Effects of Extraction Process Parameters on the Quality Characteristics of *Parinari Polyandra B*. Seed Oil

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ABSTRACT: Extraction process parameters can influence the quality of oil obtained from seeds during extraction process. The effect of extraction process parameters on the quality of parinari seed oil, a potential renewable industrial raw material, is yet to be reported. This research was aimed at investigating the effects of some extraction process parameters on some quality characteristics of parinari oil (acid, iodine and saponification values). This work reports for the first time the effects of extraction process parameters on the properties of parinari seed oil. The parinari seeds were harvested and oil was obtained from the seeds by solvent extraction method based on the experimental design. The experimental design followed central composite design (CCD). Effects of extraction parameters on the quality characteristics were investigated. The study parameters were time (2-6 h), temperature (60-70 °C), solid- solvent ratio (0.03 - 0.08 g/cm³) and solvent types (n-hexane and petroleum ether). The responses were acid, saponification and iodine values. The results indicated that time and temperature significantly influenced the physicochemical properties of parinari oil. Response Surface Methodology (RSM) based analysis of variance indicated that the models obtained were all significant (p < 0.0001). The set of conditions for the optimal quality was obtained at temperature (60 °C), time (2 h), solid to solvent ratio (0.07 g/cm³) and n-hexane solvent with 89.7% desirability. The effects of the extraction process parameters on parinari oil quality were obtained. The information provided from this work will be useful for potential scaling up of the parinari oil extraction process.

KEYWORDS: Parinari seed oil, quality, acid value, iodine value, extraction, response surface methodology.

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I. INTRODUCTION

Vegetable oils are lipids that are extracted from plants seeds, fruits or seedlings (Zielinska et al., 2014). Solvent extraction is a commonly used separation method for obtaining industrial vegetable oil from oil-bearing plant parts (Islam et al., 2015). Extraction process parameters such as temperature, time and agitation are important parameters which have significant effects on the quality (Lee et al., 2013) and spoilage (Orji and Mbata, 2008) of seed oils. Hence, various researches have been tailored towards the determination of the effects of extraction parameters on the quality of various seed oil extracted (Tasan et al., 2011; Ikya et al., al, 2013; Myung-Hee et al., 2013; Samuagam et al., 2013; Lee et al., 2013). Several reports have shown that the quality of various oil were significantly affected by the extraction parameters, these include sunflower oil (Tasan et al., 2011), olive oil (Giovacchino et al., 1994), palm oil (Ngando-Ebongue et al., 2013), coconut oil (Sereviratne & Dissanayake, 2005), Jatropha oil (Akowuah et al., 2012) and ginseng seed oil (Myung-Hee et al., 2013). However, some workers have reported that the technique used for oil processing does not markedly alter the quality of argan oil. (Tariback et al., 2013).

Parinari polyandra Benth (or Maranthes polyandra) plant is found in West Africa, extending from Mali to Sudan (Keay, 1989). The plant is known as 'abo idofin' and 'gwanja kwosa' in Yoruba and Hausa languages in Nigeria (Abolaji *et al.*, 2007). The parinari fruits (Figure 1) contains a relatively oil – rich kernel which yields up to 64% oil (Afolabi *et al.*, 2014). Our earlier works indicated that parinari seed oil is a potential non-edible oil which can be utilized as a replacement for edible soya oil used in the production of alkyd polymer resin, a main raw material in the paints industries (Odetoye *et al.*, 2013; Odetoye *et al.*, 2014). Other earlier works on parinari oil include investigation of the effects of some extraction parameters on the oil yield (Afolabi *et al.*, 2015) and variation of parinari oil characteristics with season of harvest (Motojesi *et al.*,2011).

The quality of oil is of commercial interest and quality is indicated by the physico-chemical properties of oil which include acid, iodine, peroxide, hydroxyl and saponification values. The acid value is an important quality characteristic in the specification of fats and oils because acid value indicates the level of free fatty acid present in the oil (Liauw, 2008). A relatively lower acid value implies better storage and shell life of the oil. Acid value is regarded as the number of milligrams of potassium hydroxide necessary to neutralize the free acid in

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one gram of oil. Iodine value is a measure of the level of unsaturation of fats and oils, and is expressed in terms of the weight of iodine absorbed per weight of the sample. Iodine value is an indicator for double bonds in the fatty acid chain. Iodine value is also indicative of the long term stability properties of the oil, a factor to be considered in storage of oil. Iodine value is measured as the number of grams of iodine absorbed by 100 grams of oil sample (AOAC, 2006; Ikya *et al.*, 2013).

Higher iodine values are indicative of higher degree of unsaturation, which contributes to the functionality and reactivity of the oil (Murphy, 2012). The double bonds and the carboxylic ends provide sites for crucial industrial reactions in the development of building blocks for polymers as the reaction are carried out on the double bonds of the unsaturated glycerides. These reactions include autoxidation, dimerization, epoxy ring-opening and ozonolysis useful in the production of polymers, paints, inks, resins, coatings and other oil-based chemicals (Ogunniyi, 2006). However, lower iodine values are desirable in oils meant for food uses and biodiesel production.

There is a need to determine the effect of extraction conditions on the quality of the oil obtained from parinari seeds, to provide necessary information towards the establishment of parinari oil as a new industrial feedstock. Little work has been done on parinari oil, the variation in lipid composition of the seed oil with time of harvest had been reported (Motojesi *et al.*, 2011). In our earlier work (Afolabi *et al.*, 2014), the optimization of extraction process of parinari oil for optimal yield was reported. However, in this work, we report the effect of extraction parameters on the quality characteristics of oil obtained from parinari seed by solvent extraction.

II. MATERIALS AND METHODOLOGY

A. Sample Preparation

Ripe fruits of Parinari polyandra fruits as shown in Figure 1 were picked from trees at different locations in Ilorin, Kwara State, Nigeria in April, 2014 and identified at the herbarium of the Department of Biology, University of Ilorin, Nigeria. The fruits were manually broken into halves to release the whitish seed kernels containing the oil. The seeds were cleaned and air-dried at room temperature after which size reduction was achieved by pounding the seeds with laboratory mortar and pestle to increase the contact surface for extraction. A particle size of approximately 2 mm was obtained after passing through a set of standard laboratory mesh sieve. All reagents were of analytical grade and were used as purchased from BDH Chemicals, Poole, England.

Table 1: Experimental Design Summary.

B. Design Experiment

The design of experiment was based on central composite design (CCD) using Response surface methodology (RSM) function of the commercial package, Design Expert version 6.0.8. (Stat-Ease Inc, Minneapolis, U.S.A.). The experimental process variables time t (hr), temperature T (°C) and solid/solvent ratio V (g/cm3) were transformed respectively to the coded variables A, B, and C thus;



Figure 1: Parinari fruits, leaf and kernel.

| A = (t - 4)/2 | (1) |
|----------------------|-----|
| B = (T-65)/5 | (2) |
| C = (V - 0.05)/0.025 | (3) |

Based on preliminary studies (Afolabi *et al.*, 2014), a five level, four-factor design was employed in this study requiring 40 experiments. The summary of the experimental design is as presented in Table 1. The categorical factor; solvent type, was coded as D.

C. Sample Extraction

Solvent extraction method was used to study the effect of extraction conditions on the quality characteristics of parinari oil. The predicted 40 extraction experiments were conducted using a 250 cm3 capacity laboratory Sohxlet apparatus mounted on a regulated heating mantle by varying the parameters temperature, time, solid-solvent ratio and solvent types according to the experimental design (Table 1).

D. Determination of Effects of Parameters on Oil Quality

Acid values, and iodine values were determined according to AOCS methods (Firestone, 1996). Saponification values were determined according to AOAC (2006) Official method methods for the 40 different samples.

E. Statistical Analysis and Optimization

In the present study, response surface methodology was employed to obtain the optimal extraction condition giving oil

| Factor | Name | Unit | Туре | Level | | | | |
|--------|---------------------|-------------------|-------------|-------|----------|------|-----------|-------|
| | | | | -α | -1 | 0 | 1 | α |
| А | Time | hrs | Numeric | 0.64 | 2 | 4 | 6 | 7.36 |
| В | Temperature | °C | Numeric | 56.21 | 60 | 65 | 70 | 73.36 |
| С | Solid/solvent ratio | g/cm ³ | Numeric | 0.01 | 0.03 | 0.05 | 0.08 | 0.09 |
| D | Solvent type | C | Categorical | | n-Hexane | | Pet ether | |
| | $\alpha = 1.68$ | | | | | | | |

of optimal quality within the experimental domain. The optimum oil quality condition was achieved by setting optimization goals of minimizing the acid value, maximizing iodine value and minimizing the saponification value within the range of values obtained. Design Expert 6.0.8. tool was also employed to achieve model fitting and statistical analyses.

III. RESULTS AND DISCUSSION

A. Effects of Independent Variables on Parinari Oil Quality Characteristics

The response variables representing three oil quality characteristics (acid valueY1, iodine value Y2 and saponification value Y3) were all best fitted as quadratic model. All the models were significant with values of "Prob > F less than 0.05.

Acid value

The statistical analysis for acid value response Y1, indicated that the main effects were due to the coded factors B, A2, D, A, and BD, corresponding to temperature, quadratic effect of time, solvent type and linear interaction effect between temperature and solvent type respectively. The coded factors C corresponding to solid solvent ratio did not have significant effect on the acid value. The relationship was represented by a reduced quadratic model as stated in eqn 4.

$Y_1 = 4.92 - 0.04A + 1.02B - 0.12D - 0.95A^2 - 0.34BD \quad (4)$ where $Y_1 = Acid$ value

The summary of the analysis of variance (ANOVA) and the experimental and predicted acid values for response equation (Y₁) are as shown in Tables 2 and 3. The predicted coefficient of determination (R2) and adjusted coefficient of determination (R2adj) for Parinari oil acid value response model were obtained as 0.8555 and 0.8342 respectively, indicating the regression model as acceptable. The Prob > F value of less than 0.0001 was significant. The normal probability plots of residuals obtained from parinari oil acid value response equation analysis is as shown in Figure 2. The effects of extraction temperature and time on the acid value for both the n-hexane and petroleum ether solvents at 60 °C and 70 °C followed the same trend as indicated in Figure 3. The acid value was found to increase with increasing extraction temperature while extraction time tends not to have appreciable effect on the acid value. Relatively higher values were obtained at the temperature of 70 °C compared to 60 °C for both n-hexane and petroleum ether solvents, however, the trend was more pronounced in petroleum ether. These results indicated that relatively lower temperatures are desirable to obtain lower acid values in parinari oil.

This trend in acid value agrees with the trend reported in Jatropha oil and neem oil extractions respectively (Akowuah, 2012; Adewoye & Ogunleye, 2012). This relatively lower temperature requirement favoured a more economical process when considering heating costs among other costs for the solvent extraction process. In Figure 4, the 3D response surface plots clearly show the linear relationship of acid value with temperature and the effects of temperature on acid values. The same trends were observed when n-hexane or petroleum ether was used, indicating that solvent type did not have appreciable effect on the acid value of parinari oil. In essence, the plots indicates that the main linear effects were due to the coded terms B, A2, D corresponding to temperature, time and solvent type, indicating that temperature, time and solvent type were factors responsible for the acid value of parinari oil obtained during extraction.

Iodine value

The final quadratic equation, Iodine value, Y_3 in terms of coded factors was given as in eqn 5.

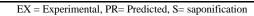
 $Y_3 = 166.12 - 0.48 \text{ A} - 3.04 \text{B} + 0.59 \text{A}^2 - 0.33 \text{B}^2 - 0.68 \text{AB}$ (5)

The test for the significance and adequacy of the model showed that the main effects were due to the coded term B, A2

| Source | Sum of Squares | Degree of Freedom | Mean Square | F Value | Prob > F |
|-------------|-------------------|----------------------|----------------|---------|------------------------|
| Model | 58.96 | 5 | 11.79 | 40.25 | < 0.0001 significant |
| Residual | 9.96 | 34 | 6.10 | | |
| Total | 68.92 | 39 | | | |
| А | 0.044 | 1 | 0.044 | 0.15 | 0.6994 |
| В | 28.41 | 1 | 28.41 | 96.96 | < 0.0001 |
| D | 0.59 | 1 | 0.59 | 2.02 | 0.1641 |
| A^2 | 26.68 | 1 | 26.68 | 91.05 | < 0.0001 |
| BD | 0.067 | 1 | 0.067 | 0.011 | 0.9170 |
| Lack of Fit | 6.08 | 24 | 0.25 | 0.65 | 0.8123 not significant |
| Pure Error | 3.38 | 10 | 0.39 | | |
| Std. Dev. | 0.54 | R-Squared | | 0.8555 | |
| Mean | 4.27 | Adj R-Squared | | 0.8342 | |
| C.V. | 12.68 | Pred R-Squared | | 0.8034 | |
| PRESS | 13.55 | Adeq Precision | | 24.131 | |

| Coded values | | | | | Responses | | | | | |
|--------------|-------|-------|-------|---------------------------|-----------|-------|----------------------|--------|--------|--------|
| Run A B | | С | D | D Acid value Iodine value | | | Saponification value | | | |
| | | | | | Ex | Pr | Ex | Pr | Ex | Pr |
| 1 | 1 | 1 | -1 | 1 | 5.48 | 5.17 | 162.09 | 162.18 | 250.30 | 248.40 |
| 2 | -1 | 1 | -1 | -1 | 3.87 | 4.80 | 165.65 | 164.50 | 231.23 | 226.08 |
| 3 | 0 | 1.68 | 0 | 1 | 6.75 | 7.09 | 162.21 | 160.07 | 252.12 | 252.24 |
| 4 | -1 | 1 | 1 | 1 | 5.30 | 5.25 | 165.11 | 164.50 | 252.56 | 251.19 |
| 5 | 0 | 0 | 0 | -1 | 4.94 | 5.04 | 167.99 | 166.12 | 254.81 | 251.78 |
| 6 | -1 | -1 | 1 | 1 | 2.30 | 2.52 | 169.40 | 169.23 | 256.20 | 255.27 |
| 7 | 0 | -1.68 | 0 | -1 | 3.61 | 3.90 | 170.18 | 170.29 | 251.98 | 254.45 |
| 8 | 0 | 1.68 | 0 | -1 | 6.24 | 6.18 | 160.20 | 160.07 | 246.13 | 245.06 |
| 9 | 0 | 0 | 0 | 1 | 5.25 | 4.80 | 165.21 | 166.12 | 252.12 | 253.59 |
| 10 | 0 | 0 | 0 | -1 | 5.54 | 5.04 | 165.32 | 166.12 | 254.81 | 251.78 |
| 11 | -1.68 | 0 | 0 | -1 | 2.10 | 2.21 | 170.10 | 168.61 | 226.12 | 227.08 |
| 12 | -1 | -1 | 1 | -1 | 3.84 | 3.45 | 168.19 | 169.23 | 247.14 | 248.68 |
| 13 | 1 | 1 | 1 | 1 | 5.10 | 5.17 | 162.75 | 162.18 | 243.14 | 242.57 |
| 14 | 0 | 0 | 0 | 1 | 4.25 | 4.80 | 166.21 | 166.12 | 252.12 | 253.59 |
| 15 | 1 | -1 | -1 | -1 | 3.25 | 3.37 | 170.19 | 169.23 | 251.21 | 252.07 |
| 16 | 0 | -1.68 | 0 | 1 | 3.13 | 2.50 | 169.20 | 170.29 | 252.30 | 250.90 |
| 17 | -1 | 1 | -1 | 1 | 5.41 | 5.25 | 163.82 | 164.50 | 242.50 | 245.57 |
| 18 | 1 | -1 | 1 | -1 | 3.23 | 3.37 | 170.30 | 169.61 | 252.20 | 247.99 |
| 19 | 0 | 0 | 0 | 1 | 4.50 | 4.01 | 166.30 | 166.12 | 256.00 | 253.59 |
| 20 | 0 | 0 | 0 | 1 | 4.14 | 4.80 | 167.14 | 166.12 | 252.92 | 253.59 |
| 21 | 0 | 0 | 0 | -1 | 4.94 | 5.04 | 165.32 | 166.12 | 244.81 | 251.78 |
| 22 | 0 | 0 | -1.68 | 1 | 4.21 | 4.80 | 168.11 | 166.12 | 252.27 | 252.11 |
| 23 | 0 | 0 | 1.68 | -1 | 5.42 | 5.04 | 165.32 | 166.12 | 252.45 | 251.59 |
| 24 | 1.68 | 0 | 0 | 1 | 2.80 | 2.03 | 168.50 | 166.98 | 253.14 | 248.65 |
| 25 | -1 | 1 | 1 | -1 | 6.10 | 4.80 | 160.65 | 164.50 | 234.40 | 238.22 |
| 26 | 0 | 0 | 0 | -1 | 5.74 | 5.04 | 166.99 | 166.12 | 254.81 | 251.78 |
| 27 | 1 | 1 | -1 | -1 | 4.56 | 4.72 | 160.12 | 162.18 | 250.15 | 251.36 |
| 28 | 1 | -1 | 1 | 1 | 2.10 | 2.44 | 170.13 | 169.61 | 226.12 | 232.12 |
| 29 | 1.68 | 0 | 0 | -1 | 2.10 | 2.41 | 165.31 | 166.98 | 248.15 | 247.76 |
| 30 | 0 | 0 | -1.68 | -1 | 4.65 | 5.04 | 164.58 | 166.12 | 240.40 | 244.81 |
| 31 | 0 | 0 | 0 | -1 | 4.94 | 5.04 | 165.32 | 166.12 | 254.81 | 251.78 |
| 32 | 0 | 0 | 0 | 1 | 5.25 | 4.80 | 166.21 | 166.12 | 252.12 | 253.59 |
| 33 | 1 | -1 | -1 | 1 | 2.20 | 2.44 | 169.11 | 169.61 | 246.12 | 242.72 |
| 34 | 0 | 0 | 0 | -1 | 4.94 | 5.04 | 165.32 | 166.12 | 250.81 | 251.78 |
| 35 | 0 | 0 | 1.68 | 1 | 4.26 | 4.80 | 167.32 | 166.12 | 251.20 | 247.92 |
| 36 | -1 | -1 | -1 | 1 | 2.15 | 2.52 | 169.34 | 169.23 | 254.32 | 254.43 |
| 37 | -1 | -1 | -1 | -1 | 3.53 | 3.45 | 170.15 | 169.23 | 243.35 | 241.32 |
| 38 | 1 | 1 | 1 | -1 | 4.12 | 4.72 | 160.14 | 162.18 | 249.65 | 252.26 |
| 39 | 0 | 0 | 0 | 1 | 6.25 | 4.80 | 166.21 | 166.12 | 252.12 | 253.59 |
| 40 | -1.68 | 0 | 0 | 1 | 2.10 | 168.3 | 168.61 | 168.32 | 248.23 | 247.78 |

Table 3: Design layout for parinari oil extraction for coded, uncoded values and responses.



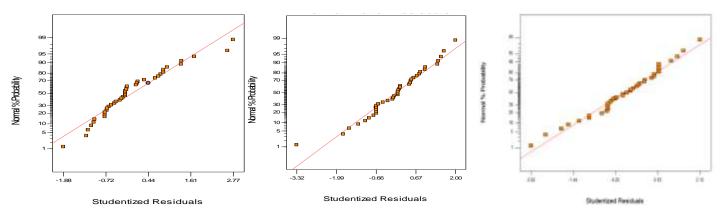


Figure 2. Normal probability plots of residuals for acid, iodine and saponification values obtained from parinari oil response data analyses.

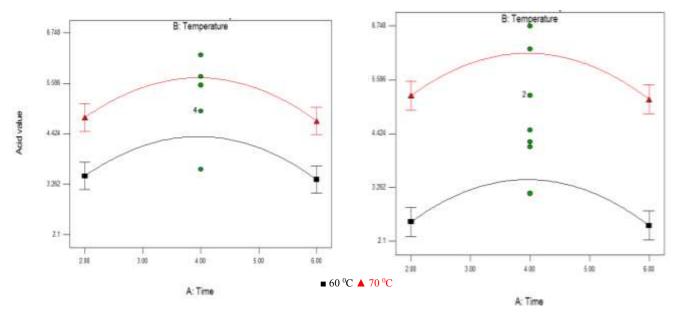


Figure 3: Acid value interaction graphs of temperature with time for n-hexane (A) and Petroleum ether (B) solvent types.

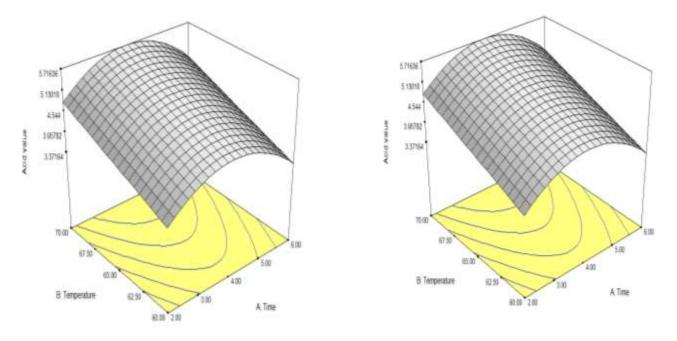


Figure 4: 4D response surface plots showing effect of temperature and time on acid value for n-hexane (A) and petroleum ether (B) solvent types.

and AB, indicating that temperature was the most significant model term. The significance of the coded terms A2 and AB also indicated that the quadratic effect of time and interactive effect of time and temperature were important. The summary of the analysis of variance (ANOVA) obtained for equation Y3 is shown in Table 4. The predicted and adjusted coefficients of determination (R2) and (R2adj) for Parinari oil iodine value response model equation were obtained as 0.8356 and 0.8114 respectively indicating the regression model as acceptable.

The ANOVA results of the regression quadratic model equation Y_3 demonstrated that the model was highly significant, as it was evident from the calculated F-value (34.56) and a very low probability value (0.0001). The R2

value of 0.7564 is in fairly in agreement with the R2adj value of 0.8114. The normal probability plot of residuals for data analysis obtained for parinari oil iodine values is shown in Figure 2. Figure 5 shows the interaction graph of temperature (60 °C, 70 °C) with time for n-hexane and petroleum ether solvents while Figure 6 shows the effects of extraction parameters on iodine values. Temperature had a negative effect on iodine values when either of the solvent was used as indicated in the interaction graphs and response surface plots.

The iodine value was found to increase slightly with increasing extraction temperature and time. Extraction temperature tends to have more effects on the iodine value compared to time. However, solid-solvent ratio and solvent

| Source | Sum of Squares | Degree of Freedom | Mean Square | F Value | Prob > F |
|----------------|-------------------|----------------------|----------------|---------|------------------------|
| Model | 280.37 | 5 | 56.07 | 34.56 | <0.0001 significant |
| Residual | 55.17 | 34 | 5.78 | | |
| Total | 415.63 | 39 | | | |
| А | 6.39 | 1 | 6.39 | 3.94 | 0.0554 |
| В | 252.16 | 1 | 252.16 | 155.4 | < 0.0001 |
| A^2 | 10.14 | 1 | 10.14 | 6.25 | 0.0174 |
| \mathbf{B}^2 | 3.23 | 1 | 3.23 | 1.99 | 0.1671 |
| AB | 7.30 | 1 | 7.30 | 4.50 | 0.0413 |
| Lack of Fit | 46.50 | 24 | 1.94 | 2.23 | 0.0930 not significant |
| Pure Error | 8.67 | 10 | 8.67 | | - |
| Std. Dev. | 2.41 | | R-Squared | 0.8356 | |
| Mean | 166.03 | | Adj R-Squared | 0.8114 | |
| C.V. | 1.45 | | Pred R-Squared | 0.7564 | |
| PRESS | 247.12 | | Adeq Precision | 20.715 | |

Table 4: Analysis of Variance (ANOVA) table for Parinari oil extraction iodine value response model Y₃.

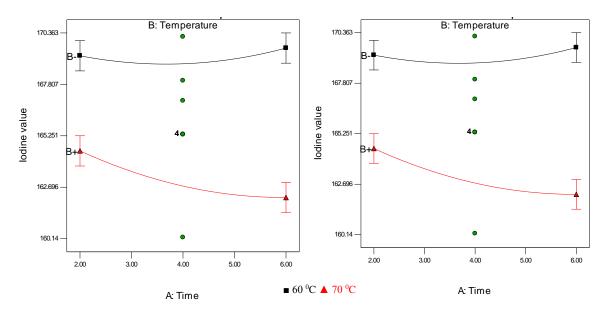


Figure 5: Iodine value interaction graphs of temperature with time for n-(A) and Petroleum ether (B) solvents.

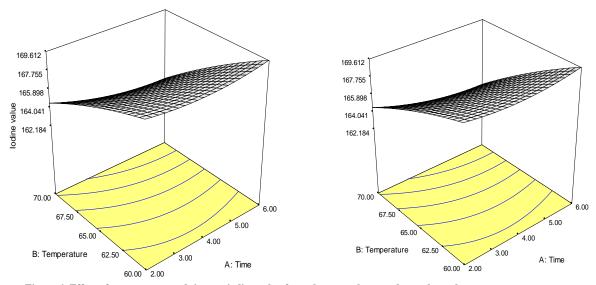


Figure 6: Effect of temperature and time on iodine value for n- hexane solvent and pet ether solvent type.

type did not have a significant effect on iodine value. Relatively lower temperatures and short extraction times tend to favour obtaining relatively high iodine value being an important property when considering the industrial utilization of the oil for reactions that depends on the methylenic bonds of the fatty acid chain e.g. hydrogenation, epoxidation, polyesterification (Murphy, 2012). Also, vegetable oils that have iodine values within the range obtained for parinari oil can be classified as drying oil.

Drying oils are important in the production of binders, resins and surface coatings in the paints industry (Murphy, 2012; Odetoye *et al.*, 2013). However, high iodine values are generally undesirable in oils which are to be used as biodiesel feedstock. Relatively higher extraction temperatures and longer extraction times tend to give parinari oil of reduced iodine values which may be more favourable for biodiesel production. However, longer residence times and extraction temperatures will have additional cost implications on the extraction process.

Saponification value

The statistical analysis indicated that the quadratic model equation Y4 was significant as shown by the "Prob > F" value which was less than 0.05. The values of R2 and R2adj for Parinari oil extraction were obtained as 0.8729 and 0.8067 respectively, indicating the regression model having more than 80% acceptability. The probability plots of residuals obtained from parinari saponification value response data analysis is shown in Figure 2.

The main linear interaction effect was due to the coded terms A, B, C, D. The quadratic effect of time (A2) and the coded factors A2, AB, AC, AD, BD, and CD were also significant model terms. The insignificant terms C, BC, C2 and D2 were excluded from the model and the ANOVA summary obtained for the reduced response equation Y4 is shown in Table 5. The response model equation for saponification value in terms of coded factors is given in equation eq.6 as:

$$252.69 + 0.53 \text{ A} - 1.2 \text{ B} + 0.38\text{C} + 0.91 \text{ D} - 5.08 \text{ }A^2 - 0.72B^2 - 1.26 \text{ }C^2 + 3.63 \text{ AB} - 2.86 \text{ AC} - 5.61 \text{ AD} + 1.19 \text{ BC} - 1.59 \text{ BD} + 1.63 \text{ CD}$$
(6)

Higher saponification values are indicative of the presence of lower molecular weight compounds/ short chain fatty acids in the oil. Higher saponification values are more desirable when considering oil for the soap industry. However, it is undesirable in the production of biodiesel. There is need to minimize the saponification value during extraction process of parinari oil that will be utilized for biodiesel production and the alcoholysis reaction stage of alkyd resin production.

For the interaction plots, Figure 7 illustrates the effect of extraction time on saponification value for the two different solvents. Saponification value increased gradually as extraction time increased in n-hexane while saponification value decreased gradually as extraction time increased in petroleum ether. Relatively lower saponification values were obtained at shorter extraction time when n-hexane solvent was used compared to that of petroleum ether. Higher saponification values suggest the presence of lower molecular weight molecules and breaking down of the oil triglyceride into lower molecular components at relatively higher temperature. The plot (Figure 7) indicates that extraction at lower temperatures favoured lower saponification values during the extraction of parinari oil when n-hexane was used. For the interaction plots, Figure 7 illustrates the effect of extraction time on saponification value for the two different solvents.

Saponification value increased gradually as extraction time increased in n-hexane while saponification value decreased gradually as extraction time increased in petroleum ether. Relatively lower saponification values were obtained at shorter extraction time when n-hexane solvent was used compared to that of petroleum ether. Higher saponification values suggest the presence of lower molecular weight molecules and breaking down of the oil triglyceride into lower molecular components at relatively higher temperature. The plot (Figure 7) indicates that extraction at lower temperatures favoured lower saponification values during the extraction of parinari oil when n-hexane was used. This observation may indicate that prolonged heating time using petroleum ether may lead to certain polymerization reactions of the oil molecules of parinari, (having a relatively high iodine value) leading to lower saponification values and higher molecular weight.

B. Extraction Process Optimization

A standard approach (Uzoh *et al.*, 2013) to the optimization exercise involves the formulation of global optimization criteria, considering necessary trade off in order to give an economically viable process with best oil properties within the design space. The global approach was adopted bearing in mind the optimization goals with concern for factors and responses that are indicative of minimal costs and maximal oil quality and profit (yield).

The optimization was achieved by setting the optimization goals as follows; minimize acid value, maximize iodine value, maximize oil yield, minimize temperature, minimize time maximize solid/solvent ratio within the design space. Since no unique solution was obtained, the optimal solution selected out of the 18 available options was based on economic considerations (Uzoh *et al.*, 2013) that is, reduced temperature and time corresponds to reduced operating costs of the extraction process and the desirable oil characteristics. Table 6 shows the optimum values of process parameters obtained for corresponding optimal quality of parinari oil. The yield of 54% which corresponds to optimal quality was relatively lower than 64.04% obtained without consideration for optimum quality characteristics (Afolabi *et al.*, 2014).

The desirability of the optimization solution was 0.897, indicating about 90% acceptability limits considering favorable independent variables; lower extraction times, lower extraction temperatures. Further validation experiments conducted at the predicted optimal conditions were in reasonable agreement with the predicted optimal values. Parinari oil has a relatively high iodine value and the oil can be conveniently classified as a drying oil comparable with linseed oil. High iodine value and refractive index are _

| Source | Sum of | Degree of Mean | | F Value | Prob > F |
|----------------|---------|----------------|----------------|---------|---------------------|
| | Squares | Freedom | Square | | |
| Model | 1909.12 | 13 | 146.86 | 13.20 | <0.0001 significant |
| Residual | 278.09 | 25 | 11.12 | | |
| Total | 2187.21 | 38 | | | |
| А | 6.54 | 1 | 0.59 | 6.54 | 0.4503 |
| В | 39.07 | 1 | 3.51 | 39.07 | 0.0726 |
| С | 4.04 | 1 | 4.04 | 0.36 | 0.5524 |
| D | 31.46 | 1 | 31.46 | 2.83 | 0.1051 |
| A ² | 14.51 | 1 | 14.51 | 1.30 | 0.2642 |
| B^2 | 46.30 | 1 | 46.30 | 4.07 | 0.0544 |
| ĀB | 211.07 | 1 | 211.07 | 18.97 | 0.0002 |
| AC | 130.91 | 1 | 130.91 | 11.77 | 0.0021 |
| AD | 728.11 | 1 | 728.11 | 65.46 | 0.0001 |
| BC | 22.83 | 1 | 22.83 | 2.05 | 0.1643 |
| BD | 69.43 | 1 | 69.43 | 6.24 | 0.0194 |
| CD | 72.60 | 1 | 72.60 | 6.53 | 0.0171 |
| Lack of Fit | 182.72 | 15 | 12.18 | 1.28 | 0.3548 |
| Pure Error | 95.38 | 10 | 9.54 | | |
| Std. Dev. | 3.34 | | R-Squared | 0.8729 | |
| Mean | 248.31 | | Adj R-Squared | 0.8067 | |
| C.V. | 1.34 | | Pred R-Squared | 0.6379 | |
| PRESS | 792.06 | | Adeq Precision | 14.606 | |

Table 5: Analysis of Variance (ANOVA) table for Parinari oil saponification value response surface reduced quadratic model Y₄.

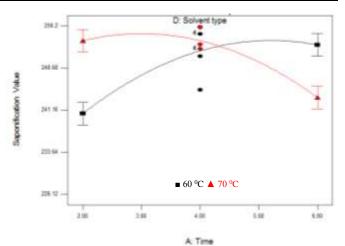


Figure 7: Saponification value interaction of solvent type with time.

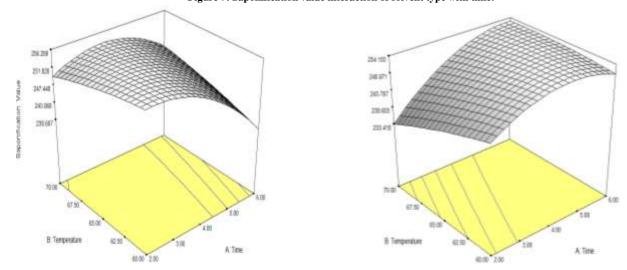


Figure 8: 3D response surface plots showing effect of temperature and time on iodine value for petroleum ether and n-hexane solvent type.

indicative of high level of unsaturation in oil. Drying oils are raw materials for the oleochemical industry.

IV. CONCLUSION

Extraction parameters were found to have varying effects on the acid, iodine and saponification values of the parinari oil. However, the solvent type did not have appreciable effect on the acid value of parinari oil. The temperature of extraction had the most significant effect on acid and iodine values while the extraction time had the most significant effect on the saponification value of parinari oil extraction process. Also, the optimum conditions for desirable quality of oil were obtained as an extraction time of 2 hours and an extraction temperature of 60 OC. Further work should be done on the effect of extraction parameters on the oil quality characteristics of parinari oil using other extraction methods.

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