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Optimization of the Oxidative Desulphurization of Residual Oil Using Hydrogen Peroxide

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Abstract: The role of fuel in global economy cannot be overemphasized, it is necessary to develop new and more efficient technologies in desulphurization processes at a low cost. This research focuses on optimization of desulphurization using oxidative method for higher yields, utilizing dual acetic/formic acid catalyst on residual oil with sulphur concentration > 0.50%wt and emphasizes the improvement of physicochemical properties primarily suitable for use in fuels where regulation is becoming more stringent. The process was conducted using H_2O_2 oxidant concentration 12.5-25.0% (w/w), $CH_3COOH/HCOOH$ acid catalyst mixture 12.5-22.0% (w/w), and reaction temperature 40-60°C. Optimization of the desulphurization parameters was done using response surface methodology based on Box-Behnken design. The optimum yield of desulphurization (60.93%) was achieved at the oxidant 18.75% (w/w), acetic/formic mixture of 17.25% (w/w), and reaction temperature of 50°C. In general, the experimentally confirmatory figures in two solutions of 63.29 ± 0.47% and 61.04 ± 0.13% match the predicted values of 62.82% and 60.91%, respectively. The total sulphur content in residual oil was reduced from 0.67 to 0.26%wt. GC-MS of the untreated sample confirm the presence of 1,2-benzisothiazole,3-(hexahydro-1H-azepin-1-yl)-1,1-dioxide, Nickel(II)bis(N,N-dihexyldithiocarbamate and Diethyl[3-[n-octadecylmercapto]-P-n-butyl-anilino methy lene] malonate with a total percentage peak area of 11.83%. In the treated sample shows no sulphur compounds. The physicochemical analysis for both treated and untreated residual oil according to ASTM were found to be within acceptable limit except sulphur content of untreated sample. After the desulphurization, treated residual oil shows a remarkable improvement in the physicochemical parameters. Hence can be applicable in industrial process and automobiles with very low sulphur emission.

Keywords: Optimization, Oxidative, Desulphurization, Residual Oil

1. Introduction

It is well known that the age of fuel oil is still young, and in the scenario under the current regulations, oil demand growth is still strong in part as a result of increased usage in shipping, aviation, and road transportation. Comes with the risk of rapid adoption of electric vehicles, aided by additional policy and infrastructure support insufficient to result in a significant reduction in global oil consumption. Light and intermediate distillates are in high demand on the market. However, there is less availability of light oils that produce a high proportion of light or middle distillates used in transportation fuels. The primary industrial problem is to

modify refineries so that they can process larger crude oils as well as heavier cuts, which can then be refined to create light distillates. The principal components of these crude and residual cuts are high molecular weight hydrocarbons and a complex mixture of contaminants, including sulphur, nitrogen, aromatics, asphaltenes, and heavy metals [1].

Sulphur was already identified as one of the main contaminants that has a negative impact on the final refined product's quality and frequently raises the cost of processing. In addition, when products burn, sulphur-containing compounds in crude oil cause several operational problems and air pollution. One of the known difficulties with this approach is that petroleum products contain sulphur, which destroys the catalyst and renders it inactive. Sulphur dioxide and sulphuric acid are produced during the burning of petroleum fuels containing sulphur components [2].

In accordance with Regulation 14 of MARPOL Annex VI, the International Maritime Organization (IMO) has established a maximum of less than 0.50%wt for sulphur in fuel oil used on board ships operating outside designated Emission Control Areas in contrast to the previous restriction of 3.50%wt. [3]. High sulphur content is not only affecting the environment but also causing adverse effects on the quality of petroleum and natural gas products as it may reduce API gravity, decrease octane rating, and release toxic hydrogen sulphide [4]. In order to produce greener fuels, the desulphurization operation is essential in the petroleum refining industry. The predominant desulphurization process used widely up to this point is hydrodesulphurization. Traditional hydrodesulphurization cannot generate ultralow-sulphur fuel due to the hardening of sulphur regulations. Alternative desulphurization processes such as adsorptive desulphurization, bio-desulphurization, and oxidative desulphurization are being widely discussed as potential technologies for producing ultralow sulphur fuel as the refinery industry becomes more reliant on the development of new technologies [5].

The correct method of eliminating sulphur content in liquid fuels is crucial since it is considerably more difficult to remove sulphur from liquid fuels than from natural gas, such as kerosene, gasoline, diesel fuel, and residual oil. The traditional method for removing sulphur, hydrodesulphurization, employs a costly catalyst and hydrogen gas under high working conditions [6]. The most promising alternative sulphur removal technique in terms of efficiency and cost is oxidative desulphurization. In this study, efficient catalysts were used to evaluate and optimize the oxidative desulphurization process on residual oil sample, lowering the sulphur content to meet liquid fuel standards (< 0.50 wt%).

Currently, oxidative desulphurization is effective but not without problems. In oxidative desulphurization, the two major problems are: Firstly, the catalysts do not always perform effectively and selectively. For example, using acetic acid leads to low yields of desulphurization. According to Haruna *et al.* [7], the CH_3COOH catalyzed system gave a sulphur reduction of (27.02%), which is 0.87 wt%, while the

HCOOH catalyzed system was able to reduce the sulphur to 0.32 wt% (73.00%). This is an indication that sulphur reduction is enhanced by a strong acidic catalyst (HCOOH) [8]. Secondly, the selection of a suitable solvent for the extraction of the oxidized sulphur compounds has been problematic because using the wrong solvent may result in removing desirable compounds from the fuel [9]. To mitigate the potential effects, we use optimization oxidative desulphurization at moderate temperature with a dual acetic and formic acid as catalyst on hydrogen peroxide as the oxidant to provide high yields of valued products with the lowest sulphur level possible at a low cost.

2. Materials and Methods

2.1. Sample and Chemical Reagents

The residual oil sample was collected from the Kaduna Refinery and Petrochemical Company, Kaduna, Nigeria. Analytical grade (BDH) hydrogen peroxide (35%wt), acetic acid (99.5%), formic acid (98.0%), and ethanol (99.7%) were used without additional purification.

2.2. Physicochemical Properties of Residual Oil

The sulphur content, specific gravity, flash point, pour point, and kinematic viscosity, were determined using ASTM D1552, ASTM D6751, ASTM D93, ASTM D97, and ASTM D445.

2.3. Characterization of the Residual Oil

GC-MS analysis was carried out using an Agilent Technologies GC 7890B coupled to MSD 5977 at electron ionization energy of 70 eV. Helium was used as carrier gas at a flow rate of 1.2 cm^3/min. The inlet temperature was kept at 300°C, and the sample injection volume was 1 μl. The oven temperature was set initially at 50°C for 1 min and then ramped to 310°C at 10°C per minute holding the temperature for 10 minutes. The MS transfer line was kept at 300°C, the source temperature was at 230°C, and the MS Quad was kept at 150°C. A fused silica capillary column (30 m × 0.25 mm i.d.) coated with 0.25 μm dimethyl polysiloxane (DB-5ms) stationary phase was used. The mass spectra of the separated compounds were compared with the spectra of known compounds in the NIST02 Reference Spectral Library [10].

2.4. Experimental Design

MINITAB 17 Statistical Software was used for the experimental design based on the Box-Behnken response surface methodology [10]. The effects of three (3) factors were investigated: namely, reaction temperature, acetic/formic acid mixture as a catalyst, and hydrogen peroxide as oxidant. The same software was used to analyze the experimental data at 95% confidence level [10]. Table 1 shows the lower and upper levels of the factors employed.

Independent Variables	Unit	Level of Variables	
		Low (-)	High (+)
Temperature	°C	40	60
Acetic/Formic acid catalyst	% (w/w)	12.5	22.0
Oxidant concentration	% (w/w)	12.5	25.0

2.5. Description of the Experimental Runs

The oxidation reaction of the residual oil was performed by adopting the method of Dana *et al.* [11] with a slight adjustment. About 40 g of the residual oil was introduced into a 250 cm^3 beaker, and then 12.5 to 22.0% (w/w) of the dual acetic/formic acid catalyst were separately added. The mixture was stirred at a temperature (40–60°C), and then 12.5-25.0% (w/w) of hydrogen peroxide were separately added as an oxidizing agent. For 120 minutes, the vigorous stirring was maintained. Thereafter, the mixture was introduced into a separatory funnel and allowed to settle for 120 minutes. Then, the lower aqueous phase was removed, and the upper organic phase was extracted with 40 g of ethanol in a 250-cm^3 beaker placed on a magnetic stirrer at ambient temperature under stirring for 30 minutes. And then a separatory funnel was used to separate the mixture into polar and non-polar phases. The non polar oil recovered was subjected to sulphur and other physicochemical analyses. The desulphurization yield (y) was calculated from equation 1.

$$y = \frac{S_b - S_a}{S_b} \times 100 \tag{1}$$

where S_b and S_a are the sulphur content of the oil before and after the desulphurization.

2.6. Data Analysis

The desulphurization yield (y) was fitted to a full quadratic model (Equation 2) using MINITAB 17 statistical software. The fitness of the model was evaluated by the coefficient of determination (R^2), and the effects of terms were evaluated using analysis of variance (ANOVA) at a 95% confidence level. Also, contour plots were developed using the fitted quadratic polynomial equation. Optimizer on the MINITAB 17 was used to optimize the factors, and the optimal level obtained was experimentally validated [10].

$$y = \beta_0 + \sum_{i=1}^{3} \beta_i x_i + \sum_{i=1}^{3} \beta_{ii} x_i^2 + \sum_{i<1}^{3} \beta_{ij} x_{ixj} + e \tag{2}$$

where y is the response (dependent); x_i and x_j are the variables (Independent); β_o is the intercept; β_i is the first order coefficient of the model; β_{ii} is the quadratic coefficient of i factor; β_{ij} is the linear coefficients of the model for the interaction between i and j factors; e is the error associated with response.

3. Results and Discussion

3.1. Analysis of the Model

Table 2 shows the design matrix and the desulphurization yield from the various experimental runs. The yield ranges from 25.59 to 60.93%.

Table 2. The experimental design matrix and the desulphurization yields.

Std Order	Temperature (°C)	Catalyst% (w/w)	Oxidant% (w/w)	Yield (%)
1	40	12.50	18.75	52.06
2	60	12.50	18.75	42.38
3	40	22.00	18.75	47.00
4	60	22.00	18.75	40.30
5	40	17.25	12.50	26.93
6	60	17.25	12.50	37.31
7	40	17.25	25.00	43.72
8	60	17.25	25.00	55.85
9	50	12.50	12.50	55.02
10	50	22.00	12.50	56.85
11	50	12.50	25.00	60.33
12	50	22.00	25.00	55.18
13	50	17.25	18.75	60.93
14	50	17.25	18.75	59.66
15	50	17.25	18.75	58.77
16	40	12.50	18.75	49.42
17	60	12.50	18.75	43.31
18	40	22.00	18.75	44.50
19	60	22.00	18.75	41.80
20	40	17.25	12.50	25.59
21	60	17.25	12.50	35.61
22	40	17.25	25.00	44.02
23	60	17.25	25.00	55.18
24	50	12.50	12.50	55.36
25	50	22.00	12.50	57.18
26	50	12.50	25.00	58.98
27	50	22.00	25.00	53.69
28	50	17.25	18.75	60.63
29	50	17.25	18.75	59.96
30	50	17.25	18.75	59.26

Table 3 shows the results of the analysis of variance (ANOVA) on the data. The model is a significant representation of the experimental data (P < 0.05). In the linear terms, temperature and catalyst of the variables are statistically insignificant except for oxidant, which is significant (p < 0.05, at α = 0.05). It also demonstrates that the square terms temperature*temperature is significant (p < 0.05, at α = 0.05) while the other terms are not. Results in the 2-way interactions of the variables are statistically insignificant (p > 0.05, at α = 0.05). The "lack of fit" is statistically significant (p < 0.05, at α = 0.05). The model though has high coefficient of variation (R^2 = 78.75%) which it adequately accounts for about 79% of the empirical data.

Table 3. Analysis of Variance (ANOVA) for oxidative desulphurization yield.

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	2289.85	254.43	8.23	0.000
Linear	3	418.22	139.61	4.52	0.014
Temperature (θ)	1	21.39	21.39	0.69	0.415

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Catalyst (c)	1	25.91	25.91	0.84	0.371
Oxidant (h)	1	371.53	371.53	12.02	0.002
Square	3	1840.06	613.35	19.85	0.000
Temperature*Temperature (θ^2)	1	1753.56	1753.56	56.74	0.000
Catalyst*Catalyst (c^2)	1	3.00	3.00	0.10	0.758
Oxidant*Oxidant (h^2)	1	114.19	114.19	3.70	0.069
2-Way interaction	3	30.96	10.32	0.33	0.801
Temperature*Catalyst ($\theta*c$)	1	5.10	5.10	0.17	0.689
Temperature*Oxidant ($\theta*h$)	1	1.04	1.04	0.03	0.856
Catalyst*Oxidant (c*h)	1	24.82	24.82	0.80	0.381
Error	20	618.06	30.90		
Lack-of-Fit	3	601.81	200.60	209.88	0.000
Pure Error	17	16.25	0.96		
Total	29	2907.91			

Key: DF= degree of freedom, Adj SS= adjusted sum of squares, Adj MS= adjusted mean squares, F-Value = F-statistic values, P- value = probability value.

When the insignificant terms of the model are eliminated, the new regression model Equation 3 with three significant terms is as good as the previous model in representing the data (adjusted R^2 = 69.48% compared to 69.18%). The prediction power of the new model is better than the old one (R^2 predicted = 61.72% compared to 45.72%). Similarly, the error of the new model slightly reduced compared to the old one (SE = 5.53 compared to 5.56).

$$y = -341.6 + 15.29\theta + 0.771h - 0.1517\theta^2 \qquad (3)$$

where θ = temperature, h = concentration of oxidant, θ^2 = temperature*temperature.

3.2. Effect of the Reaction Variables on the Yield

Figure 1 shows the absolute effects obtained from coded variables on the desulphurization yield. It is clear that the quadratic term (θ^2) has the largest effect though negative, which is about three times greater than oxidant load.
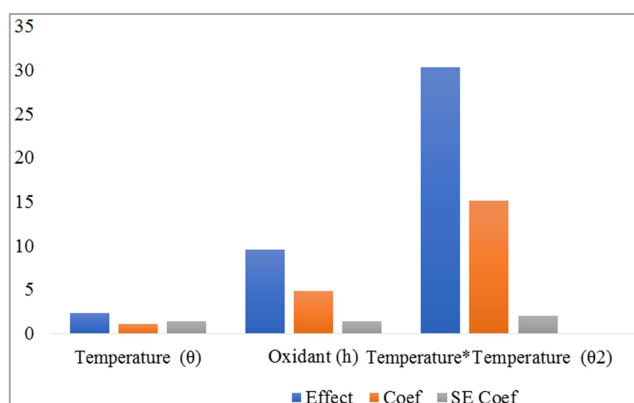

Figure 1. Effect of the coded variables on the desulphurization yield.

The effects of temperature, and oxidant concentration were presented on contour plots as shown in Figure 2.
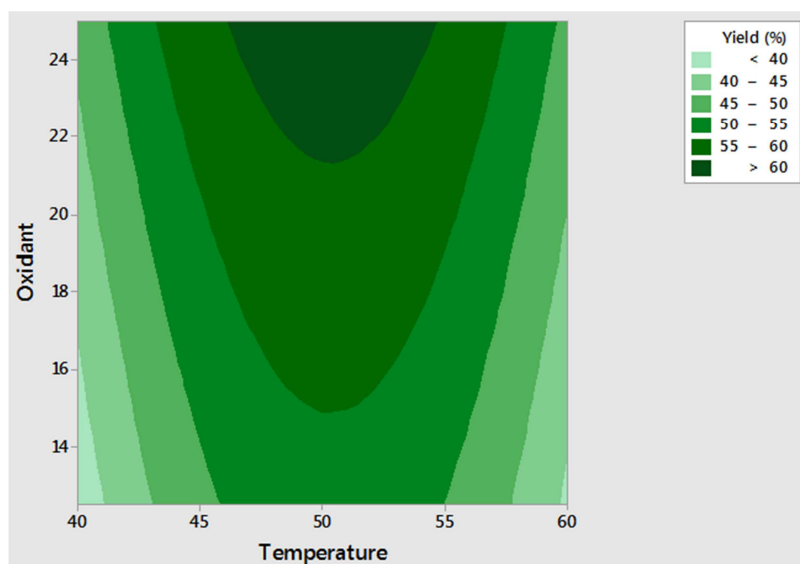

Figure 2. Effects of oxidant concentration and reaction temperature on the yield of desulphurization's.

The results of regression analysis show that only temperature and oxidant concentration are significant. From figure 2, when the oxidant concentration is < 16.1% (w/w) and temperature < 41°C, the desulphurization yield is < 40%, maximum yields of the desulphurization > 60% are obtained when the oxidation is carried out at oxidant > 21% (w/w) and temperature of 46°C

to 55°C. However, increase in temperature from 55°C to 60°C results in decrease in desulphurization. Temperature is the most important variables in oxidative desulphurization using hydrogen peroxide, even at high oxidant concentration led to low yield of desulphurization when temperature above 50°C [12] and 80°C [8]. Hence increase in temperature above 55°C using hydrogen peroxide oxidant should be avoided where it starts to degraded.

3.3. Response Optimization and Validation

Optimization of the desulphurization yield was carried out on Minitab 17 Statistical Software using Response Optimizer. The expected outcomes for two optimal solutions attained through optimization are shown in Table 4. The two solutions had maximal amounts of oxidant at 25.0% (w/w) and catalyst mixture at 22.5% (w/w) in accordance with results in Figure 2. The reaction temperature is where the differences between

the solutions are most noticeable. In solution 1, a comparatively high desulphurization yield of about 62.82% is predicted at a relatively high temperature (50°C). On the other hand, solution 2 is less desirable than solution 1 due to the lower yield. With a predicted desulphurization yield of 62.82% and a temperature requirement of 50°C. Solution 1 may, therefore, be more desirable for the oxidative desulphurization of residual oil using hydrogen peroxide.

Validation experiments were carried out at the levels of the process variables predicted in solutions 1 and 2, and the resulting desulphurization yields were 63.29 ± 0.47% and 61.04 ± 0.13%, respectively. The empirical yields (Table 4) are much higher than the model predictions respectively. According to a one-sample t-test ($p < 0.05$), yet the two are only separated by less than 1% for each solution. This further supports the prediction power of the model derived from the response surface design.

Table 4. *Predicted Result of Optimization and Validation of the desulphurization.*

Solutions	Temperature (°C)	Oxidant conc. % (w/w)	Cat. mix. conc. % (w/w)	Predicted yield (%)	Validated yield (%)
1	50.30	25.0	22.0	62.82	63.29 ± 0.47
2	46.83	25.0	22.0	60.91	61.04 ± 0.13

The result of the GC-MS analysis of the untreated residual oil sample is projected in Table 5 shows the dominant sulphur compound is Diethyl[3-[n-octadecylmercapto]-p-n-butylanilinomethylene] malonate, followed by Nickel(II)bis(N,N-dihexyldithiocarbamate, and the least is

1,2-benzisothiazole,3-(hexahydro-1H-azepin-1-yl)-1,1 dioxide. The sulphur compounds account for about 11.8% of the total compounds in the sample based on relative peak area. Habib *et al.* [13], reported the presence of sulphurous acid, butylheptadecyl ester compounds in the residual oil.

Table 5. *Organic sulphur compounds found using GC-MS.*

Name of compounds	Molecular Formula	Percentage peak area (%) untreated	Percentage peak area (%) treated
1,2-benzisothiazole,3-(hexahydro-1H-azepin-1-yl)-,1,1-dioxide	$C_{13}H_{16}N_2O_2S$	1.95	ND
Nickel(II)bis(N,N-dihexyldithiocarbamate	$C_{26}H_{52}N_2NiS_4$	4.24	ND
Diethyl[3-[n-octadecylmercapto]-p-n-butylanilinomethylene] malonate	$C_{36}H_{61}NO_4S$	5.64	ND

Key: ND- Not detected

3.4. Physicochemical Properties

The results of the physicochemical analyses carried out on residual oils before and after desulphurization are presented in Table 6 alongside the ASTM standard limits for residual oil.

Table 6. *The physicochemical Properties of untreated and desulphurized residual oils.*

Parameter	Test method	ASTM limit	Untreated	Treated
Sulphur content (wt.%)	ASTM D1552	<0.50	0.67	0.26
Specific gravity	ASTM D6751	0.90-0.99	0.93	0.94
Flash point (°C)	ASTM D93	100-150	130	110
Pour point (°C)	ASTM D97	< 30	14	11
Kinematic Viscosity @ 82.2°C (cst)	ASTM D445	< 50.0	35.9	31.0

The untreated residual oil 0.67%wt sulphur content which did not comply with the sulphur emission standard. The combustion of such kinds of fuels results in the production of SOx pollutants, which has a detrimental impact on both the environment and human health. In the atmosphere, these SOx can combine with water to form acid rain. Furthermore, the sulphur compounds can also cause corrosion issues in pipelines, pumping equipment, and refining equipment, as

well as the deactivation of catalysts during refining procedures [14]. After the desulphurization, the sulphur content reduced to 0.26%wt which was below the standard limit.

Desulphurization of crude oil at 60°C using $KMnO_4+H_2O$ and a formic acid oxidant/catalyst system resulted in 73.00% desulphurization yield [7, 8], which was higher than the reduction achieved in this work. Another study on oxidative

desulphurization found that using ozonized air reduced sulphur in residual oil to 0.40%wt (86.01%) from 2.86%wt [15]. The result is also higher than the reduction achieved in the current work. The best desulphurization result was 90.70%, which was achieved after 4 recursive extractions using ethanol as the solvent [9]. Despite the fact that, the effectiveness of the current work is it achieved lower sulphur content of 0.26%wt compared to the 0.32%wt and 0.40%wt obtained by Haruna *et al.,* [7] and Kazakov *et al.,* [15], respectively.

The use of two catalyst systems, i.e., acetic/formic acids had significantly improved the oxidative desulphurization reaction at a lower temperature of 50°C compared to 80°C used by Haruna *et al.* [8] and Kazakov *et al.* [15] at 150°C. The result from the current work is significant in that it achieved an acceptable sulphur limit of less than 0.50%wt as prescribed by the International Maritime Organization [3]. Hence, it has improved the fuel quality, such fuel can be used on boards and in auxiliary engines and boilers [3].

The desulphurization yield at the optimal conditions identified was characterized using ASTM standard methods. Table 6 contains the properties of the untreated and treated residual oil in comparison with ASTM standard. The desulphurization technique employed has generally lower all the parameters except in specific gravity with a slightly increase from 0.93 to 0.94 which is less significant. The decrease in the parameters may be due to breaking of higher molecular weight organic compounds in the desulphurization process. Except in sulphur content, both the treated and the untreated residual oil parameters are however in agreement within the ASTM standard specifications.

4. Conclusion

Finally, the oxidative desulphurization of residual oil at a reaction temperature of 50°C was significantly optimized using an oxidant concentration of 18.75% (w/w) and a catalyst mixture of 17.25% (w/w). In the presence of H_2O_2 oxidant, a $CH_3COOH/HCOOH$ mixture was found to be a better catalyst for organic sulphur removal. The treated residual oil sulphur content was reduced from 0.67 to 0.26%wt and found to be as low as the stringent environmental conditions of less than 0.50%wt. The physicochemical properties analyzed for the untreated and treated samples are within the ASTM standard with the exception of the sulphur content of the untreated; the treated samples show remarkable improvements on the physicochemical parameters. As a result, desulphurized residual oil could be used in applications such as boilers, automobiles, and industries such as cement kiln processes that would emit very little sulphur.

Acknowledgements

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