BE-P32: FABRICATION OF NAHAR SEED OIL FOR BIOLUBRICANT PRODUCTION

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Abstract

In this study, a laboratory scale for extraction and analysis of Nahar (*Mesua ferrea L.*) seed oil (NSO) for biolubricant production was conducted. The oil was extracted then analyzed the chemical and physical properties and studied its current and potentially future use in lubricant applications, as both base oil and additives. The analysis includes moisture content, free fatty acids (FFA%), saponification value (SV), iodine value (IV), unsapoifiable matters and phosphorus content. After that the NSO was undergo an esterification process and two-step transesterification processes to increase its viscosity for production of biolubricant. The reaction temperature, the reaction time, and the catalyst dosage (sodium methoxide) were the chosen parameters in the optimization processes of the Nahar seed oil (NSO) biolubricant production. From the result obtained, the maximum viscosity of NSO biolubricant was achieved when the temperature was 150^{o}C, 80 min in reaction time and 0.8% catalyst dosage.

Key word: *Biolubricant, Esterification, Nahar (Mesua ferrea), Nahar seed oil (NSO), Transesterification.*

INTRODUCTION

Nahar (*Mesua ferrea L.*) is from the Clusiaceae family. Nahar is one of India's highly regarded and sacred trees. The Nahar tree is also called as *Mesua ferrea*, Ceylon ironwood, Indian rose chestnut, Cobra's saffron, Penaga Lilin or Nahar. It is also found in Nepal, Sri Lanka, Thailand, Vietnam, Myanmar (Burma) and Cambodia.

Oil from the seeds of Nahar are popularly used in the topical treatment of various skin problems and also commonly used in Buddhist temples. The fresh blossoms of Nahar are said to aid digestion and cough while dried flowers helped in relieving bleeding hemorrhoids, while the root is an antidote for snake poison. In such assured applications, firm situation on various environmental themes, such as biodegradability, occupational health safety, and emissions, have become obligatory. This has encouraged the search for environmentally friendly lubricants.

Nahar Seed Oil (NSO)

Nahar seed oil (NSO) can be used in industrial application such as biodiesel and biolubricant, used in medical treatment and other uses. NSO has antibacterial, antifungal and anthelmintic properties and shows excellent anti-inflammatory and styptic activity (Adewale *et al*., 2011). In Malaysia, Nahar tree commonly called as Penaga Lilin. This tree can be seen popularly grown as avenue trees, not yet in plantation form.

The kernels contain about 70% oil, constituted by the glycerides of common fatty acids such as linoleic, oleic, stearic, and arachidic acids. A few reports on the utilization of NSO in the field of polymer (Dutta *et al*., 2004; Mahapatra and Karak, 2004; Dutta and Karak, 2005, 2006) along with some other fields such as biodiesel (Konwer *et al*., 1989) and medicine (Baruah and Sarma, 1984) have already been published.

Dutta *et al*. (2004) claimed that Nahar (*Mesua ferrea*) is such a plant that produces high oil content seeds. In India, it is available in Assam, Uttar Pradesh and Western ghats. Nahar seeds contain a large amount of oil (75%), which is non-drying, comprising oleic acid (52.3%) and linoleic acid (22.3%) as unsaturated fatty acids and stearic acid (9.5%) and palmitic acid (15.9%) as saturated fatty acids and hence it can be utilized for the synthesis of different types of resins. The authors reported the utilization of NSO as raw material for coating applications.

The NSO has already been used in many research areas. For example, Das & Karak, (2009) have made research on the NSO based epoxy resin. Due to the exhaustion of fossil fuels, tremendous increase of materials demand, and unpredictable prices of petroleum based products urge upon the sustainable development of synthesized resins as coating materials. Bora & Nath (2006) reported on the use of NSO as a potential source of biodiesel.

Nahar Seed Oil (NSO) as Biolubricant

To meet up the increasing demand for vegetable oils, improvements are being made with conventional crops as well as with selected plant species that have the ability to produce unique, desirable fats and oils (Lin, 2009). The depletion of world oil pool, rising price of crude oil and increased environmental concerns are pressurizing the scientists for the use of renewable natural resources in different fields of applications as they are eco-friendly and cost effective materials. In this regard, vegetable oils have a number of excellent properties, which could be utilized in production for variable polymeric materials such as alkyd, epoxy, polyesteramide, polyurethane, etc. in addition to many applications in other fields (Dutta & Karak, 2005). Vegetable oils are feedstock for the oleochemical industry to produce a wide variety of chemical materials which are used in many applications, including lubricants, either as additives or for the production of synthetic materials such as ester base fluids (Crawford *et al*., 2010). This study will focus on the production of biobased lubricant from Malaysian NSO.

MATERIALS AND METHODS

Seed oil Extraction

There is a variety of manufacturing methods of manufacture associated with the large range of oil source. Many methods can be used for the seed oil extraction such as the mechanical pressing, solvent extraction method, prepress followed by solvent extraction and supercritical fluid extraction (SFE) methods.

Soxhlet extraction was used for the extraction of the oil and the solvent used was n-hexane to extract oil from Nahar seed kernels (NSK). Solvent extraction has various steps which include raw material preparation such as cleaning, cracking and dehulling and size reduction (grinding). In addition, the NSK was pre-dried to avoid the presence of water in the extracted products (Houghton & Raman, 1998).

Chemical Properties of Oil

1. Iodine Value

The iodine value is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. One application of the iodine number is the determination of saturation of fatty acids as double bonds in fatty acids that react with iodine compounds. It shows that the higher the iodine number, the more unsaturated fatty acid bonds are present in a fats.

2. Saponification Value (SV)

Saponification value (SV) or saponification number represents the number of milligrams of potassium hydroxide (KOH) required to saponify 1 g of fat under the conditions specified. If there are more moles of KOH used for 1g of fat, then there are more moles in fat. Therefore, the chain lengths are smaller, due to the equation:

$$\boxed{\text{Number of moles} = \text{mass of oil} / \text{relative atomic mass}}$$

The relative atomic mass would be smaller with smaller fatty acid chains, meaning more moles. The higher the SV the smaller the chain lengths of fatty acids. Low SV showed that the oil is good edible oil (Ajiwe *et al*., 2006).

3. Unsaponifiable Matter

This refer to the whole quantity of substances present in the oil or fat which after saponification by KOH and extraction by a specific solvent, there are not soluble in aqueous alkali and non-volatile under the condition test. The amount of unsaponifiable matter in oil is important in characterizing such products as it indicates the level of non-acidic material, free and combined, present in test material. The unsaponifiable is primarily composed if higher molecular weight alcohols, sterols, and hydrocarbon.

Free fatty acids (FFA), Moisture and phosphorus content and other parameters were measured following the American oil chemists' society official methods (AOCS, 1997) and PORIM test methods (1995).

Design of Experiment on the Biolubricant Production of NSO

In this research, Design Expert program is chosen to optimize the process conditions. Design Expert consists of factorial, crossed, mixture and response surface methodology (RSM) consists of an empirical modelization technique devoted to the evaluation of relation existing between a group of controlled experimental factors and the observed results of one or more selected criteria. RSM allows prediction of the best performance conditions with minimum number of experiments in esterification and transestrification of NSO. It also helps in quantifying the relationships between one or more measured responses and the vital input factors. The statistical software package Design-Expert 6.0.8 (Stat Ease Inc., Minneapolis, USA) was used to identify the experimental design as well as to generate a regression model to predict the optimum combinations considering the effects of linear, quadratic and interaction on viscosity of the oil. This could be a maximum, a minimum or an area where the response (viscosity) is stable over a range of the factors, which were Temperature, time and catalyst dosage (sodium methoxide).

Central Composite Design (CCD)

CCD is one of the designs available in RSM. It is the most popular and easier design to use. CCD has three groups of design points which are two level factorial or factional factorial design points, axial points and center points.

Statistical Analysis

Analysis of results will be done statistically with the aid of Design Expert Software. In this project, analyzed was done using analysis of variance (ANOVA). ANOVA is similar to regression. It used to investigate and model the relationship between a response variable and one or more independent variables. Nevertheless, ANOVA differs from regression method because the independent variables are qualitative and no assumption is made about the nature of the relationship. In effect, ANOVA extend the two sample T-tests for testing the quality of two populations means to a more than two means, versus them not all being equal. ANOVA, p-test and t-test was done in order to get the optimum equation for the transesterification of NSO.

RESULTS AND DISCUSSION

Oil Percentage

In the determination of the Nahar seed oil (NSO) percentage, the oil percentage was determined by measuring the oil collected after evaporating the solvent. The result of three replicates is shown in Table 1.

Table 1: Oil Percentage

Sample	1	2	3	Average $\pm$ *SD*
% Nahar seed oil	68.10	66.17	65.25	66.51 $\pm$ 1.19

Therefore, from the result, it can be said that the percentage of NSO is very high which more than 66% of the seeds' kernel.

Characterization of NSO

The characteristics and specifications of feedstock are very important during the initial research and production stage (Canakci and Gerpen, 2001). In addition, study of characteristics of the material can estimate the right way of selection of process, subsequently decreasing the cost of process and increasing the selectivity of desired products. Hence, Table 2 illustrates the specifications of NSO that were used in this study. The table 2 also shows range of NSO specification in other studies. It was found that the characteristics of Nahar seed oil used in this study are within the ranges of other feedstocks in low grade consequently it conceder as non-edible oil.

Table 2: Specification range for low grade oils with high FFA

Parameters	Malaysian NSO	Low grade oils with high FFA (specifications range)
Free fatty acid, FFA (%)	7.26	(5-45) [a]
Peroxide value (ml mol/kg)	16.4	(1.36-21.81) [a]
Moisture content (%)	1.31	<2 [a]
Iodine value, IV	77.3	40.2-55.9 [a]
Saponification value (mg KOH/g)	101.55	(173.82-197.86) [a]
Impurities (%)	-	(0.004-8.1) [c]
Phosphorus (ppm)	33.5	(10-55) [c]

[a] (Dutta, *et al*., 2004; Dutta & Karak, 2005) ; [c] (Lin, 2009).

From Table 2, it can be seen that the FFA content of NSO used in this study was 7.26% which would not be suitable for biolubricant production by two stages transesterification process. As the study by Canakci and Van Gerpen (2001) indicated that transesterification reaction will not occur if the FFA content in the vegetable oil is more than 3%. Ramadhas *et al*. (2005) recommended <2% level of FFA for transesterification reaction using homogeneous base catalyst. Therefore, the limit of FFA was set to maximum of 2% for all esterification experiments. Average molecular weight was calculated based on saponification value, and it was 539.74 g/mole. The value of average molecular weight was used in calculation of molar ratio.

Thus, an acidic catalyst presence in the pretreatment step by esterification reaction was conducted to convert the FFA to FAME followed by two stage transesterification reaction offer an effective and efficient method to convert NSO to biolubricant.

Fatty acid compositions of NSO are very important to identify the carbon chains and its properties. The literature showed that the highest fraction of fatty acids were palmitic acid, oleic acid, palmitoelic, linoeic acid and stearic acid (Canakci and Van Gerpen, 2001).

Analysis of the Results Using Design Expert

A total of 17 runs were executed according to the CCD. These runs covered all the extreme cases of the parameter values. By using Design Expert software, the results were analyzed statistically to evaluate the data obtained and to determine the optimum condition of the process. RSM was used in order to analyze the result obtained from the optimization of the process condition and to study the effect of the reaction temperature, reaction time and catalyst dosage on the viscosity of NSO biolubricant. Table 3 showed the result obtained from the optimization processes during the production of NSO biolubricant.

It was found that within the given range, the highest viscosity response was achieved in run 3 with 150^oC in reaction temperature, 80 minutes of reaction time and 0.8% catalyst dosage. The maximum viscosity of NSO biolubricant obtained by the above optimized variables was 0.1722kg/m^3.s.

Regression Analysis

The final equation developed (in term of actual factors) was presented as in the following equation:

$$\text{Viscosity (Y)} = 1.09494 - 4.93975E - 003*A - 0.012857*B - 0.92211*C + 0.51268*C^2 + 1.03438E - 004*A*B \quad (1)$$

Where: A = Reaction temperature; B = Reaction time; C = Catalyst dosage

The model represents a relationship between the dependent variables which was the viscosity (Y) of the NSO biolubricant, Y with the independent variables, namely the reaction temperature, the reaction time and the catalyst dosage denoted by A, B and C respectively. This model was also used in order to determine the optimum values of the three variables A, B and C based on the highest predicted viscosity of biolubricant.

The developed regression model was evaluated by analyzing the values of regression coefficients, analysis of variance (ANOVA) and F-values. The quality of fit of the polynomial model equation was expressed by the coefficient of determination (R^2). The results that obtained from the optimization process were further analyzed by using the standard analysis of variance (ANOVA) in Table 3.

It showed that the model F-value of 15.18 implies that the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise.Values of "Prob > F" less than 0.0500 indicated that the model terms are significant. In this case A, B, C, C^2, AB are significant model terms. The lack of fit 4.3385 was not significant, showed that the model was fitted.

The correlation between the experimental and predicted values is better when the value of R^2 is closer to 1. In this experiment, the value R^2 was 0.8732, for the viscosity of the NSO biolubricant produced. These values indicate a high degree of correlation between the experimental and the predicted values. The relationship of both the actual and predicted values can be seen in Figure 1.

Table 3: Results of Analysis of Variance (ANOVA)

Source	Sum of Squares	DF	Mean Square	F Value	Prob > F	
Model	0.01383	5	0.00277	15.1811	0.0001	Significant
A	0.00642	1	0.00642	35.2166	< 0.0001	
B	0.00139	1	0.00139	7.6426	0.0184	
C	0.00085	1	0.00085	4.68109	0.0534	
C2	0.00173	1	0.00173	9.50466	0.0104	
AB	0.00274	1	0.00274	15.0339	0.0026	
Residual	00.002	11	0.00018			
Lack of Fit	0.00157	5	0.00031	4.33856	0.0512	Not significant
Pure Error	0.00043	6	7.2E-05			
Cor Total	0.01583	16				

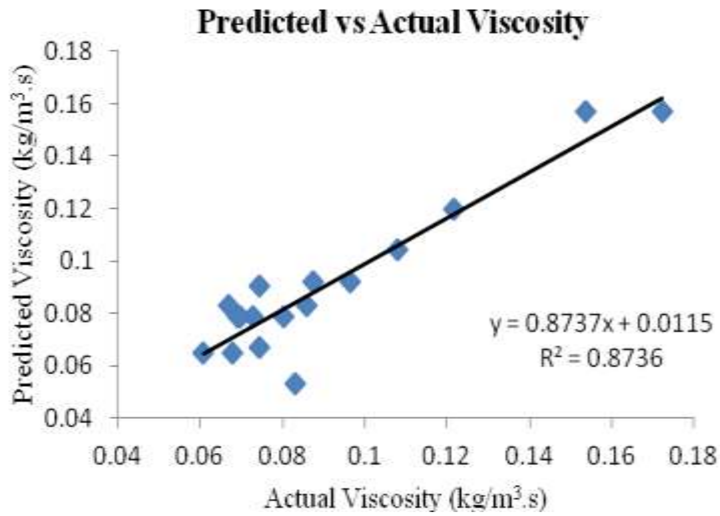

Figure 1: The graph shows the interpretation of the predicted value and the actual value

Table 4, proved that the model demonstrates a good determintaion coefficient (R^2) which was 87.35% explaining that 87.35 of the variables (the reaction temperature, the reaction time and the catalyst dosage) validated in the model to ensure a satisafactory adjustment of the quadratic model to the experimental data. This implies that the sample variation of 87.35% for the NSO biolubricant viscosity was attributed to the independent variables. It was observed that the variable that was highly significant was the temperature. Furthermore, the linear effect of time (B) was significant at the level of $p < 0.01$ and the catalyst dosage was at the level of $p < 0.05$. While the square term of the catalyst dosage and the interactive term of temperature and time (AB) were significant at the level of $p< 0.01$. The temperature and time played a significant role in the higher production of NSO biolubricant.

According to the Table 4, the adjusted of R^2 also gives high value which was 81.59% which was more suited for comparing model with different numbers of independent variable. Meanwhile, the predicted sum of squares (PRESS), which was a measure on how particular model fits each point in the design, was 0.0042. Adequate precision measure signal to noise ratio; a ratio greater than 4 was desirable. An adequate precision of 12.93 for Nahar biolubricant viscosity indicate an adequate signal. The predicted R-Squared of 0.7359 is in reasonable agreement with the adjusted R-Squared of 0.8159.

Table 4: Regression Analysis

Parameter	**value**
Std. Dev.	00.0135
Mean	0.09081
C.V.	14.8644
PRESS	0.00418
R-Squared	0.87343
Adj R-Squared	0.81589
Pred R-Squared	0.73585
Adeq Precision	012.931

Response surface plot is presented to study the interaction among the various factors used and to find out the optimum value of each factor for maximum production. The 3D response surface plot with the effects of the reaction temperature, the reaction time and the catalyst dosage are shown in the Figure 2 which was obtained from the Design Expert software.

The main target of response surface is to hunt efficiently for the optimum values of the variables such that the response is maximized (Tanyildizi et al., 2005). The maximum predicted value is identified by the surface confined in the smallest ellipse in the contour diagram. Elliptical contours are obtained when there is a perfect interaction between the independent variables (Muralidhar et al., 2001).

Figure 2 depicted the response surface by the model equation to estimate the viscosity of the NSO biolubricant production over the independent variables; temperature and time.

Based on the Table 4, the interaction between the temperature and time, AB is significant. But it does not contribute to the optimum value since the Figure 2 did not contained the maximum or minimum point (which is should be in parabola shape). From the figure, we can see that the viscosity of NSO biolubricant was increased with the increased in the temperature and time.

The main target of the response surface is to obtain the optimum values of the variables efficiently so that the response is maximized. The maximum predicted value is represented by the surface confined in the smallest ellipse in the contour diagram. A perfect interaction between the independent variables occurs when elliptical contours are obtained.

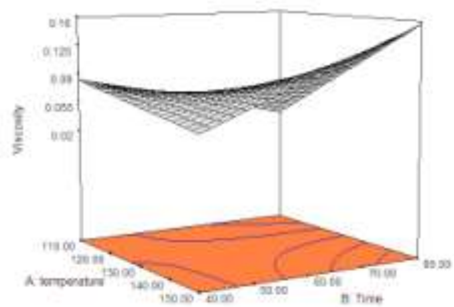

Figure 2: Response surface 3D surface plot showing the effect of Temperature and Time in the viscosity of the NSO biolubricant

CONCLUSION

The NSO obtained after the extraction processes was dark yellow. The characterization processed done in this project showed that the free fatty acid content of the NSO is high which about 7%, the IV is 77.3 mg Iodine/ g oil, the phosphorus value is 33.5 ppm and the SV is 101.5 mg KOH/ g oil. The average molecular weight of the NSO was determined from the SV of the oil which had give 539.74 g or approximately 540g. On the other hand, the experimental results of NSO biolubricant viscosity optimization to obtain the optimum condition to produce high viscosity indicated that the reaction temperature, the reaction time and the catalyst dosage were the main factors affecting the optimization processes. In addition, the data analysis using Design Expert software had shown a significant interaction between the NSO biolubricant viscosity, the temperature, the time and the catalyst dosage. The viscosity achieved was nearer to the benchmark value when the temperature was more than 150^{o}C, 80 minutes reaction time and about 0.8% of the catalyst dosage.

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