression equations as in (1) and (2) were opbtained. The regression equation shows that all parameters have a positive effect on the cetane number. However, the effect is rational on octane number and flash point which means there is a negative effect from some additives. The effect of each parameter is determined by a factor in regression equations.

A. Effect of the Added Chemicals on the Cetane Number

Figure 2 demonstrated the relationship between the contour plot of the determined additives and cetane number, while Figure 3 showed the surface plot of the obtained additives and cetane number. The effect of the additives m-nitrophenol, 4-nitro toluene, and nitrobenzene on cetane number was positive. The greatest estimated impact was recorded from nitro phenol followed by 4-nitro toluene, and nitrobenzene by 0.3545, 0.0054, and 0.0035 respectively as shown in regression equation (1). The correlation between the parameters is very strong and equal to 98.92%. Table IV contains the coefficients and ANOVA parameters obtained from the current experiment, and Table V demonstrates the cetane numbers results from the tested samples.

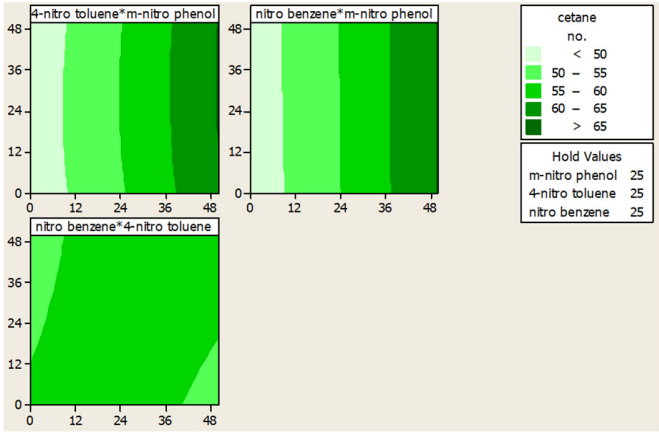


Fig. 2. Contour plot for the determination of additives effect on cetane number.

TABLE IV. COEFFICIENTS AND ANOVA PARAMETERS

Term	Coeficient	SE coeficient	T	F	P
Constant	46.6417	0.534102	87.3273		0.000
Regression				336.62	0.000
m-nitro phenol	0.3545	0.011157	31.7737	1009.57	0.000
4-nitro toluene	0.0050	0.011157	0.4481	0.20	0.666
Nitro benzene	0.0035	0.011157	0.3137	0.10	0.762
Model summary	S = 0.788921, R-Sq = 99.21%, R-Sq(adj) = 98.92%, PRESS = 11.2031, R-Sq(pred) = 98.23%				

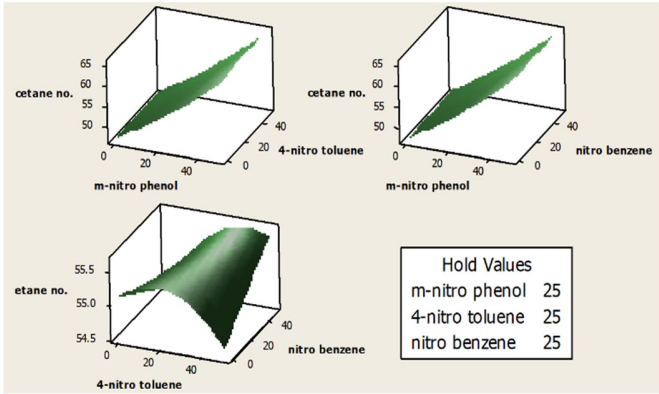


Fig. 3. Surface plot for the determination of additives effect on cetane number.

According to the test, the correlation equation between the cetane number and the additive becomes:

$$Cetan\ number = 46.6417 + 0.3545\ m-nitro\ phenol + 0.005\ 4\ nitro\ toluene + 0.0035\ nitro\ benzene \quad (3)$$

TABLE V. CETANE NUMBER RESULTS

No. of run order	Nitro benzene (PPM)	4-nitro toluene (PPM)	M-nitro phenol (PPM)	Cetane number
1	25	0	0	46.9
2	25	0	50	64.1
3	25	50	0	47.3
4	25	50	50	65.2
5	0	25	0	47.3
6	0	25	50	65.3
7	50	25	0	47.4
8	50	25	50	65.2
9	0	0	25	55.3
10	0	50	25	54.3
11	50	0	25	54.9
12	50	50	25	55.4
13	0	0	0	46.9

B. *Effect of the Added Chemicals on Flash Point*

Figures 4 and 5 exhibit the contour and surface plots on the flash point obtained from the present work. The effect of the additives on flash point temperature has been investigated. The results show that the additives present a negative effect on flash point temperature. This means that when the concentration of additives is increasing, the flash point temperature decreases by factors of 0.135, 0.005, and 0.06 respectively as shown in regression equation (3). The resulted correlation was about 45.41%. Table VI illustrates the coefficients and ANOVA parameters estimated from the runs, whereas Table VII consists of the results of all tests with their run order. It is worth mentioning that the mixture flash point reaches the requirement of the international standards which is about 51-60 [17].

The equation between the flashpoint and the additive becomes:

$$Flash\ point = 90.25 - 0.135\ m-nitro\ phenol - 0.005\ 4\ nitro\ toluene - 0.06\ nitro\ benzene \quad (4)$$

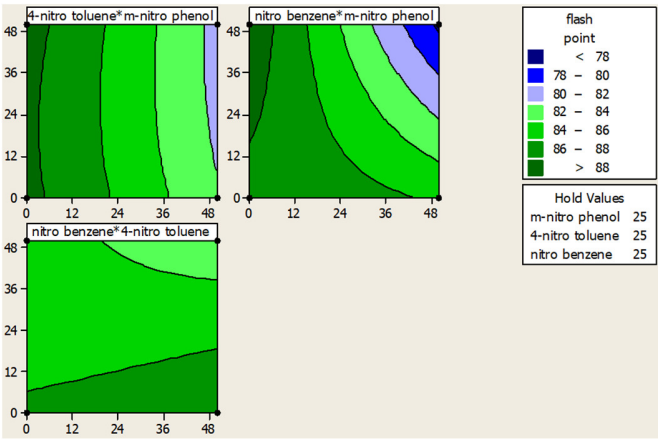


Fig. 4. Contour plot for thedetermination of additives effect on cetane number.

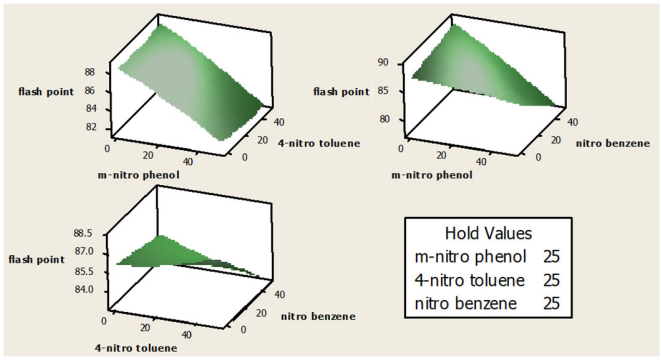


Fig. 5. Surface plot fo ther determination of additives effect on flash point temperature.

TABLE VI. COEFFICIENTS AND ANOVA PARAMETERS

Term	Coeficient	SE coeficient	T	F	P
Constant	90.250	1.41605	63.7335		0.000
Regression				8.3238	0.007655
m-nitro phenol	-0.135	0.02958	-4.5638	20.8286	0.002
4-nitro toluene	-0.005	0.02958	-0.1690	0.0286	0.870
Nitro benzene	-0.060	0.02958	-2.0284	4.1143	0.077
Model summary	S = 2.09165 R-Sq = 75.74% R-Sq(adj) = 66.64% PRESS = 78.75 R-Sq(pred) = 45.41%				

TABLE VII. FLASH POINT TEMPERATURE RESULTS

No. of run order	Flash point	Nitro benzene (PPM)	4-nitro toluene (PPM)	M-nitro phenol (PPM)
1	89	25	0	0
2	83	25	0	50
3	88	25	50	0
4	81	25	50	50
5	88	0	25	0
6	86	0	25	50
7	89	50	25	0
8	77	50	25	50
9	85	0	0	25
10	88	0	50	25
11	85	50	0	25
12	84	50	50	25
13	91	0	0	0

C. *Effect of the Added Chemicals on Viscosity*

The effect of the selected additives are exhibited in Figure 6. All additives had a negative effect on viscosity. This means that when the concentration of additives increased, viscosity decreased by the factors of -0.000080, -0.00044, and -0.00008 as shown in (5). Nevertheless, the effect is very weak. Table VIII shows the coefficients and ANOVA parameters obtained from the tests, while Table IX states the results of the viscosity values. The regression equation is:

$$Viscosity = 3.15 - 0.00008\ m-nitro\ phenol - 0.00044\ 4\ nitro\ toluene - 0.00008\ nitro\ benzene \quad (5)$$

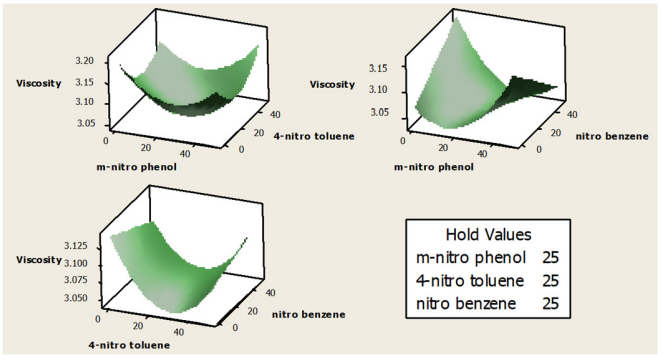


Fig. 6. Surface plot for the determination of additives effect on kinematic viscosity.

TABLE VIII. COEFFICIENTS AND ANOVA PARAMETERS

Term	Coeficient	SE coeficient	T	F	P
Constant	3.14867	0.04942	63.71		0.000
Regression				0.06	0.977
m-nitro phenol	-0.000080	0.001032	-0.08	20.8286	0.940
4-nitro toluene	-0.000440	0.001032	-0.43	0.0286	0.681
Nitro benzene	-0.000080	0.001032	-0.08	4.1143	0.940
Model summary	S = 0.0729989 R-Sq = 2.4% R-Sq(adj) = 0.0%				

TABLE IX. KINEMATIC VISCOSITY RESULTS

No. of run order	Kinematic Viscosity Cts/s	Nitro benzene (PPM)	4-nitro toluene (PPM)	M-nitro phenol (PPM)
1	3.256	25	0	0
2	3.172	25	0	50
3	3.148	25	50	0
4	3.132	25	50	50
5	3.08	0	25	0
6	3.22	0	25	50
7	3.104	50	25	0
8	3.048	50	25	50
9	3.08	0	0	25
10	3.076	0	50	25
11	3.112	50	0	25
12	3.176	50	50	25
13	3.182	0	0	0

D. Effect of the Added Chemicals on Refractive Index

The influence of the chosen additives is shown in Figure 7. M-nitrophenol, 4-nitro toluene, and nitrobenzene were studied with regard on their effect on the refractive index. The additives presented a very low impact on the refractive index which means their effect is negligible as shown in regression equation (6). Table X demonstrates the coefficients and ANOVA values obtained from the runs, and Table XI shows the summed values of the tests with their run order. The regression equation is:

$$Refractive\ index = 1.46 - 0.000013\,m - nitro\ phenol - 0.0000224\,nitro\ toluene + 0.000007\,nitro\ benzene \quad (6)$$

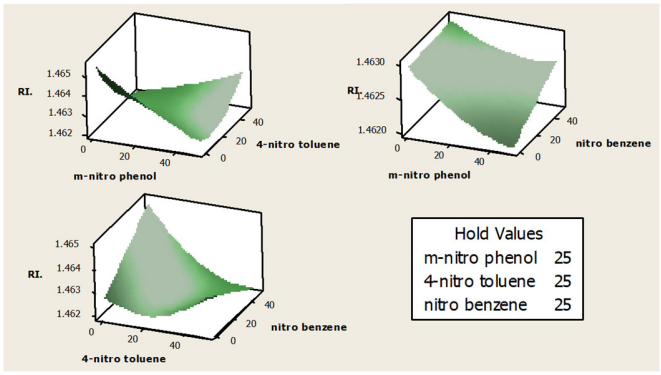


Fig. 7. Surface plot for the determination of additives effect on refractive index.

TABLE X. COEFFICIENTS AND ANOVA PARAMETERS

Term	Coeficient	SE coeficient	T	F	P
Constant	3.14867	0.04942	63.71	----	0.000
Regression				0.06	0.977
m-nitro phenol	-0.000080	0.001032	-0.08	20.8286	0.940
4-nitro toluene	-0.000440	0.001032	-0.43	0.0286	0.681
Nitro benzene	-0.000080	0.001032	-0.08	4.1143	0.940
Model summary	S = 0.0729989 R-Sq = 2.4% R-Sq(adj) = 0.0%				

TABLE XI. REFRACTIVE INDEX RESULTS

No. of run order	Refractive index	Nitro benzene (PPM)	4-nitro toluene (PPM)	M-nitro phenol (PPM)
1	1.4623	25	0	0
2	1.4624	25	0	50
3	1.4621	25	50	0
4	1.4631	25	50	50
5	1.4632	0	25	0
6	1.463	0	25	50
7	1.462	50	25	0
8	1.4624	50	25	50
9	1.4618	0	0	25
10	1.4632	0	50	25
11	1.4653	50	0	25
12	1.4629	50	50	25
13	1.4653	0	0	0

IV. CONCLUSION

The current statistical and experimental analyses have been performed to study the effect of three aromatic compounds as diesel cetane number improvers and their impact on flash point, refractive index, and viscosity of Tawke oil well diesel. Sample 6 gave the best result. To the best of our knowledge, no similar study has been conducted with the certain components to contrast the present outcome, however, many investigations to improve the cetane number of fuel have been performed including the transesterification and higher alcohol-diesel blends [17], the oxygenated compound for cetane number improvement di-n-pentyl-ether (DNPE) [18], and the ethanol with 2-ethyl hexyl nitrate (EHN) component [3].

Mixtures of additives were added to the diesel samples and were measured regarding the cetane number improvement and

flash point. Three different organic chemicals were selected for the current research, namely m-nitrophenol, 4-nitro toluene, and nitrobenzene. Statistical analysis was performed to determine the effect of each component and to calculate the regression equation. Besides, the experimental design was utilized to calculate the most active mixture composition that presents the best performance and attains the international standards. The best mixture composition turn out to be the addictive consisting of run number 6 that consisted of no nitrobenzene, 25PPM 4-nitro toluene, and 50PPM m-nitrophenol. Viscosity and refractive index were measured as well and their effect was significant.

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