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Mathematical Modelling and Optimization of Alkyl-Phenol Based Additive – Aki-56 for Motor Oils: a Full Factorial Design Approach

Abstract

Motor oil performance enhancement is excessively crucial, as the industrial demand and the need for electrical vehicles evolve. In this context, the development and optimization of multi-functional alkyl-phenol based additive – AKI-56 (as detergent and dispersant) as part of the lubricant performance packages can potentially serve for the mentioned objective, as has been studied in this chemical engineering analysis. The study covered the Full Factorial Design methodology where the impact of the mass of formaldehyde (CH_2O), amino acid (glycine – NH_2CH_2COOH) and $Ca(OH)_2$ on the total base number of final product after the one-stage condensation and neutralization reactions was mathematically analysed. The harmony of chemical, mathematical and engineering analysis has indicated the critical ranges for reagent proportions, achieving a total base number of 105.1 mgKOH/g while minimizing the acceptable levels of corrosion. The research findings can be utilized as a foundation for further advancements in dispersant-detergent based additive performance optimization and therefore, longevity of the modern engines.

Keywords: *FFD, modelling, TBN, motor oil additives, detergents, dispersants*

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Introduction

17.1 Introduction to Tribology and Modern Lubricant Performance Packages

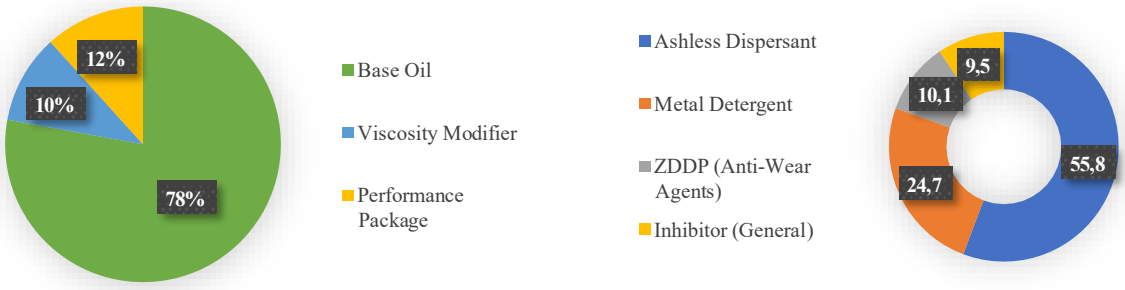
Moving further to the Industrial era 4.0, with the considerable forecasted rise in electrical vehicles, the perspective of lubricant and its performance improvement has become vital. The specific science called "tribology" provides essential insights on this perspective of optimizing the engine performance by studying the friction, wear and lubrication (Tribology – Lubricants and Lubrication, 2011).

ABBREVIATIONS & DEFINITIONS

FFD	Full Factorial Design
TBN	Total Base Number
PPD	Pour Point Depressant
AKI-56	Name of the product
MATLAB	MATLAB is simulation software employed to solve the mathematical equations with more than 3 unknowns.
ASTM	American Society for Testing and Materials
ANOVA	Analysis of Variance

The particular demands of various machinery, such as automotive engines, industrial equipment, even wind turbines or food-processing machinery form the design specifications of modern lubricants that are indeed the sophisticated blends of base oils and additives. These additives are critical in ensuring that the lubricant can perform multiple roles, including minimizing wear, controlling temperature through efficient heat transfer, preventing corrosion, and maintaining cleanliness by controlling soot, sludge, and deposit formation (D'Amico, Rinaldi, 2023; Effect of Additives on Lubrication, 2014). These sophisticated blends are inevitable components of lubricants called "performance package". The development of a performance package is not straightforward, it instead is a complex process which demands vigorous expertise and robust performance testing (Rudnick, 2017). To provide vivid imagination on the importance of performance package in lubricants, the following figure can be worked out. The figure illustrates that the finished engine oil includes the addition of two essential additive categories – performance package (~ 12.0%) and viscosity modifier (~ 10.0%) in addition to its base oil (~ 78.0%) (D'Amico, Rinaldi, 2023; Handbook of Industrial Catalysis, 2011).

Figure 1. Lubricant and Performance Package Compositions (Average for Motor and Heavy Duty Diesel Oil) [2]



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1.0 Literature Review

2.1 Detergent and Dispersant-based Additives for Lubricants

The performance package as part of finished engine oil can compose of several additives serving for the various specific functions contributing to the overall effectiveness of the lubricant. Key additives include: detergents, dispersants, pour point depressants (PPDs), foam depressants, anti-wear additives, friction modifiers, oxidation and rust & corrosion inhibitors, extreme pressure additives, etc. (Vasudevan, Rao, 2013).

As can be seen from figure 1, the majority of additives in performance package for lubricants consists of combination of detergents (~ 56.0%) and dispersants (~ 25.0%) which play a crucial role in maintaining the performance and longevity of motor oils, particularly in the demanding environments of modern engines. These additives are designed to neutralize acidic by-products formed during combustion with the following primary functions (D'Amico, Rinaldi, 2023):

- **Neutralizing Acidic Combustion By-Products**
- **Neutralizing Oxidation Products**
- **Cleaning High-Temperature Surfaces**

The effectiveness of these additives is strongly interconnected to maintaining a high total base number which primarily refers to the oil quality being a measure of oil's acid neutralization capacity (Lubricant Science and Technology, 2010; Naghiyeva, 2022).

The historical background behind the optimized detergents is comprehensive and includes various modification phases. Referring to the patent developed by the Institute which has a dedicated structure of laboratory to develop multifunctional alkyl-phenol based additives that can be used as part of performance package for lubricants, the additives formed after the one-staged condensation perform essentially well in modifying the motor oil properties (Patel, 2014).

2.2 Optimization of Multifunctional Alkyl-phenol Additives for Enhanced Oil Performance

The alkyl-phenol based additives do serve the multi-functional advantages where detergent and dispersant functions are more effective (Naghiyeva, 2022). The Institute's dedication in the field of optimized lubricants for motors has resulted in various products formulated over the years. This chemical and engineering research paper has the clear objective of optimizing the already formed additives where it takes the condensation stages as the reference and employing the full factorial design (FFD) – statistical evaluation technique. It is necessary to note that FFD is only the first step for optimization studies and the findings from this mathematical modelling will form a basis for further chemical and simulation-based engineering analysis (Kazimzadeh et.al., 2006).

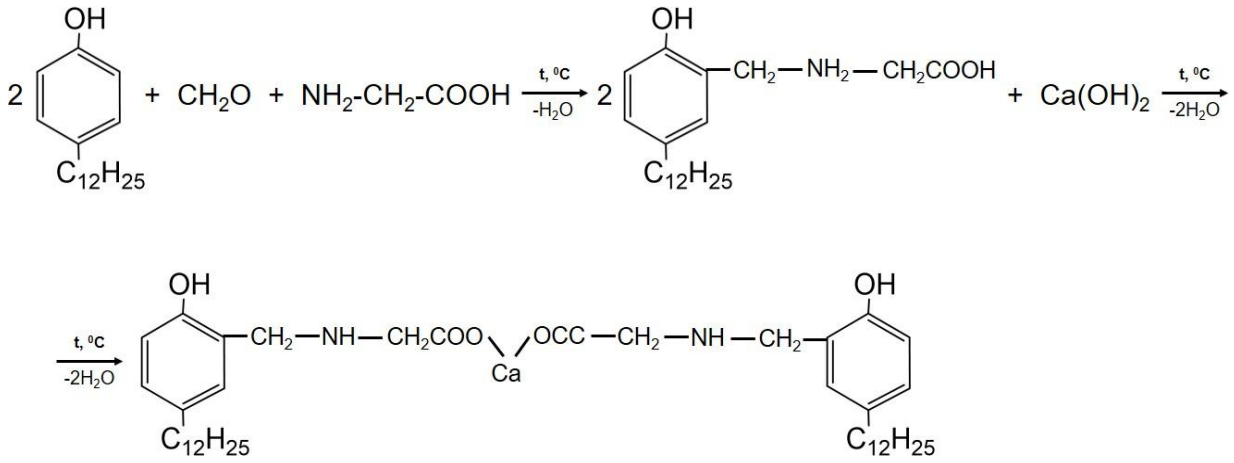
FFD model has referenced the one-stage condensation and neutralization reaction experimental values on AKI-56. AKI-56 is synthesized with the base reaction feeds of dodecyl phenol, formaldehyde and glycine (amino acid). The first stage is called the condensation process where the intermediate product is formed from three compounds. The second stage of the reaction is neutralization where the intermediate is treated with proper portion of $Ca(OH)_2$ to produce the calcium salt of condensation product.

Research

The statistical approach was dedicated to the optimization trials on the reactions described below where the total base number – TBN of product (additive) was the primary output of the mathematical model (Naghiyeva, n.d.).

Following the analysis of the experimental values of TBN resulted from the various proportions of the major reagents – CH_2O and NH_2CH_2COOH, the optimization trials were carried out on the neutralization stage of intermediate with $Ca(OH)_2$ (Naghiyeva, n.d.).

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3.0 Method Statement

MATLAB two-level full factorial design together with DataTab software was employed to analyze experimental values results from above reaction. As mentioned above, the total base number of the product formed after one-stage condensation and neutralization was modelled referring to the experimental data.

The purpose of optimizing / modelling the TBN was to comprehend the impact of reagent proportions. In addition to this objective, the study focused on the provision of the most affecting one and the best proportion of reagents leading to the minimum level of corrosion.

FFD as a statistical model can be employed in various experiments to express the simultaneous impact of multiple factors – independent variables on the final dependent variable (AKI-56 TBN). The model involves utilization of every plausible combination of the factors together with their levels. The levels in the context refer to the various trials on the factors (Naghiyeva, n.d.). For instance, mass of formaldehyde is one of the factors, the different mass combinations (13 and 14 gram) employed in this study is called level.

The factors and their levels chosen for this study are as follows:

Table 1. The factors and their levels used in experimental setup

	TBN Optimization	
Factors and Levels	Formaldehyde mass, gram	13.0
		14.0
	NH_2CH_2COOH mass, gram	7.4
		8.0
	$Ca(OH)_2$ mass, gram	14.0
		15.0

This setup resulted in eight experimental runs, each corresponding to a unique combination of the factor levels which was resulted from $N = 2^k = 2^3 = 8$ where (Tribology – Lubricants and Lubrication, 2011):

- N – number of experimental runs;
- k – number of factors.

ISSN: 2707-1146
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TBN (referring to ASTM D2896) of the resulting mixture was measured for each run. Developing the possible combinations of each factor and level below table was formed before the analysis:

Table 2. Design of Experiment on the combination of factors – TBN *Data taken from [9]*

Run Order	Formaldehyde mass, gram	NH_2CH_2COOH mass, gram	$Ca(OH)_2$ mass, gram	The Total Base Number (mg KOH/g)
1	14.0	7.4	15.0	84.5
2	14.0	7.4	14.0	72.0
3	14.0	7.0	15.0	77.6
4	14.0	7.0	14.0	81.2
5	13.0	7.4	15.0	73.2
6	13.0	7.4	14.0	70.0
7	13.0	7.0	15.0	101.5 (non-effective result due to corrosion effect of product)
8	13.0	7.0	14.0	72.8

The response variable (the refractive index and TBN) was taken as the major output from a multiple linear regression model which incorporated the main effects of each factor as well as the combined influence of factors on the dependent variable.

The analysis involved fitting a multiple linear regression model to the data, with the refractive index as the response variable. The model incorporated the main effects of each factor as well as interaction terms to capture the combined influence of factors on the response. The model was expressed as:

$$TBN = \beta_0 + \beta_1(m_1) + \beta_2(m_2) + \beta_3(m_3) + \beta_{12}(m_1 \text{ x } m_2) + \beta_{13}(m_1 \text{ x } m_3) + \beta_{23}(m_2 \text{ x } m_3)$$

Where:

- m_1, m_2, m_3 – CH_2O, NH_2CH_2COOH & $Ca(OH)_2$ mass;
- β_0 – intercept;
- $\beta_1, \beta_2, \beta_3$ – coefficients of main effects; $\beta_{12}, \beta_{13}, \beta_{23}$ – coefficients of interactions.

The impact factor of each variable and the potential effect of their interaction has been analyzed using ANOVA (Analysis of Variance) and the standardized effects were simulated via Pareto chart to visually represent the influence of each factor on the major dependent variables – the refractive index and TBN. In addition to the analysis carried out, the main and interaction plots were generated to form a detailed perspective image which can be further implemented in upcoming chemical process interpretation and analysis. The following section of the report clearly outlines the primary outcomes of the FFD study on the mathematical modelling development and optimization of the refractive index in first and TBN in second reactions.

4.0 Results & Discussion

Using the input data containing the two-levels of every factor with the experimental TBN results, the FFD model was driven using Analysis of Variance and Pareto standardized effects for clearly demonstrating the influence of each factor on total base number of AKI-56. The analysis has shown that the optimal mass range for glycine (NH_2CH_2COOH) analysis should be between 7.0 and 8.0 grams. Within this range, there is a specific optimal mass value that has the most significant impact on TBN value. Experimental results indicate that this value is 7.4 grams. However, mathematical analyses suggest that repeating the experiments with 7.6 and 7.8 grams of glycine may further optimize the results.

Additionally, it appears that an excessive amount of $Ca(OH)_2$ does not necessarily increase the total base number of the additive. Therefore, the optimal range for $Ca(OH)_2$ is between 14 and 15 grams. Although the 7th experiment achieved a TBN of 105.1 mgKOH/g, the corrosion rate was high. This phenomenon can be explained by the lower amount of $Ca(OH)_2$ acting as a neutralizing agent in the

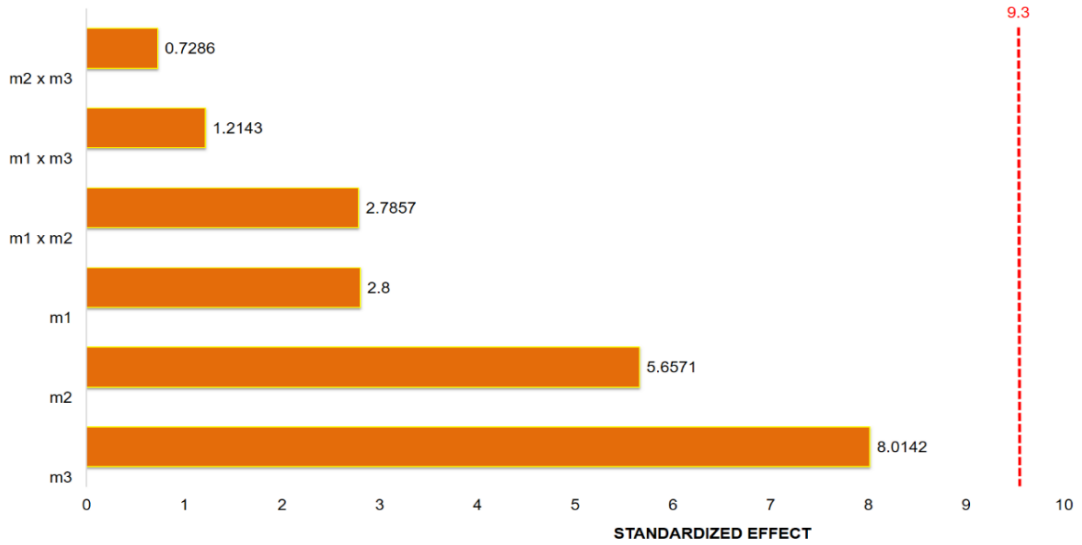
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reaction. The results also indicate that the CH_2O-$Ca(OH)_2$ combination has a synergistic effect on the TBN value. To optimize this mechanism, the following conditions should be applied:

- **Optimal range for CH_2O:** 12–14 grams
- **Optimal range for $Ca(OH)_2$:** 14–15 grams

The Pareto chart of standardized effects have been developed to express the above-mentioned effects.

Figure 2. Pareto Chart of Standardized Effects for Impact Analysis (TBN).



The figure above known as a Pareto diagram, is used as a mathematical tool for optimizing reactions or effects. The x-axis represents a standardization effect within the range of 0–10, where a higher value indicates a stronger impact. For instance, according to our analysis, the mass of m_3 (i.e., $Ca(OH)_2$) is the most critical parameter for this reaction. Following this, the mass of glycine and CH_2O also significantly influence the TBN. Based on mathematical modeling, the amount of $Ca(OH)_2$ is the most important factor in optimizing the base number. Selecting its optimal quantity will directly contribute to the overall optimization of the reaction.

The results received from FFD analysis was used as a basis to develop a mathematical regression model for optimized TBN of the final product. The factors which excessively influence the magnitude of this significant additive property as represented in figure 1 are mathematically combined in below regression model. This model can be further employed for promoting the higher TBN for the final product by manipulating the factors determined via the carbonization stage of AKI-56:

$$\text{TBN} = \frac{[10{,}1234 + 0{,}5678(m_1) + 1{,}2345(m_2) + 0{,}6789(m_3) + 0.1234(m_1 x\, m_2) + 0.2345(m_1 x\, m_3) + 0.3456(m_2\, x\, m_3)]}{1.63056}$$

Conclusions

This study explored the key factors influencing the Total Base Number (TBN) of AKI-56 using a Fractional Factorial Design (FFD) approach, supported by variance analysis and Pareto effect evaluation. The results indicate that glycine (NH_2CH_2COOH) within 7.0–8.0 grams plays a crucial role in optimizing TBN, with 7.4 grams emerging as the most effective amount. However, additional trials at 7.6 and 7.8 grams may offer further refinements. Similarly, while $Ca(OH)_2$ is essential in neutralization, excessive amounts do not proportionally increase TBN. The optimal range for $Ca(OH)_2$

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is 14–15 grams, balancing efficiency and minimizing corrosion risks. Additionally, the interaction between CH_2O and $Ca(OH)_2$ has a noticeable synergistic effect, reinforcing the importance of keeping CH_2O between 12 and 14 grams for optimal performance.

The Pareto analysis confirmed that $Ca(OH)_2$ has the most significant influence on TBN, followed by glycine and CH_2O. The mathematical regression model developed in this study provides a structured approach to fine-tuning these factors for maximum effectiveness. By leveraging this model, the TBN of AKI-56 can be further optimized, improving overall additive performance while maintaining process stability. Future research could explore additional variables or advanced modeling techniques to enhance the predictive accuracy and adaptability of the formulation process.

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