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STATISTICAL OPTIMIZATION AND SENSITIVITY ANALYSIS OF RHEOLOGICAL MODELS USING CASSAVA STARCH

M. E. Ojewumi*, G.O. Kayode, J. A. Omoleye and D. T. Oyekunle
Chemical Engineering Department, Covenant University, P.M.B 1023, Km 10, Idiiroko.
Canaan Land, Sango Ota, Ogun state, Nigeria.
*Corresponding author

ABSTRACT

Models are sometimes employed to determine some parameters that can be used to distinguish between different types of food samples. Rheological models can be used to predict flow for severe conditions where it is difficult to determine the nature of the fluid flow, consequently it is essential to select the appropriate rheological models. This study aims to propose a rheological model that describes an ideal cassava starch rheological behavior and its influence on state variables such as concentration and temperature in order to validate the rheological models. In this study, five rheological models (namely; Power-law model, Robertson-stiff model, Herschel-Bulkey model, Prandtl-Eyring model and Bigham plastic model) were amended into various statistical model by adding the error variance (e). This study concludes that Herschel-Bulkley model and Robertson-stiff model closely explain the rheological patterns occurring during the production of cassava starch. The sensitivity evaluation of other rheological models demonstrate that the validity of Power-law model, Herschel-Bulkley model and Robertson stiff model is not notably influenced by changes in concentration and temperature of the cassava starch. Nevertheless, the Prandtl-Eyring and Bingham plastic models are noted to have less reliable prediction at lower temperature and higher concentration respectively.

Keywords: Statistical optimization, Sensitivity analysis, Rheological models, Cassava

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1. INTRODUCTION

Native starches have been used as colloidal, gelling, thickening, water retention and bulking agent [1], this is to enhance viscosity and stability of food products [2]. Starch could enhance the texture of different types of food [3]. Starch has its main origin from plant, and it's mostly used in food processing as a gelling or thickening agent, in textiles as a sizing agent, and it's applied in paper and paper products as adhesive [4-6]. Starch solution rheological property is largely dependent on its concentration and this is required to determine its use [7]. Starch is a significant component of cassava roots which compose of about 80% of its dried weight [8]. The stability of the starch based food products is usually enhanced by the use of non-starch hydrocolloids to improve the properties of the food products; to preserve its gross quality throughout its storage time and by influencing its textural and rheological properties during processing [9-12].

Cassava, *Manihot esculenta crantz* is a tuberous plant which grows best in tropical and subtropical areas of the world all through the year. By virtue of its high starch content and tolerance to drought, it is one of the most essential crops in the tropics with Nigeria being the highest producer in the world [13-15]. Cassava is mostly regarded as a source of carbohydrate, nicotinic, thiamin and riboflavin acid but not including proteins [16]. Apart from some waste materials [17-19] cassava has been used as an emphasis of research and practice for the production of ethanol and biofuel in the view of the limited fossil fuel reserve throughout the last decade [2, 20]. It is used in soups as a thickener, fruit pies, sauces, puddings and in the processing of baby foods, as raw material in fillers and it serves as bonding agent in confectioneries and biscuits [21]. Various functions of wheat, rice and maize starches can be performed by cassava starch [22]. It has a flat taste with an appealing textural characteristics that can be used as simple processes in comparable to other starches [23]. Cassava starch poses various properties for various applications such as stabilizing and thickening agent in baby food; as material for fillers and in industrial manufacture of biscuits and confectionaries, it's also applied to cloth for brightness [22, 24]. For an effective formulate on of product and engineering enlargement, it's important to determine the rheological properties of starch solution [7].

Several researchers have investigated the rheological properties of starch concentration [25, 26]. The effects of temperature, overlap concentration (C), cooking time and pH value have been carried out by Chen and Ramaswamy, [27] on parameters of rheological properties (such as consistency index and flow behavior index (n) of tapioca starch applying a second order composite design. It was reported that the three models (power law model, Casson model, and Herschel-Bulkley model) illustrate tapioca solutions flow behavior. Solutions of gelatinized starch were studied at different ranges of concentration and temperature by Nurul [28]. The behavior of the flow was determined by the power law model, Arrhenius equation was used to evaluate the temperature effect. It was suggested that as K increases, C increase while it decreases as temperature increases.

Mathematical model is regarded as a decision tool that assists decision makers in effectively dealing with complex issues such as oil spillage on soil surfaces [29-31].

2. TOOLS FOR MODEL DEVELOPMENT

Tools for the developments of Rheological models involved in this research were listed and described below:

2.1. Power law model

Power law model **is o**therwise called the Ostwald-de waele equation, the flow relationship is useful because of its simplicity; the model is limited because it only approximately describes the behavior of real non-Newtonian fluids. This model describes the flow behavior of pseudo-plastic fluids.

The power law model can be expressed mathematical as:

$$\tau = K\gamma^{n} \qquad (1)$$

τ = Shear stress

K represents the index consistency

n represents flow behavior index

The consistency index (K) depicts the thickness of the fluid while the flow behavior index (n) the extent of non-Newtonian behavior.

2.2. Herschel-Bulkley Model

Herschel-Bulkley model is used to evaluate rheological behavior of non-Newtonian fluids. It is also used to depict the flow behavior of certain fluids like food products. The Herschel-Bulkley model is more complicated than the power law model because of the introduction of the yield stress. The model is mathematically described as:

$$\tau = \tau_o + K\gamma^{n} \qquad (2)$$

Three model parameters characterize this relationship;

K representing the index consistency

n representing flow behavior index

τ_o representing yield stress

The yield stress describes the amount of stress that the fluid experiences before it yields and begins to flow.

2.3. Bingham Plastic model

This rheological model is characterized by two model parameters which describe the flow dynamics of the fluid. Fluid that exhibits Bingham plastic are characterized by plastic viscosity and yield point which does not depend on shear rate. It is also an expression of the attractive forces that exist within the fluid under dynamic conditions. The Bingham plastic model can be expressed mathematically as

$$\tau = \tau_o + \mu_p\gamma \qquad (3)$$

$\boldsymbol{\tau_o}$ representing the yield stress

μ_p representing the plastic viscosity

2.4. Prandtl-Eyring model

A distinct option to the power law is the Prandtl-Eyring model which tends to a constant viscosity in the limit of γ tending towards zero. Although, the viscosity function tends towards zero as γ tends towards infinity. The Prandtl-Eyring model can be represented mathematically as:

$$\tau = A\sinh^{-1}(\gamma/B) \qquad (4)$$

A and B are constant and specific to the fluid which describes the flow behavior of the fluid.

The model evokes Newtonian behavior at very low shear rates, with a gradual transition into even stronger pseudo-plasticity as the shear rate increases.

2.5. Robertson-Stiff Model

Robertson-Stiff model was propagated by Robertson & Stiff in 1976, and like the Herschel-Bulkley model it also has three fluid characterizing model parameters. It consolidates the Power law and Bingham Plastic Model. The model tends to Bingham plastic model if B = 0; on like power law model when γ_o approaches zero. It is widely used for flow characterization in the oil industry.

The model is mathematically expressed as

$$\tau = A\,(\gamma_o + \gamma)^{B} \tag{5}$$

A, γ_o and B represents the model parameters characteristic to each fluid.

3. REGRESSION ANALYSIS

Regression analysis is a statistical tool for the examination of relationships between independent and dependent variables of a model [26]. This tool can be used to estimate the degree of certainty at which the true relationship is close to an estimated relationship. Regression can also be used to estimate the quantitative effect of the causal variables upon the variable they influence. Regression is also used for model parameter estimation, especially for nonlinear complex model which cannot easily be linearized and further estimated.

Least-square is one of the methods of regression analysis commonly used to estimate model parameters. It is based on the assumption that the scatter plot follows a Normal distribution [27]. Hence, it is a viable method of estimating model parameters used in this research.

4. RHEOLOGICAL MODEL OPTIMIZATION

This involves selecting the best rheological model that most accurately predicts the flow behavior of a given fluid. A lot of statistical methods have been used to select models that best fits rheological data. Amongst which are the mean sum of squares criterion, absolute percentage error criterion, coefficient of determination (R^2). The best model for characterization is the model that gives the lowest mean sum-of-squares while the model with the lowest absolute percentage error gives the best fit, and hence is the best model for characterization.

5. SENSITIVITY ANALYSIS

Sensitivity analysis examines how uncertainties in the output of a model are apportioned to different sources of uncertainties in inputs. It also involves a process of recalculating outputs under different conditions to ascertain the impact of these conditions on the model. In this study, state variables such as temperature and concentration were used in perturbing the models by using the multiple factor at a time approach. Temperature was held constant while concentration and shear rate were varied; Concentration was also held constant while temperature and shear rate were varied. The effect of changes in these variables on the accuracy of all the models were ascertained.

6. MATERIALS AND METHOD

Freshly harvested Cassava starch tubers were purchased from the local market in Ota, Ogun State, Nigeria.

6.1. Flow properties determination

This was done according to [32].

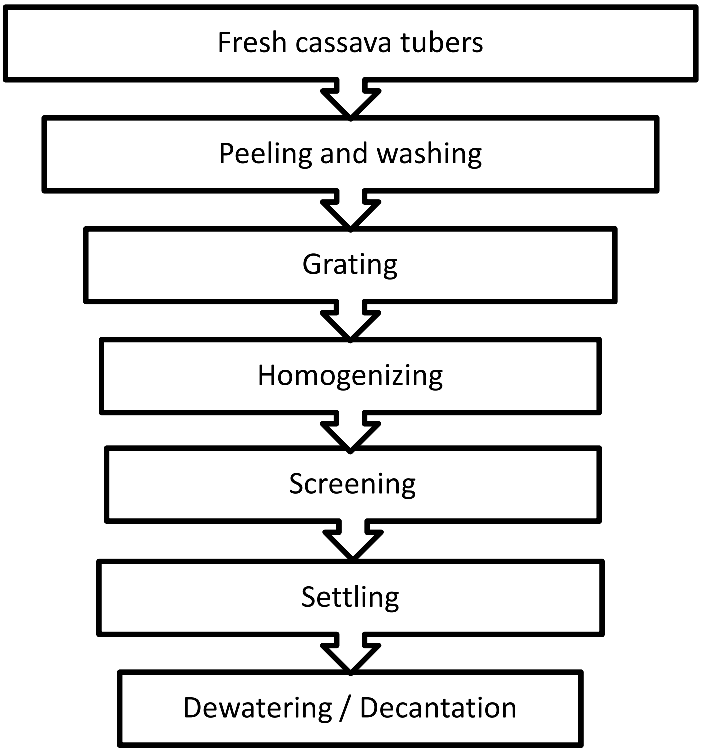

Figure 1 Flowchart for the extraction of Starch from Cassava roots

6.2. Determination of moisture content of starch

The moisture content was evaluated using [28,[33, 34].

$$\% \text{ Moisture} = \frac{W1-W2}{W3} \text{X } \mathbf{100\%} \qquad (7)$$

Where:

W_1= weight of sample ± Petri dish before drying (g)

W_2=Weight of sample ± Petri dish after drying (g)

W_3=Weight of sample (g)

6.3. Rheological experiment

Different quantity of cassava starch was weighed [0.00, 30.00, 40.00, 50.00 g], dissolved in a 450 ml of clean warm water inside a bigger beaker until a solution was formed. Dissolved homogenous sample were put inside controlled water bath in order to form an aqueous gel. The formed gel were later transferred into a cold water bath (4^0C) to the drop the temperature of the gel to 70, 60, 50, 40 and finally 30^0C**.** The flow characteristics was determined by Viscometer in terms of shear rate and shear stress. 1.8415cm radius bob was used at different speeds of 3, 6, 30, 60,100,200,300 and 600 rpm to effectively determine the dial deflection so as to evaluate the shear stress and shear strain [32].

6.4. Determination of gelatinization temperature: This was done using method [32].

6.5. Model parameter estimation

The least square method was used in evaluating model parameters for each model based on the data obtained from the rheological experiment. This method was chosen due to the following assumptions:

a) The scatter follows a Normal distribution
b) Errors are random errors that are independent and identically distributed with mean of zero and variance, σ2.

Considering P number of data points (τ_i, γi), least-square is expressed mathematically in equation 10 below.

$$\mathrm{RSS}\ (\mu) = \sum_{i=1}^{N}(\boldsymbol{\tau \mathrm{i}} - \mathbf{f}(\boldsymbol{\gamma \mathrm{i}}, \mu))^2 = \epsilon^2 \tag{8}$$

RSS (μ) representing the residual sum of squares.

∈ Representing random errors.

μ representing the value(s) of model parameters that gives minimum RSS (also called Least-Square estimators). μ has to be determined such that RSS (μ) will be minimum. Therefore, for the sum of squares to be minimum the partial differential $\boldsymbol{\frac{\delta \mathrm{RSS}\ (\mu)}{\delta \mu} = 0}$

6.5.1 Power-law model

$$\tau = K \gamma^{n} \tag{9}$$

$$\mathrm{RSS}\ (\mu) = \sum_{i=1}^{N}(\tau_i - (K \gamma_i^{\ n}\ ))^2 \tag{10}$$

$$\frac{\delta \mathrm{RSS}\ (\mu)}{\delta K} = \sum_{i=1}^{N} 2(\tau_i - K \gamma_i^{\ n}\ )\gamma_i^{\ n} = 0 \tag{11}$$

$$\frac{\delta \mathrm{RSS}\ (\mu)}{\delta n} = \sum_{i=1}^{N}(\tau_i - K \gamma_i^{\ n}\ )\gamma_i^{\ n} \ln\gamma_i = 0 \tag{12}$$

The system of equations (11-12) were solved using Matlab in order evaluate the model parameters and RSS.

6.5.2. Bingham-Plastic model

$$\tau = \tau_o + \mu_p \gamma \tag{13}$$

$$\mathrm{RSS}\ (\mu) = \sum_{i=1}^{N}(\tau_i - (\tau o + \mu_p \gamma_i))^2 \tag{14}$$

$$\frac{\delta \mathrm{RSS}\ (\mu)}{\delta \tau_o} = \sum_{i=1}^{N}(\tau_i - \tau_o - \mu_p \gamma_i) = 0 \tag{15}$$

$$\frac{\delta \mathrm{RSS}\ (\mu)}{\delta \mu_p} = \sum_{i=1}^{N}(\tau_i - \tau_o - \mu_p \gamma_i)\gamma_i = 0 \tag{16}$$

The system of equations (15-16) were solved using Matlab in order evaluate the model parameters and RSS.

6.5.3. Herschel-Bulkley model

$$\tau = \tau_o + K \gamma^{n} \tag{17}$$

$$\mathrm{RSS}\ (\mu) = \sum_{i=1}^{N}(\tau_i - (\tau_o + K \gamma^{n}))^2 \tag{18}$$

$$\frac{\delta \mathrm{RSS}\ (\mu)}{\delta \tau_o} = \sum_{i=1}^{N}(\tau_i - \tau_o - K \gamma_i^{\ n}) = 0 \tag{19}$$

$$\frac{\delta \mathrm{RSS}\ (\mu)}{\delta K} = \sum_{i=1}^{N}(\tau_i - \tau_o - K \gamma_i^{\ n})\gamma_i^{\ n} = 0 \tag{20}$$

$$\frac{\delta \mathrm{RSS}\ (\mu)}{\delta n} = \sum_{i=1}^{N}(\tau_i - \tau_o - K \gamma_i^{\ n})\gamma_i^{\ n} \ln\gamma_i = 0 \tag{21}$$

The system of equations (19-21) were solved using Matlab in order evaluate the model parameters and RSS.

6.5.4. Robertson-Stiff model

$$\tau = A\,(\gamma_o + \gamma)^{B} \tag{22}$$

$$\text{RSS}\,(\mu) = \sum_{i=1}^{N}[\tau_i - (A\,(\gamma_o + \gamma_i)^{B})\,]^2 \tag{23}$$

$$\frac{\delta \text{RSS}\,(\mu)}{\delta A} = \sum_{i=1}^{N}[\tau_i - A\,(\gamma_o + \gamma_i)^{B}\,]\,.\,(\gamma_o + \gamma_i)^{B} = 0 \tag{24}$$

$$\frac{\delta \text{RSS}\,(\mu)}{\delta B} = \sum_{i=1}^{N}[\tau_i - A\,(\gamma_o + \gamma_i)^{B}\,]\,.\,(\gamma_o + \gamma_i)^{B}\,.\,\text{In}(\gamma_o + \gamma_i) = 0 \tag{25}$$

$$\frac{\delta \text{RSS}\,(\mu)}{\delta \gamma_o} = \sum_{i=1}^{N}[\tau_i - A\,(\gamma_o + \gamma_i)^{B}\,]\,.\,(\gamma_o + \gamma_i)^{B-1} = 0 \tag{26}$$

The system of equations (24-26) were solved using Matlab in order evaluate the model parameters and RSS.

6.5.5. Prandtl-Eyring model

$$\tau = A\sinh^{-1}(\gamma/B) \tag{27}$$

$$\text{RSS}\,(\mu) = \sum_{i=1}^{N}[\tau_i - (A\sinh^{-1}(\gamma_i/B))\,]^2 \tag{28}$$

$$\frac{\delta \text{RSS}\,(\mu)}{\delta A} = \sum_{i=1}^{N}[\tau_i - (A\sinh^{-1}(\gamma_i/B))\,]\,.\,[A\sinh^{-1}(\gamma_i/B)\,] = 0 \tag{29}$$

$$\frac{\delta \text{RSS}\,(\mu)}{\delta B} = \sum_{i=1}^{N}[\tau_i - (A\sinh^{-1}(\gamma_i/B))\,]\,.\,\left[\frac{\gamma_i}{B^2\sqrt{1+(\gamma_i/B)^2}}\right] = 0 \tag{30}$$

The system of equations (29-30) were solved using Matlab in order evaluate the model parameters and RSS

7. RESULTS AND DISCUSSION

7.1. Analysis using statistical tools (RMS, RSS AND R^2)

Residual plots only are not sufficient in model optimization especially when the data points are less than fifty (<50). Other statistical tools such as the Coefficient of determination (R^2), Residual mean squares (RMS) and Residual sum of squares (RSS) were used to ascertain the best model for characterization. The model with the highest R^2 value gives the best fit, while the model with the lowest RMS and RSS values gives the best fit.

For better illustration the values were plotted in charts as shown in Figures 2 and 3 respectively.

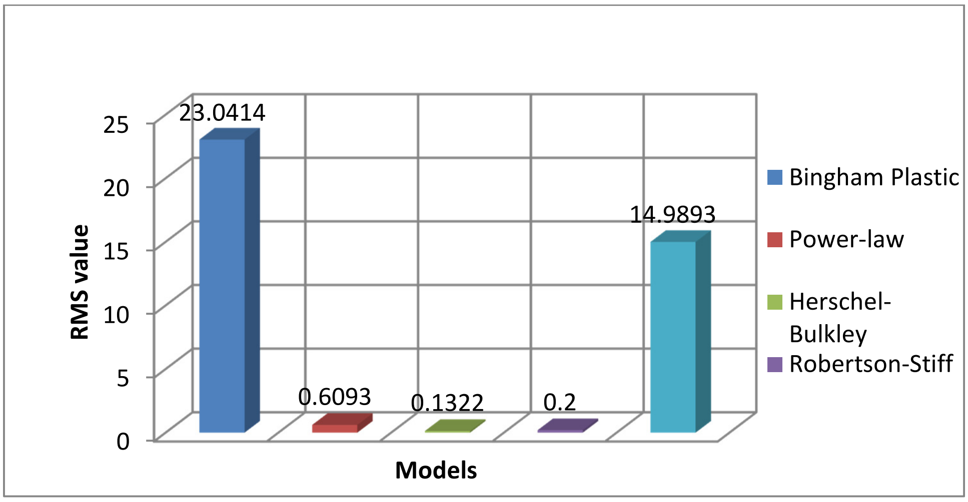

Figure 2 Bar chart showing the RMS values for the various Model

From the above plot, it can be seen that the power-law model, the Herschel-Bulkley model and the Robertson-stiff model all gave very low RMS values relative to the other models, while the Prandtl-Eyring model and Bingham Plastic model gave relatively high RMS values.

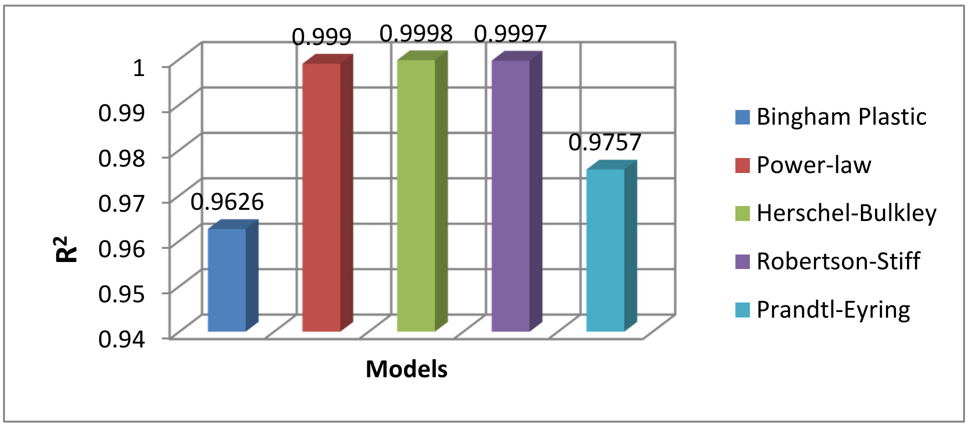

Figure 3 Bar chart showing the R^2 values for the various Model

From the above plot it can be seen that the Power-law model, Herschel-Bulkley model and Robertson-Stiff model all have very high R^2 values relative to the other models, while Bingham plastic and Prandtl-Eyring model have relatively lower R^2 values.

It can therefore be concluded from the above that Herschel-Bulkley model is the best model for characterization since it gave the lowest RMS value and the highest R^2 value. Although the R^2 value of the Bingham plastic model is high (0.9626), which depicts relative closeness of fitting, this however negates the analysis presented by its flow curve as shown in Figure 2. The plot clearly shows that the Bingham plastic model gives a poor fit. This is however one of the limitation of the coefficient of determination (R^2) in that the presence of predictors or explanatory variables in a model always increases the value of the coefficient of determination (R^2). That is, even if the fit is bad it may still display a very high value of R^2. It should be noted that the R^2 value is merely a descriptive measure to give a quick assessment of the model. There are other methods for ascertaining the goodness of fit, one of which is the RMS value which was also used in this study.

A lot of the industrially accepted models such as the Bingham plastic model may not necessarily be the best model for characterization as shown in this study, hence the constant need for rheological model optimization.

7.2. Sensitivity analysis

Sensitivity analysis was carried out on each model using the Multiple-factor-at-a-time approach.

7.2.1. Sensitivity Analysis on Bingham plastic model

The influence of state variables like concentration and temperature on the accuracy of the Bingham Plastic model was examined. Figure 4 shows the result when the sensitivity analysis at constant concentration and varied temperature was carried out on the Bingham plastic model.

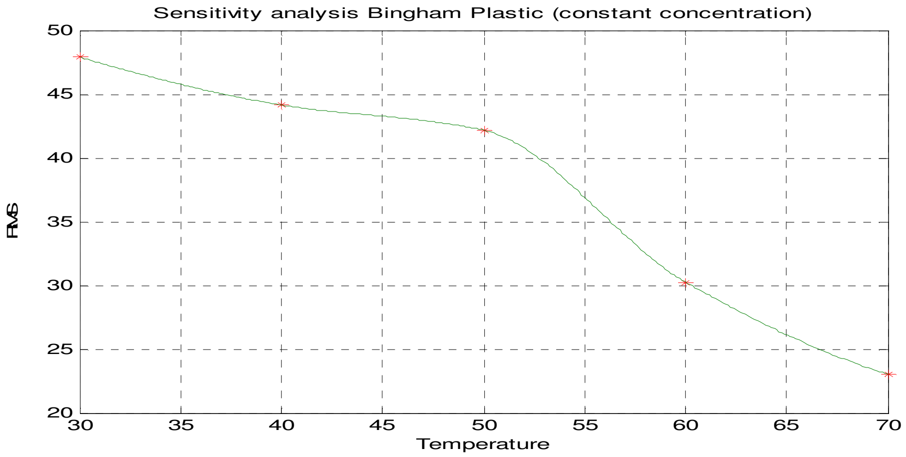

Figure 4. Sensitivity analysis on Bingham Plastic model (constant concentration)

From the plot above it can be seen that the RMS values decreases as the temperature increases. It can therefore be deduced that the accuracy of the model increases as the temperature of the fluid is increased. This is because the smaller the RMS value the better the model fits.

Figure 5 represents the result of the sensitivity carried out at constant temperature and varied concentration.

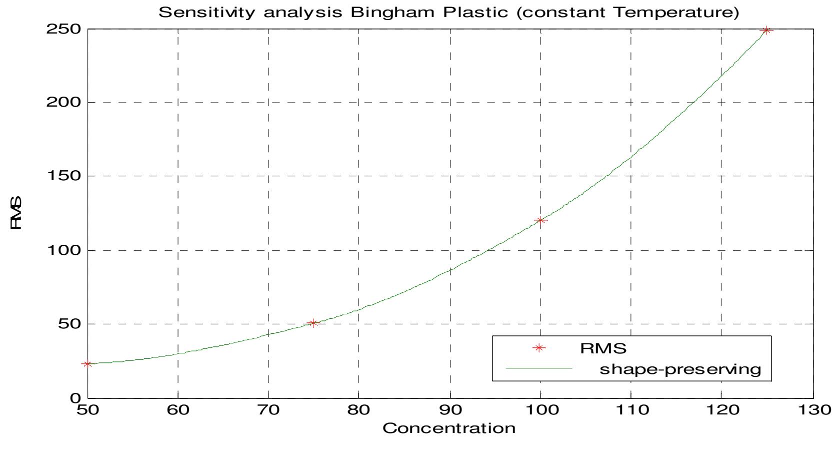

Figure 5 Sensitivity analysis on Bingham Plastic model (constant temperature)

From the plot above it can be observed that the RMS value increases as the concentration increases. It can therefore be deduced that the accuracy of the model decreases with increasing concentration.

7.2.2. Sensitivity Analysis on Power-law model

At constant concentration the sensitivity analysis of the power-law model differs greatly from that of the Bingham plastic model. It can be observed from Figure 6 below that the plot follows an oscillatory pattern with the RMS value increasing and decreasing as the temperature increases. It can therefore be deduced that temperature has no significant effect on the accuracy of the Power-law model.

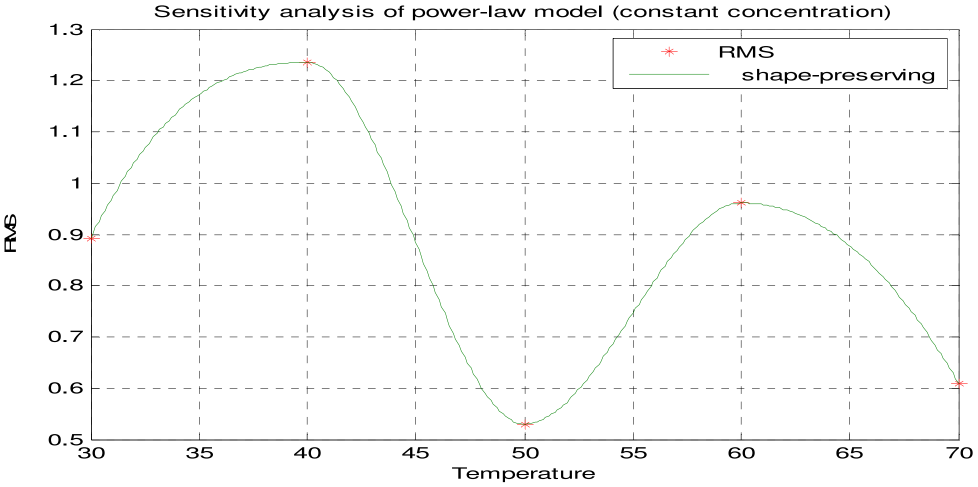

Figure 6 Sensitivity analysis on Power-law model (constant concentration)

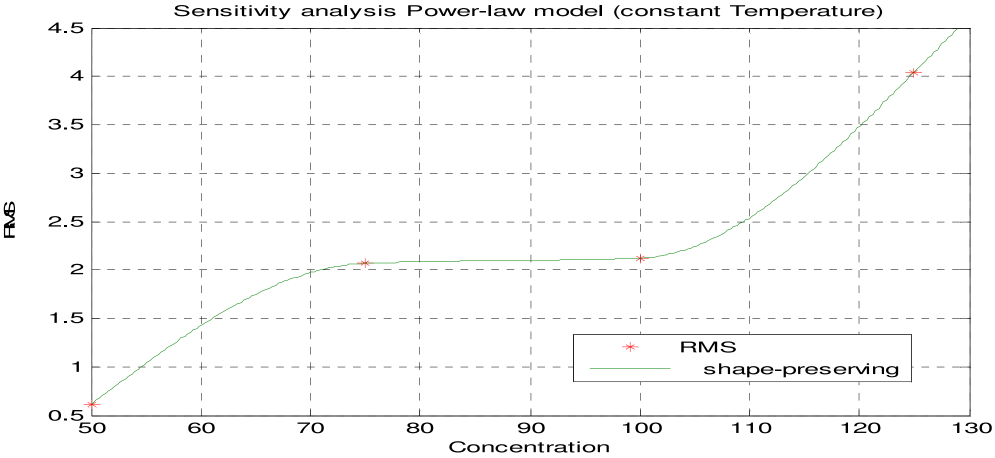

Figure 7 Sensitivity analysis on Power-law model (constant Temperature)

At constant temperature and varied concentration it can observed that the RMS value increases as the concentration of fluid is increased. It can also be deduced that the accuracy of the model decreases with increasing concentration.

7.2.3. Sensitivity Analysis on Herschel-Bulkley model

The sensitivity analysis of the Herschel-Bulkley model at constant temperature is quite similar to that of the power-law model in that both plots follow an oscillatory pattern, increasing and decreasing as the temperature increases. Hence temperature has no significant effect on the accuracy of the Herschel-Bulkley model.

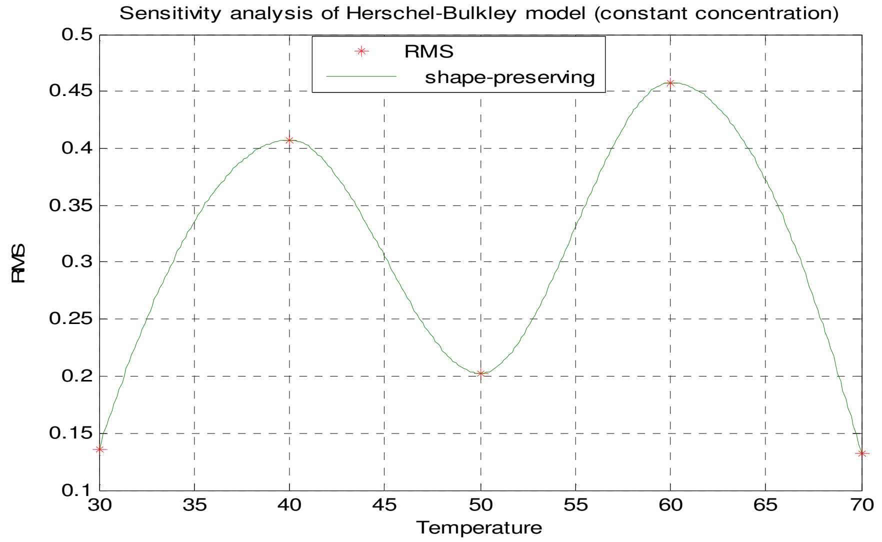

Figure 8 Sensitivity analysis on Herschel-Bulkley model (constant concentration)

At constant temperature as shown in Figure 9, the sensitivity analysis showed that the RMS value increased up to a certain point and then began decreasing. Since the RMS values do not follow any definite pattern, it can be concluded that concentration has no significant effect on the accuracy of the Herschel-Bulkley model.

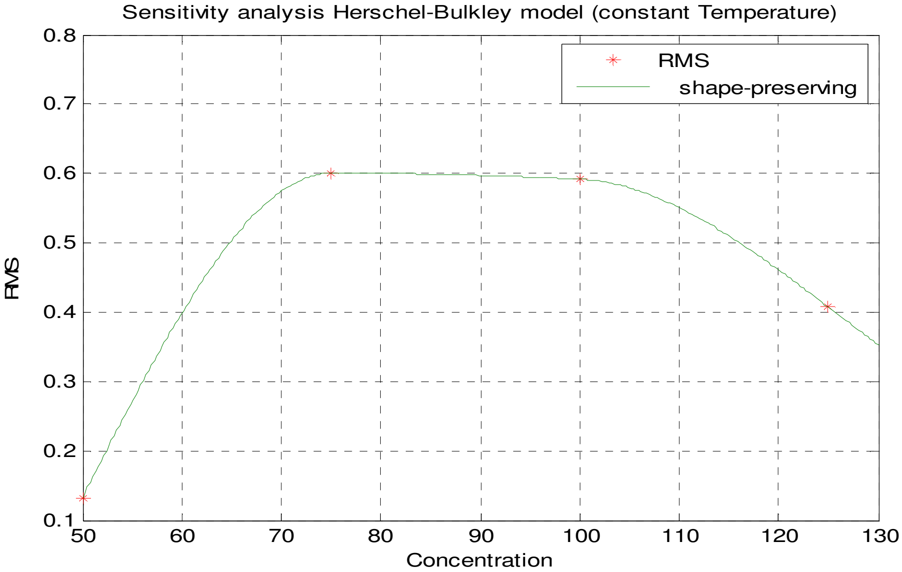

Figure 9 Sensitivity analysis on Herschel-Bulkley model (constant temperature)

7.2.4. Sensitivity Analysis on Robertson-Stiff model

At constant temperature, the sensitivity analysis represented in figure 10 below is also quite similar to that of the Power-law and Herschel-Bulkley model. It also follows an oscillatory pattern with the RMS value increasing and decreasing with increasing temperature. Hence temperature has no significant effect on the accuracy of the Robertson-Stiff model

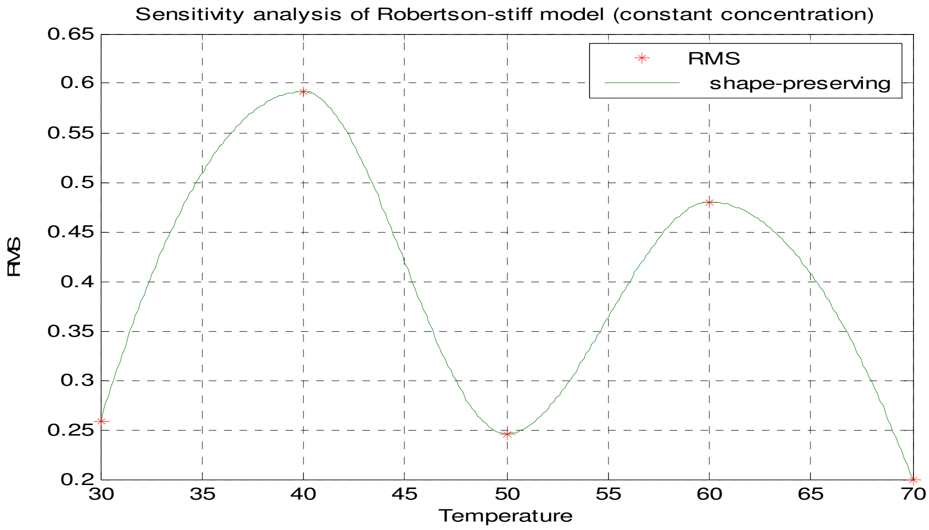

Figure 10 Sensitivity analysis on Robertson-Stiff model (constant concentration)

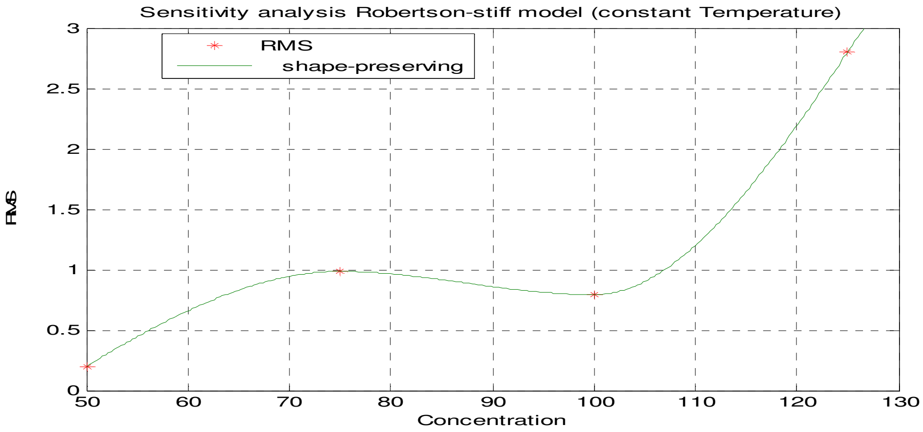

Figure 11. Sensitivity analysis on Robertson-Stiff model (constant temperature)

At constant temperature, the sensitivity analysis on the Robertson-Stiff model showed the RMS value increasing and decreasing as the concentration value increased following an oscillatory pattern. Hence concentration has no significant effect on the accuracy of the model.

7.2.5. Sensitivity Analysis on Prandtl-Eyring model

At constant concentration, the sensitivity analysis of the Prandtl-Eyring model is quite similar to that of the Bingham plastic model. As shown in Figure 12, the RMS value decreases with increasing temperature. This depicts that the accuracy of the Bingham plastic model increases with increasing temperature.

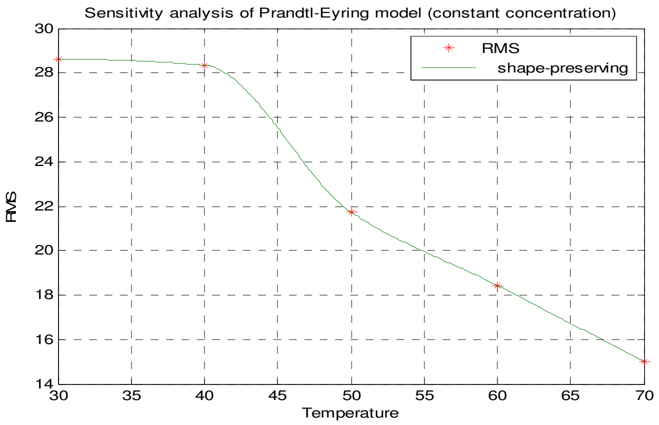

Figure 12 Sensitivity analysis on Prandtl-Eyring model (constant concentration)

At constant temperature, as shown in Figure 13 the RMS value increases with increasing concentration. This depicts that the accuracy of the model decreases with increasing concentration.

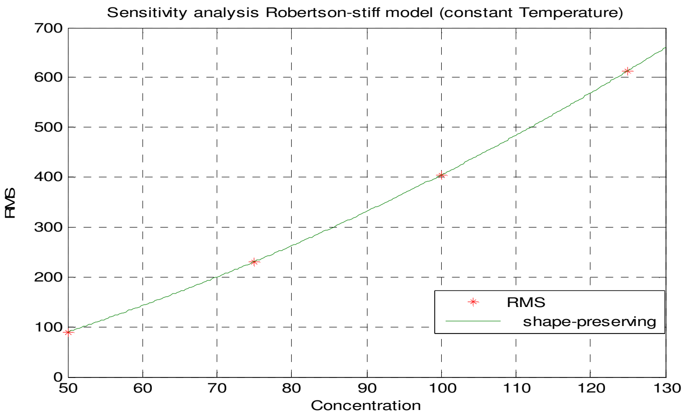

Figure 13. Sensitivity analysis on Prandtl-Eyring model (constant temperature)

7.3. Sensitivity comparison

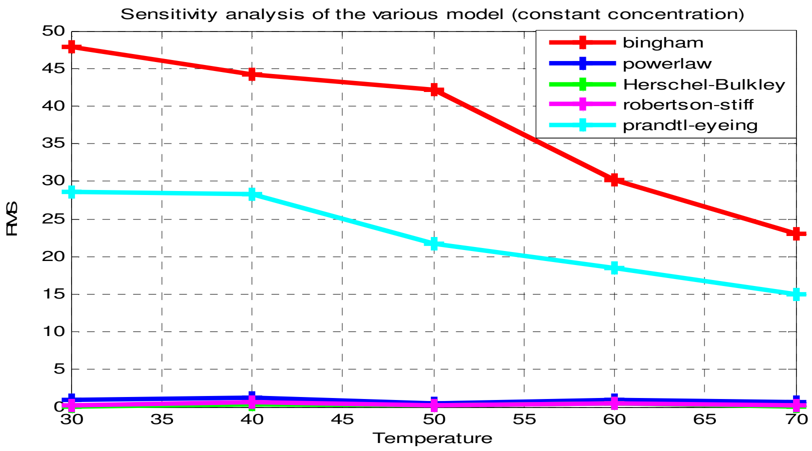

Figure 14. Sensitivity Comparison of the Various Models (Constant concentration)

From Figure 14, it can be seen that the Power-Law model, Herschel-Bulkley and the Robertson-Stiff are not all significantly affected by variations in temperature relative to the other models.

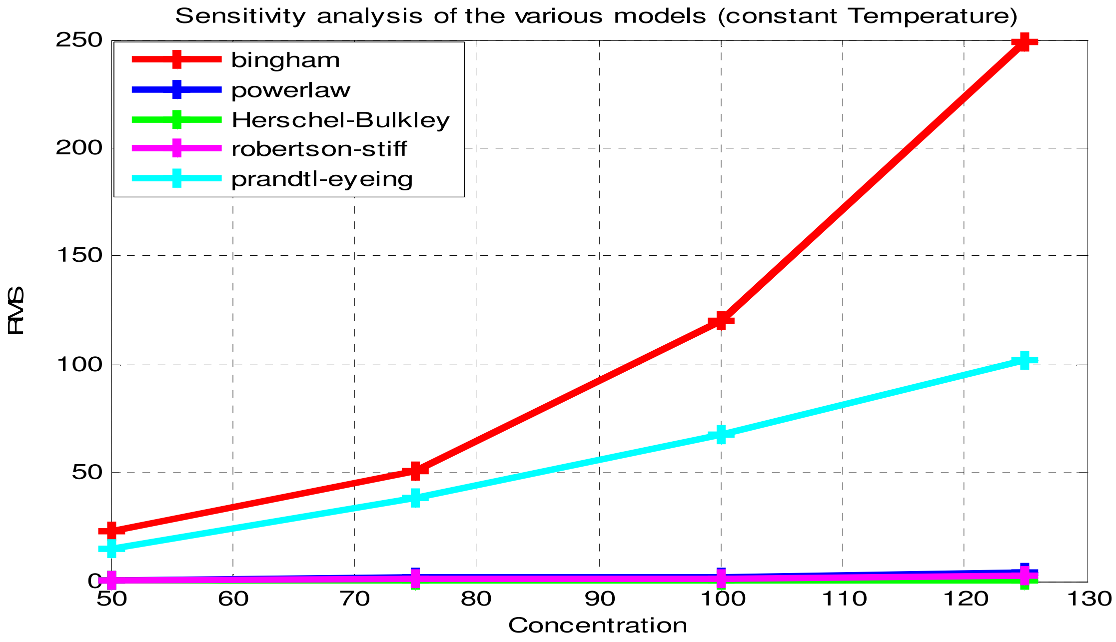

Figure 15 Sensitivity Comparison of the Various Models (Constant temperature)

From Figure 15, it can be seen that the Power-Law model, Herschel-Bulkley and the Robertson-Stiff are not all significantly affected by variations in concentration relative to the other models.

8. CONCLUSION

Rheological characterizations of cassava starch using different rheological models as well as sensitivity analysis of the selected models have been investigated in this study. It can therefore be concluded from this study that the Herschel-Bulkley model and the Robertson-Stiff model most accurately described the rheological behavior of cassava starch. Both models had the lowest RMS values as well as the highest R^2 values as shown in the study. On the other hand, both the Bingham plastic model and the Prandtl-Eyring model both gave the poorest description of the flow behavior of cassava starch.

From the sensitivity analysis of the different rheological models, it can be concluded that the accuracy of both the Herschel-Bulkley model and the Robertson-Stiff is not significantly affected by variations in temperature of the cassava starch. However, it was observed that the Robertson-Stiff model gave less accurate predictions at higher concentration and lower temperature respectively.

9. COMPETING INTEREST

The authors declare that they have no conflict of interest.

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