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Optimization of the operating parameters for the extractive synthesis of biolubricant from sesame seed oil via response surface methodology

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ABSTRACT

This study examined the optimization of the transesterification reaction of sesame methyl esters (SMEs) with trimethylolpropane (TMP) to synthesise sesame biolubricant (SBL). Response surface methodology (RSM) using central composite design (CCD) was employed for the experimental design. Effects of temperature, mole ratio and reaction time on the yield of SBL were evaluated. The predicted yield after process optimization was found to agree satisfactorily with the experimental value. The optimum conditions were obtained at temperature of 150 °C, mole ratio of 6:1 and time of 197.26 min for 80.02% biolubricant yield. Mole ratio and reaction time were found to be the most significant variables. SBL characteristics complied with ISO VG 22 standard and holds high potential as base stock for biolubricant formulation.

1. Introduction

Lubricants used globally are commonly made from petroleum, coals or natural gases [1,2]. Due to their high utilization, there is the need to search for alternative sources for producing lubricants [3]. As a result of the long-term pollution effects associated with mineral oil-based lubricants on the environment, there is need for cheap and renewable feedstock for the production of biodegradable lubricant.

There are many alternatives to petroleum based lubricant, such as synthetic or animal fat lubricants. However, lubricants derived from vegetable oil have received greater attention due to their favourable and acceptable physical properties. Among the advantages of biobased lubricants is its high lubricity as well as much lower coefficient of friction when compared to petrobased lubricants. Furthermore, biobased lubricants have high flash points, which makes them effective in high temperature environment to impede evaporation or dissipation [4–6].

They also have relatively stable viscosity indexes, so that they are useful over a large range of temperatures. In addition, biobased lubricants are generally derived from vegetable oils, and its processing involves clean and pollution free method as well as being renewable. Finally, the non-toxic and biodegradable nature of biobased lubricant ensures easy disposal to the environment, unlike petroleum based lubricant. These properties make biobased lubricants an attractive alternative to petroleum based lubricants [7].

Despite a number of useful properties of biobased lubricant, there are few draw backs associated with them, such as high composition of organic matters that causes easy oxidation of the lubricant. This rapid oxidation leads to frequent changing of the lubricant, there by modifying its properties adversely. Secondly, the initial cost per volume of a biobased lubricant is generally two or three times more than that of a petrobased lubricant. Thirdly, biobased lubricants can only be applied over a moderate range of temperatures as they have high pour points in cold and low thermal stability in heat. Finally, specialized crops (rather than food by products) are the raw materials for higher quality lubricants, thus diminishing sources that would otherwise be applied for food production [8,9].

In general, biolubricant is produced by transesterification reaction of fatty acid methyl esters (FAME) and polyhydric alcohol. Transesterification reaction may be carried out with an acid catalyst, a base catalyst or an enzyme. There has been a lot of work reported on the transesterification reaction of vegetable oil methyl esters with trimethylolpropane (TMP) as the polyol [10–12]. However, reported model compound studies in this area of research are very few.

In this study, we present a novel synthetic approach for transesterification reaction to produce a high yield of biolubricant. It is

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typically investigated by optimizing the following reaction variables: mole ratio, reaction temperature, and reaction time involved in the process. Both the effects of the variables and their reciprocal interactions have been evaluated using response surface methodology (RSM).

Response surface methodology is a collection of mathematical and statistical techniques used for the modelling and analysis of problems in which a response of interest is influenced by several variables. The objective is to optimize the response (output variable) which is influenced by several independent variables (input variables or factors) [13]. Different levels or values of the operating conditions comprise the factors in each experiment [14]. Some may be categorical (e.g., the supplier of raw material) and others may be quantitative (feed rates, temperatures, time, etc). In practice, categorical variables must be handled separately by comparing our best operating conditions with respect to the quantitative variables across different combinations of the categorical ones. The fundamental methods for quantitative variables involve fitting first-order (linear) or second-order (quadratic) functions of the predictors to one or more response variables, and then examining the characteristics of the fitted surface to decide what action is appropriate [14].

2. Materials and methods

2.1. Materials

Sesame samples were collected from Idah, Kogi State, Nigeria. Chaffs were separated from the oilseeds by winnowing. All the chemicals and reagents used for this work were of analytical grade.

2.2. Extraction of oil from sesame seed

Dried sesame seeds were crushed and tied in a white piece of cloth. This was later soaked in hexane in a tightly sealed bucket for 3 days before collecting the extract through filtration. The cloth containing the crushed sesame seeds was further rinsed with fresh hexane to extract more oil. Hexane contained in the extracted sesame oil was removed by distillation and the crude oil extracts was collected in a beaker [15].

2.3. Synthesis of sesame methyl ester

Sesame oil extracted from sesame seed was transesterified to form sesame methyl ester (SME). In this method, a mixture of 300 g of sesame oil, 100 g methanol and 1% wt/wt orthophosphoric acid catalyst was poured into continuously stirred reactor equipped with a water-cooled reflux condenser and heated up to 65 °C for 90 min. The mixture was dosed with 0.2 M of sodium trioxocarbonate IV, which on neutralizing the acid catalyst, stopped the reaction. The neutralized mixture was later transferred to a separating funnel and subsequently allowed to stand overnight to ensure complete separation of methyl esters and glycerol phases. Glycerol phase (bottom phase) was emptied into a clean container and then allowed to stand. The obtained sesame methyl esters were heated at 65 °C to remove methanol. Entrained catalyst in the SME was removed by successive rinses with hot and distilled water. Finally, water present in the SME was eliminated by oven-heating at 70 °C [15].

2.4. Synthesis of sesame biolubricant

This was as described by Surapoj et al. [16] with modifications. A batch transesterification at predetermined conditions: TMP:SME (3:1, 4:1, 5:1, 6:1 and 7:1), temperature (80, 100, 120, 140 and 160 °C) and time (1, 2, 3, 4 and 5 h) at 110 °C was carried out in a 50 mL three-necked round bottom flask equipped with a water-cooled reflux condenser, a thermometer, kipp's apparatus and a magnetic stirrer. The mixture contained in the flask was stirred at 1000 rpm, 110 °C for 15 min under CO_2 flow. 110 °C was maintained to evolve moisture from the TMP. A required amount of catalyst was then introduced in the reaction mixture, which was allowed to react for 5 h. At the end of the reaction, the product mixture was brought to room temperature and filtered to separate the solid catalyst from the liquid mixture (SBL). The filtered sesame bio-based stock was analysed using the gas chromatography (GC) to determine the product composition. Pour point, viscosities, flash point, total base number (TBN) and viscosity index were also determined by appropriate analysis [15].

2.5. Analysis of transesterification product

Identification of functional groups present in SBL was determined using Fourier Transform Infrared (FTIR) Resonance. Samples were collected after 1, 2, 3, 4 and 5 h and analysed for SME, monoester (ME), diesters (DE), triesters (TE) and TMP by gas chromatography. The yield of each product was determined from the GC chromatogram calibrated against the known samples according to the procedure described by Yunus et al. [17].

2.6. Lubricating characteristics

The following lubricating characteristics were determined based on the corresponding referred ASTM procedures: Pour Point [18]; Kinematics Viscosities [19]; Viscosity Index [20] and Flash Point [21].

2.7. Design of experiment

The Central Composite Design (CCD) was used to study the effects of the variables of the transesterification reaction and subsequently in the optimization of the process. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyse the interaction between the parameters. In order to describe the effects of temperature, time and mole ratio on the yield of biolubricant, batch experiments were conducted based on the CCD. The coded values of the process parameters were determined by the following equation:

$$x_i = \frac{X_i - X_0}{\Delta X} \tag{1}$$

where x_i – coded value of the ith variable, X_i – uncoded value of the ith test variable and X_o – uncoded value of the ith test variable at centre point. A second-order polynomial Eq. (2) was used to express the biolubricant yield (Y) as a function of the independent variables,

$$Y = b_0 + \sum_{i=1}^{k} b_i X_i + \sum_{i=1}^{k} b_{ij} X_i^2 + \sum_{i_1<j}^{k} \sum_{j}^{k} b_i X_i X_j + e \tag{2}$$

where Y is response factor (% yield), and i and j denote linear and quadratic coefficients, respectively; b_o is the intercept, b_i is the first order model coefficient, k is the number of factors, and e is a random number.

The factors levels of independent variables for SBL synthesis is given in Table 1. The regression analysis was performed to estimate the response function as a second order polynomial. A statistical software package, Design Expert 8.7.0.1 was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. Analysis of variance (ANOVA) was further carried out to determine the adequacy of the model. The

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