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Effect of Process Parameters on NaOH Catalysed Cassava Starch Modification

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ABSTRACT

This paper reports a study on the effect of process parameters on NaOH catalysed cassava starch modification using sodium acetate as crosslinking agent as well as to optimize the process using Response Surface Methodology (RSM). Central composite design (CCD) was employed to determine the effect of process parameters: sodium hydroxide catalyst (2g-8g), reaction temperature (65 - 85 °C) and reaction time (50- 70 min), on gelatinization temperature and pH of modified cassava starch. The regression analysis showed good fit of the experimental data to the second-order polynomial (Quadratic models) for the two responses with coefficients of determination (R^2) value of 0.8907 and model *F*-value of 9.05 for gel temperature and (R^2) value of 0.8705 and model *F*-value of 7.47 for pH respectively. The models were found to be significant as its Predicted R^2 of 0.8907 was in close agreement with the Adjusted R^2 of 0.7923 for gelatinization temperature and Predicted R^2 of 0.8705 was in close agreement with the Adjusted R^2 of 0.7539 for pH respectively. A good fit of the model was further validated as the lacks of fit values for the two models were found to be greater than 5%. The conditions for modification of cassava starch were predicted by the model at optimum condition: reaction temperature of 68.77°C, sodium hydroxide catalyst of 4.16 g and reaction time of 50 min. with predicted gelatinization temperature and pH of 74.39 °C and 9.85 respectively.Validation experiments conducted at this optimum conditions gave an experimental value of 74 °C of gelatinization temperature and pH of 8.0 respectively which was in close agreement with the predicted values.

Keywords: RSM, Cassava Starch, Gelatinization Temperature, pH, Optimization, Sodium Acetate, Adipic Acid

INTRODUCTION

Starch is an odorless, tasteless white substance occurring commonly in plant tissue and gotten chiefly from cereals and potatoes. It is a polysaccharide which works as a carbohydrate store and is an important part of the human diet with the molecular formula $(C_6H_{10}O_5)n$ (Chung-wai and Daniel, 2009). Starch is one of the most abundant organic polymers on earth (Jerachaimongkol *et al.*, 2006). Starch or amylum is a polysaccharide consisting of a large number of glucose units joined together by glycosidic bonds. It comprises of amylose and amylopectin as its macromolecules. Starch is produced by all green plants as an energy store and is an important energy source for humans. It is found in potatoes, wheat, rice and other foods, and it varies in appearance, depending on its source. Starch is one of the most abundant, renewable, biodegradable and relatively cheap natural polymer, which is produced by many plants as a source of stored energy. Starches are inherently unsuitable for most applications and, therefore, must be modified chemically or physically to enhance their positive attributes and to minimize their defects. Starch derivatives are used in food products as thickeners, gelling agents and encapsulating agents, in paper making as wet-end additives for dry strength, surface sizes and coating binders, as adhesives (corrugating, bag, bottle labeling, laminating, cigarettes, envelopes, tube-winding and wallpaper pastes), for warp sizing of textiles, and for glass fiber sizing. Various starch products are used to control fluid loss in subterranean drilling, and completion fluids (for oil, gas or water production) (Abbas *et al.*, 2010). Modified starches are also used in tableting and cosmetic formulations (Chung-wai and Daniel, 2009). Modified starch is a food additive which is prepared by treating starch or starch granules, causing the starch to be partially degraded. The purposes of this modification are to enhance its properties particularly in specific applications such as to improve the increase in water holding capacity, heat resistant behavior, reinforce its binding, minimized syneresis of starch and improved thickening (Adzahan, 2002; Miyazaki *et al.*, 2006). Modification is a major tool to address the functionality of starch since its functionality depends on properties like molecular size, crystallinity degree, amylose content and viscosity properties (Ogunmolasuyi, 2015).

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In the unmodified form, starches have limited use in the food industry. In general, native starches produce weak-bodied, cohesive, rubbery pastes when heated and undesirable gels when the pastes are cooled (Adzahan, 2002). The food industry uses starch to perform variety of functions such as thickening, stabilizing, texturing, gelling, encapsulation, and shelf life extension. It plays an important role in deciding the quality and texture of many foods controlling the fitness and sweetness of most food products. Modified starches consist of starch with low to very low level of substituent group. Starch gelatinization is a process that breaks down the intermolecular bonds of starch molecules in the presence of water and heat, allowing the hydrogen bonding sites (the hydroxyl hydrogen and oxygen) to engage more water (Sobkowska, 2001). Gelatinization temperature is regarded as the temperature at which the phase transition of starch granules from an ordered state to a disordered state occurs. The gelatinization temperature of starch depends upon plant type, amount of water present, pH, types and concentrations of salt, sugar, fat and protein in the recipe, degree of cross-linking of the amylopectin, the amount of damaged starch granules as well as derivatisation technology used (Hermansson and Svegmark, 1996; Delcour *et al*., 2000). While the heat-treatment processes include heat–moisture and annealing treatments, both of which cause a physical modification of starch without any gelatinization, damage to granular integrity, or loss of birefringence. Chemical modification is the mainstream of the modified starch in the last century. Many developments of chemical modification of starches have been introduced in food, pharmaceutical and textile industries (Abbas *et al*., 2010).

Akpa and Dagde (2012) modified cassava starch using sodium acetate neutralized with adipic acid and reported that the modified starch had improved functional and physical properties than the native starch. Ameh *et al*. (2018) reported the effect of composition; time and temperature on viscosity and pH of acetic anhydride modified cassava starch and found the empirical generated by response surface methodology to be significant.

The objective of this work was to utilise response surface modelling (Design Expert) to study and optimize the effects of some process parameters (catalyst quantity, reaction time and reaction temperature) on the properties (gelatinization temperature and pH) of modified cassava starch using sodium hydroxide as catalyst and sodium acetate as crosslinking agent.

MATERIALS AND METHODS

Cassava starch preparation

Starch was prepared using the method of Akpa and Dagde (2012). Freshly harvested cassava roots were obtained from Samaru Market in Zaria. The Cassava roots and leaves were then taken to Biological Science Department of Ahmadu Bello University, Zaria and was identified to be of ZSm species. The cassava roots obtained were peeled, washed and disintegrated in a grating machine. The resulting mesh was mixed with water in ratio 1:5 (w/v %). Afterwards, the mesh was filtered with the nylon seive to obtain starch solution. The resulting starch solution was seperated from the water by sedimentation and subsequent decantation. The decanted starch was collected on a tray and air-dried at room temperature. The dried starch was then ground and sieved using 200 µm sieve.

Design of experiment for starch modification

RSM is a statistical technique for the modeling and optimization of multiple variables, which determines the optimum process conditions through combinations of experimental designs with interpolation by first- or second-order polynomial equations in a sequential testing procedure (Said and Amin, 2015). Sodium hydroxide catalyst (A), reaction temperature (B), and reaction time (C) are considered the most important factors affecting starch modifications (Barrios *et al*., 2012). For sodium hydroxide catalyst, it is considered because for this type of modification the catalyst used are basic catalysts which activate the starch by forming starch alcoxide (ST-O−) (Ačkar *et al*., 2015). In this study, design expert version 6.0.6 software was used for experimental design, regression and graphical analyses. Central Composite Design (CCD) was selected as the model for analysis due to its rotatability compared to other methods of optimization such as Box Behnken, Tauguchi and so on. CCD was employed to optimize the modified starch. 3-factors-2-level technique was employed. The total number of experiments for the three factors was obtained as 20 ($=2^k+2k+6$), where k is the number of factors (k=3). This included eight factorial points, six axial points, and six central points to provide information regarding the interior of the experimental region, making it possible to evaluate the curvature effect. Selected factors and their levels for optimization of the process factor were; reaction time (50-70 minutes), reaction temperature (65-85 ^{0}C) and sodium hydroxide catalyst (2-8 g) respectively. Generally, the reaction conditions involved a trade-off between the A, B and C. These three factors were chosen and varied as shown in Table 1.

Table 1: Factors varied for the CCD design of experiment for starch modification

S/NO	FACTOR	LOW LEVEL	HIGH LEVEL
1	A= Sodium hydroxide Catalyst (g)	2	8
2	B= Temperature (^oC)	65	85
3	C= Reaction Time (min)	50	70

while statistical analysis was performed on the output responses; (Gelatinization temperature and pH), optimization of the investigated factors was done and optimum conditions were determined.

Modified Cassava Starch Preparation

50g of the cassava starch was weighed into a beaker followed by addition of 0.05g of silicon oxide as fluxing agent and the mixture was mixed for five minutes, then various amounts of sodium hydroxide (catalyst) according to the experimental design was added and mixed for 20 minutes. Afterwards, 7.25g of sodium acetate and 3.63g of adipic acid were added to the mixture and heated for various reaction times (according to the experimental design) in a water bath maintained at various set temperatures based on the experimental design. After heating the mixture to react, it was poured into a plate to cool. This procedure was repeated for the twenty number of runs based on the design experiment matrix.

Determination of gelatinization temperature

25g of the modified starch was transferred into a beaker, 140ml of water was added and a thermometer inserted into the beaker and placed in a water bath. The mixture was heated with constant stirring until the colour became milky and the starch thickened. The temperature at which this phenomenon was observed was the gelatinization temperature. The temperature obtained was recorded. The same procedure was repeated for each sample.

Determination of pH

The pH was determined using the pH meter (3150 JENWAY).

RESULTS AND DISCUSSION

Table 2 shows the design matrix of the Central Composite Design (CCD) for starch modification and the responses obtained from the experiment.

As shown in Table 3, three different models were suggested by the Design of experiment (DOE) and from Table 4 it can be seen clearly that quadratic model came out the best model hence it is selected for the design and optimization of gelatinization temperature for the cassava starch modification because quadratic model has least standard deviation, the highest R-Squared value , a close value between the R-Squared value of 0.8907 and Adj R-Squared value of 0.7923 as well as the Predicted R-Squared value of 0.7288 compared to linear and 2 factorial (2F1) models. Also the lack of fit value for quadratic model exceeded the 5 % for the quadratic model which is one of the major createria for a model to fit. Likewise the qudratic model has the highest adequate precision of 13.085 compared to other models indicating a good signal to noise ratio since a ratio greater than 4 is desired and can be used to navigate the design space.

Also shown in Table 4, is the ANOVA of the selected quadratic model based on the p-value (0.0010) being less than 0.05 hence the model is significant and the confidence level is 95 % while the lack of fit is insignifficant thus confirming the adequacy of the quadratic model selected.

From Table 4, it can be seen that, the significant model terms are: B, C, C2 and AC. However, this does not mean the model terms A2, B2, AB and BC are not important in this study but it shows that, the model terms B, C, C2 and AC contributed more in the modification of cassava starch as compared to A2, B2, AB and BC model terms, thus the results obtained showed that the model is good. Mathematical model of gelatinization temperature of cassava starch modification.

The mathematic model developed for this response is quadratic model represented by Equation 1. The model was adopted because of its high value of R-squared (0.8907) and the insignificant value of lack of fit of 0.9606 compared to other types of model like linear, 2F1 and cubic**.**

Gel Temp. = +71.18-0.32×A-0.43×B-0.69×C+0.066×A^2-0.20×B^2+0.34×C^2-0.29×AB-1.04×AC+0.029×BC 1

Where A=Sodium hydroxide catalyst (g), B=reaction temp.(oC) and C=reaction time (min). A, B and C represent the liner terms, A2, B2 and C2 denote the quandratic terms while AB, AC, and BC

From the CCD design above in Table 1. A total of twenty (20) experimental combinations were run

Table 2: Experimental (CCD) design results for Cassava Starch Modification

EXPERINMENTAL RUN	A	B	C	RESPONSES 1 GEL. TEMP.	RESPONSES 2 pH
1	5.00	58.18	60.00	71.50	10.70
2	5.00	75.00	60.00	71.88	8.05
3	2.00	85.00	50.00	71.00	8.00
4	8.00	85.00	50.00	71.50	10.50
5	5.00	75.00	43.18	73.50	9.50
6	10.05	75.00	60.00	71.00	11.50
7	8.00	65.00	50.00	73.85	11.50
8	5.00	75.00	60.00	71.14	9.00
9	2.00	85.00	70.00	72.00	11.10
10	8.00	65.00	70.00	69.50	11.70
11	8.00	85.00	70.00	69.00	10.50
12	5.00	91.82	60.00	70.00	8.50
13	2.00	65.00	70.00	72.00	11.50
14	5.00	75.00	60.00	71.00	9.00
15	-0.05	75.00	60.00	72.00	10.90
16	5.00	75.00	76.82	71.05	10.50
17	5.00	75.00	60.00	70.00	7.00
18	2.00	65.00	50.00	71.50	9.00
19	5.00	75.00	60.00	71.14	8.67
20	5.00	75.00	60.00	71.88	7.00

Key; **A=Sodium hydroxide catalyst (g) B= Temperature (^{o}C) C= Reaction Time (min).**

Table 3: Model Statistical Summary of CCD for Cassava Starch Modification

Model type	Std Dev.	R-Square	Adj.R-square	Pred.R-square	Precision	Adeq.Precision	Lack of fit value
Linear	0.98	0.4043	0.2926	-0.0354	26.81	6.562	0.1657
2FI	0.64	0.7942	0.6993	0.6392	9.34	12.994	0.6543
Quadratic	0.53	0.8907	0.7823	0.7288	7.02	13.085	0.9606

Table 4: ANOVA for Response (Gelatinazation Temperature) Surface Quadratic Model for Cassava Starch Modification

Model	Fvalue	Pvalue	Remarks
	9.05	0.0010	Significants
A	4.86	0.0521	Insgnificant
B	8.92	0.0136	Significant
C	23.21	0.0007	Significant
A^2	0.22	0.6481	Insgnificant
B^2	2.02	0.1855	Insgnificant
C^2	5.88	0.0357	Significant
AB	2.44	0.1494	Insgnificant
AC	30.80	0.0002	Significant
BC	2.44	0.1494	Insgnificant
Lack of fit	0.18	0.9606	Insignificant

are the products terms. Equation 1 can be use to predict the gelatinazation temperature for cassava starch modification prior to laboratory experiments at different conditions of the parameters.

Predicted and Actual Yield Relationship

Figure 1 shows the relationships between the predicted and actual responses (Gel. Temp). It presented the design expert parity plot of the predicted gelatinazation temperature of cassava starch modification against their respective actual responses for the evaluation and optimization of process parameters of cassava starch modification.

As shown in Figure 1, the data points were well distributed close to the regression line, which suggested an excellent relationship between the predicted and experimental (actual) values of the response. The data points as shown in the Figure 1 are well distributed close to the regression which revealed that, the model developed is highly significant and adequate to represent the actual relationship between input variables and output response.

Interactive Effects of the Process Parameters on Gelatinization Temperature of Cassava Starch Modification.

The interaction of the process variables on gelatinization temperature are represented by Figures 2a – 2c. Figures 2a, 2b and 2c show the 3D-Surface diagram of significant model term interactions among the variables varied and the response (gelatinization temperature).

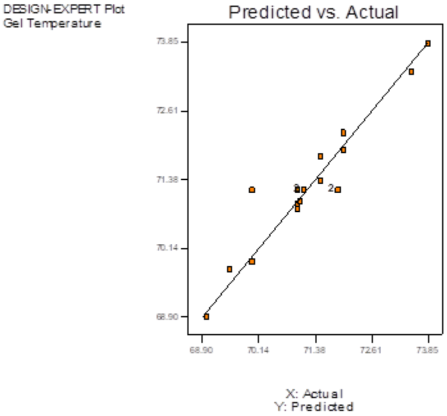

Figure 1: Correlation between Actual (experimental) and predicted value of gelatinazation temperature of cassava starch modification.

The 3D response surface plots generally illustrate the effects of the independent variables and their interactive effects on the responses. The 3D plots shown in Figures 2a and 2b and 2c illustrate the interactive effects of catalyst - temperature, catalyst-reaction time and temperature - reaction time on gelatinization temperature response respectively.

As shown in Figure 2a, increase in catalyst concentration resulted in slight increase in gelatinization temperature up to a catalysts quantity of about 4.5g. A further increase in catalyst (above 5.0g) led to a gradual decrease in gelatinization temperature. Similarly, increasing reaction temperature resulted in increase in gelatinization temperature upto 75°C, above which it began to decrease.

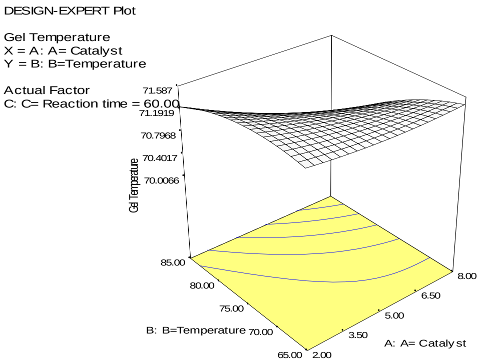

Figure 2a: 3D Response Surface Plot for temperature-catalyst interaction on gelatinization temperature of cassava starch modification.

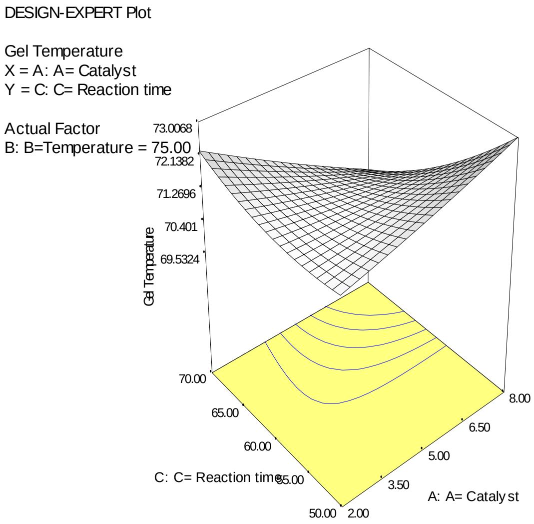

Figure 2b: 3D Response Surface Plot for catalyst–reaction time interaction on gelatinization temperature of cassava starch modification.

Catalyst and reaction time show a good interaction on gelatinization temperature. It was observed that increase in catalyst and reaction time resulted in a corresponding increase in gelatinization temperature. Also, the variations in gelatinization temperature showed that the interactions between the variables are significant, as evidenced from the elliptical nature of the plot.

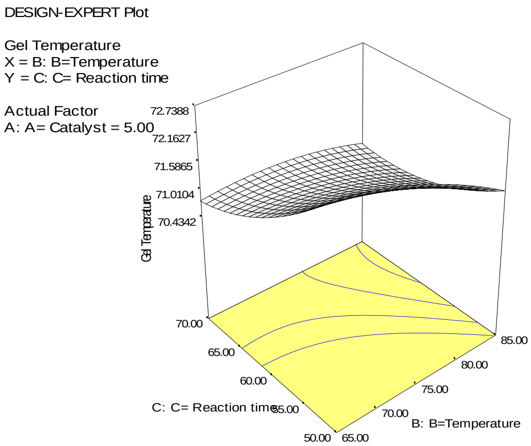

Figure 2c: 3D Response Surface Plot for temperature -time interaction on gelatinization temperature of cassava starch modification.

Figures (2a-2c), showed that catalyst quantity only slightly affected gelatinization temperature. Reaction time and temperature had more significant effect on the gelatinization temperature: gelatinization temperature increased with increase in time. In the catalyst-time interaction, the gelatinization temperature seemingly increased sharply with increase in catalyst between 2 – 3.5g before becoming invariant. As the starch gelatinization temperature is higher, the gelatinization endotherm is more defined and the energy value is increased. This is in agreement with the findings of Chung-wai and Daniel, (2009) who observed a high-amylose starch with a higher dietary fiber content. Although, under preferred conditions, linear chains within granules realign themselves in a more orderly manner, thus making it more difficult for amylase attack. The resulting granular, high-amylose starch has a high gelatinization temperature greater than 70°C. Björck (1990) also concluded that starch with high dietary fiber content, i.e. starch that is more resistant to digestion, is more desirable than traditional cereal dietary fiber which has higher water adsorbtivity and gives a gritty texture. They further concluded that in addition to its functional benefits, resistant starch has been associated with physiological benefits, such as lowering blood glucose and cholesterol concentrations and reducing the incidence of colon cancer. As expected the stronger the bond between the starch molecules, the higher the amount of heat required to break the intermolecular bond and therefore, the higher the gel temperature.

Analysis for pH

Similarly, quadratic model came out the best model hence it is selected for the design and optimization of pH for the cassava starch modification because quadratic model has least standard deviation, the highest R-Squared value, a close value between the R-Squared value of 0.8705 and Adj R-Squared value of 0.7539 as well as the Predicted R-Squared value of 0.6209 compared to linear and 2 factorial (2F1) models. Also the lack of fit value (0.8861) for quadratic model exceeded the 5 % for the quadratic model which is one of the major criteria for a model to fit. Likewise the qudratic model has the highest adequate precission of 7.132 copmapred to other models indicating a good signal to noise ratio since a ratio greater than 4 is desired and can be used to navigate the design space.

Also shown in Table 5, is the ANOVA of the selected quadratic model based on the p-value (0.0021) being less than 0.05 hence the model is significant and the confidence level is 95 % while the lack of fit is insignifficant thus confirming the adeuacy of the quadratic model selected.

Table 5 :ANOVA for Response (pH) Surface Quadratic Model for Cassava Starch Modification

Model	Fvalue	Pvalue	Remarks
	4.47	0.0021	Significants
A	4.02	0.0728	Insgnificant
B	6.81	0.0261	Significant
C	7.15	0.0233	Significant
A^2	30.73	0.0002	Sgnificant
B^2	7.33	0.0221	Sgnificant
C^2	11.67	0.0066	Significant
AB	0.14	0.7165	Insgnificant
AC	6.36	0.0303	Significant
BC	0.035	0.8555	Insgnificant
Lack of fit	0.31	0.8861	Insignificant

The Prob > F of 0.0021 , a value less than 0.0500 indicate model terms are significant. In this case B, C, A^2, B^2, C^2 and AC are significant model terms. However, this does not mean the model terms A, AB and BC are not important in this study but it shows that, the model terms B, C, A^2, B^2, C^2 and AC contributed more (enhancing the pH) in the modification of cassava starch as compared to model terms A, AB and BC.Doubly all the three factors considered ehnace the pH of the cassava starch modification.

Mathematical model of pH for cassava starch modification.

The mathematic model developed for this response is a quadratic model as represented in Equation 2. The model was adopted because of its high value of R-squared (0.8705) and the insignificant value of lack of fit of 0.8861 compared to other types of model like linear, 2F1 and cubic.

pH= $+8.12+0.41\times A-0.53\times B+0.55\times C+1.11\times A^2+0.54\times B^2+0.68\times C^2-0.100\times AB-0.87\times AC+0.050\times BC$ **2**

Where A= Sodium hydroxide catalyst (g), B= reaction temp.(^{o}C) and C= reaction time (min). A, B and C represent the liner terms, A^2, B^2 and C^2 denote the quandratic terms while AB, AC, and BC are the products terms. Equation 2 can be use to predict the pH for cassava starch modification prior to laboratory experiment at different conditions of the parameters.

Predicted verses Actual Yield Relationship

Figure 3 shows the relationships between the predicted and actual responses (pH). It presented the design expert parity plot of the predicted pH of cassava starch modification against their respective actual responses for the evaluation and optimization of process parameters of cassava starch modification.

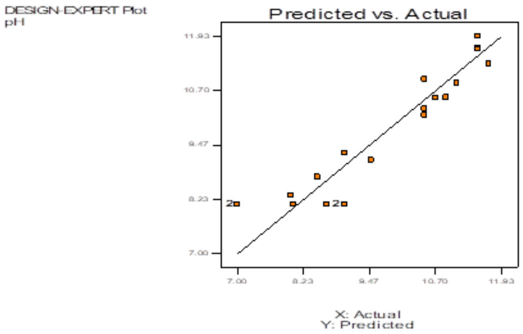

Figure 3: Correlation between Actual (experimental) and predicted value of gelatinazation temperature of cassava starch modification.

Figure 3 is indicative of a strong correlation between the actual (experimental) and predicted values: suggesting the model is significant.

Interactive Effects of the Process Parameters on pH of Cassava Starch Modification.

The interaction of the process variables on pH are represented by Figures 4a – 4c. It shows the 3D-Surface diagram of significant model term interactions among the variables varied and the response (pH). The 3D response surface plots generally illustrate the effects of the independent variables and their interactive effects on the responses. The 3D plots shown in Figures 4a, 4b and 4c illustrate the interactive effects of catalyst - temperature, catalyst-reaction time and temperature - reaction time on pH response respectively.

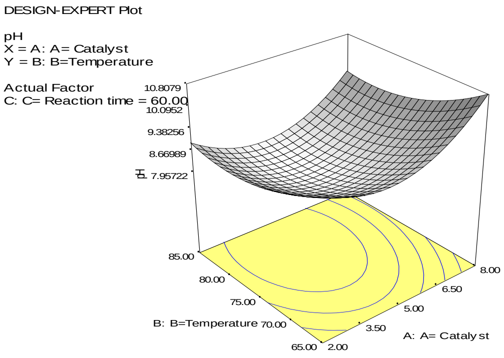

Figure 4a: 3D Response Surface Plot for temperature-catalyst interaction on pH of cassava starch modification.

Catalyst and reaction time show a good interaction on pH. It was observed that as both catalyst and reaction time increases, it leads to a corresponding increase in pH. Also, the variations in pH showed that the interactions between the variables are significant, as evidenced from the elliptical nature of the plot. Also, the variations in pH showed that the interactions between the variables are significant, as evidenced from the elliptical nature of the plot.

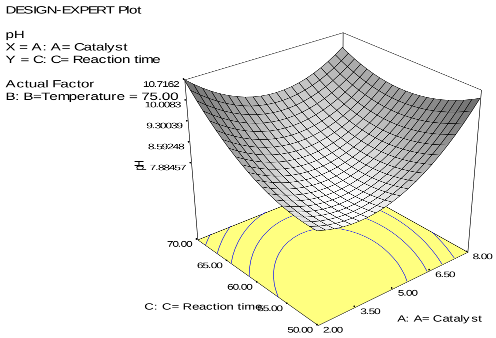

Figure 4b: 3D Response Surface Plot for catalyst–reaction time interaction on pH of cassava starch modification.

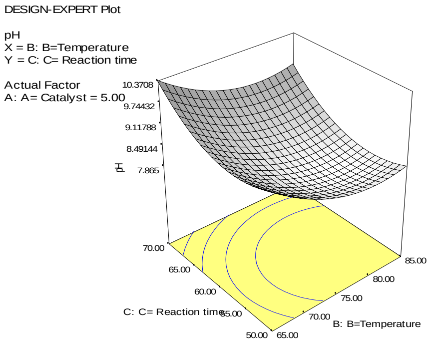

Figure 4c: 3D Response Surface Plot for temperature -time interaction on pH of cassava starch modification.

The pH of a substance is the degree of acidity or alkalinity of that substance. Starch pastes from cross-linked starches have been reported to be less likely to break down with extended cooking times and possess increased acidity or severe shear (Akpa and Dagde, 2012). Hence, modification increased the pH of the starch to about 7.00 to 11.7 this is because the modification was done with sodium acetate which neutralized the adipic acid and fumaric acid respectively. It is necessary that the pH of starch tends towards neutrality (Chung-wai Chiu and Daniel, 2009) so that it can be used in industries where a change in the pH of products is not desired. This, modification by cross-linking achieved with improved pH values of the native starch to desirable limits of neutrality. Although there was an improvement in pH compared to the results of Akpa and Dagde (2012) who obtained a pH of 5.14 that tends to be more acidic.

Optimization of Process Parameters for gelatinization Temperature and pH of Cassava Starch Modification
Having carried out statistical analysis on the input responses, optimization was done by setting goals, constraint for the investigated parameters and responses. A numerical optimization technique using the desirability approach was employed to develop new process conditions with desired responses. The selection of the optimum condition was based on the criteria for obtaining starch with maximum gelatinization temperature, neutral pH while other factors (catalyst, reaction temperature and reaction time) were set in range as shown in Table 6.

Table 6: Optimization criteria (goal and constraint) of CCD on gel. Temperature and pH of Cassava Starch Modification.

FACTORS/ RESPONSES	**GOALS**	**LOWER LIMIT**	**UPPER LIMIT**
A	Is in range	2.0	8.0
B	Is in range	65	85
C	Is in range	50	70
Gel. Temp.	Maximized	69	73.85
pH	Is Target=7	7.00	11.7

At these process conditions, the starch obtained will have the corresponding properties. It was desired that gelatinization temperature should be maximum since high gelatinization temperature means that high amount of heat energy will be required to break the intermolecular bonds in the starch. Catalyst, temperature and time were desired to be within range of experimental investigation. This is because it is preferred the best results should be obtained. It was suspected that altering all inputs to minimum because of cost of catalyst and energy might compromise the desired quality of the obtainable starch.

Ten (10) optimized solutions were predicted and five (5) out of these solutions were selected and validated in laboratory to see how well the model predict the magnitude of the responses (gelatinization temperature and pH). The solution for optimized condition is shown in Table 7.

Table 7: Solution for optimized process conditions and responses for cassava starch modification

Parameters	**Catalyst gram**	**Temperature (^oC)**	**Time (min)**	**Gelatinization Temperature (^oC)**	**pH**	**Desirability**
Predicted Solution	4.16	68.77	50	74.39	9.85	1.00
Validated solution	4.16	68.77	50	74.00	8.00	1.00

The results of the validated experiment as shown in Table 7 and the predicted and actual value are in closed range suggesting that the quadratic model is adequate and successfully predicted the responses of gel temperature and pH for the cassava starch modification. The difference between the predicted and validated gel temperature of 0.39% and that of pH of 1.85% is due to experimental error.

CONCLUSION

The modified starches showed improvements in functional properties in pH and gelatinization temperature. This starch had fairly neutral pH, the high gel temperature. The increased gel temperature gives stronger inter-molecular bonds and makes this starch more resistant to shear stress and retrogradation hence it is suitable for application in food industry. A full factorial design using Central Composite design (CCD) was used to study the effect of three process parameters on two responses. Process parameters considered were Catalyst quantity, Reaction temperature and Reaction time. Responses considered were gelatinization temperature and pH. ANOVA results of both gel temperature and pH revealed that all terms of both regression Equations (1) and (2) were significant except A, A^2 and B^2 terms which had negligible effect on gel temperature and A, AB and BC terms had little effects on pH respectively. This is because increasing catalyst quantity beyond 4.5 g had no significant effect. From the results, the optimal conditions of the modified cassava starch were determined to be at a reaction temperature of 68.77°C, 4.16 g of sodium hydroxide catalyst and reaction time of 50 min with a gel temperature of

74°C and pH of 8.00. Higher gel temperature and neutral pH enhanced the modification of cassava starch (as high gel temperature is required to break the intermolecular bonds in the starch) while a pH close to neutrality (that is pH of 7) neutralizes the effect of adipic acid and fumaric acid present in the modified cassava starch. Finally, the factors upon which the modification of cassava starch depends are largely Temperature and Reaction Time.

REFERENCES

Abbas K. A., Sahar K. Khalil, Hussin *A. S. M. M* (2010) Modified Starches and Their Usagesin Selected Food Products: A Review of Studies. *Journal of Agricultural Science*, 2(2): 90-100.

Ačkar, Đ., Babić, J., Jozinović, A., Miličević, B., Jokić, S. and Miličević, R., (2015). Starch Modification by Organic Acids and Their Derivatives: A Review. *Molecules*, 19554-19570.

Adzahan, N. M. (2002). Modification on wheat, sago and tapioca starches by irradiation and its effect on the physical properties of fish cracker (keropok). Food Technology. Selangor, University of Putra Malaysia. *Master of Science*: 222.

Akpa, Jackson Gunorubon and Dagde, Kenneth Kekpugile (2012). Modification of Cassava Starch for Industrial Uses. *International Journal of Engineering and Technology (IJET)* – Vol. 2 No. 6, ISSN: 2049-3444 © 2012 – IJET Publications UK. All rights reserved.

Ameh A. O., Abutu D., Andoor S. (2018) Effect of Process Parameters on The Viscosity and pH of Acetic Anhydride Modified Cassava Starch, *Nigerian Journal of Pharmaceutical and Applied Science Research*, 7(1): 22-28.

Barrios, S., Contreras, J., Lopez-Carresquero, F., and Muller, A. (2012). Chemical modification of cassava starch by carboxymethylation reactions using sodium monochloro acetate as modifying agent. *Revista de la Facultad de Ingenieria*, 97-105

Bjorck I., Eliasson A.-C., Drews A., Gudmundsson M., And Karlsson R. (1990) Some Nutritional Properties of Starch and Dietary Fiber in Barley Genotypes Containing Different Levels of Amylose, Cereal Chem. 67(4): 327-333.

Chung-wai, C., and Daniel, S. (2009). *Starch: Chemistry and Technology, 3rd Edn.* Elsevier Inc. p 629 – 655.

Delcour, J. A., Vansteelandt, J., Hythier, M. C., Abecassis, J., Sindic, M., and Deroanne, C. (2000). Fractionation and reconstitution experiments provide insight into the role of gluten and starch interactions in pasta quality. *J. Agric. Food Chem., 48*, 3767-3773.

Hermansson, A. M., and Svegmark, K. (1996). Developments in the understanding of starch functionality. *Trends Food Sci. Technol., 7*, 345.

Jerachaimongkol, S., Chonhenchob, V., Naivikul, O., and Poovarodom, N. (2006). Modification of Cassava Starch by Esterification and Properties of Cassava Starch Ester Films. *Natural Science*, 148-151.

Miyazaki, M. R., Hung, P. V., Maeda, T., and Morita, N. (2006). Recent advances in application of modified starches for breadmaking. *Trends in Food Science and Technology*, 17(2006): 591-599.

Ogunmolasuyi, M. A. (2015). Modification of Starch Extracted from Cassava with Acidifed Ethanol. *British Journal of Pharmaceutical Research*, 1-7.

Said K.A.M and Amin M.A.M (2015) Overview on the Response Surface Methodology (RSM) in Extraction Processes, *Journal of Applied Science & Process Engineering,* 2(1): 8 – 17.

Sobkowska, E. (2001). Skrobia i glikogen oraz produkty skrobiowe [Starch and glycogen and starch products]. In J. Gawęcki (Ed.), *Współczesna wiedza o węglowodanach* [Contemporary knowledge on carbohydrates]. Poznań [in Polish]: Wyd. AR.