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# Hydroxypropylation of Saba Banana Starch

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**Abstract.** This aim of this study is to investigate the effects of three reaction variables on the hydroxypropylation of Saba banana starch. The variables were pH (10, 11 and 12), amount of propylene oxide (5, 10 and 15% v/w, starch d.w.b ) and temperature (35, 40 and 45$^{o}$C). Response Surface Methodology (RSM) using Central Composite Design was employed to explore the effect of the three variables on the Molar Substitution (MS), pasting profile, freeze-thaw stability and thermal properties of the modified starch. Increasing the propylene oxide, pH and temperature promoted higher level of substitution. All variables resulted significant changes ($p<0.05$) on the pasting parameters and thermal behaviour of banana starch. Good negative correlation was observed between MS and pasting temperature (r=-0.727**). Starch gel syneresis during freeze-thaw cycles was reduced by increasing pH and propylene oxide ($p<0.01$) but increased with temperature ($p<0.05$). Significant correlation between MS with onset temperature (r=-0.622**) as well as peak temperature (r=-0.713**) was detected. In general, propylene oxide exerted the most pronounced effect on hydroxypropylation of Saba banana starch as compared to reaction pH and temperature. The regression equations obtained were used to predict the optimal reaction condition by specifying the desirable responses and their limits as criteria for optimization.

**Keywords:** hydroxypropylation, banana starch, pasting, thermal properties, freeze-thaw stability

## 1. Introduction

Starch is a common raw material that has economic and commercial values in both food and non-food industry. Starch is widely distributed in seeds, roots, tubers, stems, leaves, fruits and even pollen [1]. The demand of starch has increased because it is cheap, readily available, renewable, biodegradable and is also a biocompatible polymer [2, 3]. The ever-increasing demand for starch becomes reasonable to come up with new starch sources, particularly from the underutilized resources such as banana. Several studies reported that green bananas may contain up to 70% (d.w.b.) of starch [4].

Saba banana (*Musa balbisiana*) is a cooking banana that is abundantly found in the state of Sabah. This kind of banana is usually steamed to eat, or fried to produce banana fritters (*pisang goreng*), or made into banana chips (*kerepek*). Besides local consumption, part of this banana is exported to the neighbouring country, Brunei Darussalam. The cost value of *Saba* banana is as low as RM 1 per kilogram. Therefore, it creates a potential for extracting starch from this easily available, underutilized, and cheap source. It is well established that starch in native form lack of desirable functionality for industrial applications. A few studies have proven that starch from banana shares the same problem by exhibiting low solubility [5]; restricted swelling power [6]; on top of high syneresis and low stability in refrigerated and freezing cycles [7, 8].

Hydroxypropylation is an etherification process that is commonly used to modify food starch. Among the benefits of hydroxypropylation is it improves the swelling capacity, clarity, syneresis, freeze-thaw stability and enzymatic digestibility of native starch [9]. The objective of this study was to investigate the effects of a few hydroxypropylation parameters (pH, temperature and quantity of propylene oxide) on the degree of modification and physicochemical properties of Saba banana starch. The data obtained provides information on the suitable reaction combinations to prepare hydroxypropylated banana starch with desirable properties.

## 2. Material and Methods

### 2.1. Material and Sample Preparation

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Unripe and green peel Saba bananas (*Musa balbisiana*) were purchased from an orchard located in Keningau, Kota Kinabalu. Isolation of banana starch was performed according to Nimsung and co-workers [10] with slight modifications. Native banana starch was then hydroxypropylated [11].

### 2.2. Experimental Design

A Central Composite Design (CCD) study was conducted to determine the relative contributions of three independent variables on hydroxypropylation of *Saba* banana starch. The three independent variables were the amount of propylene oxide (3 mL, 6 mL and 9 mL), pH (pH 10, 11 and 12) and temperature (35˚C, 40˚C and 45˚). Each independent variable was coded at three levels between -1 and +1 and a total of 20 experimental run was generated.

### 2.3. Moisture Content and Molar Substitution

Moisture content of starch was determined using a Halogen Moisture Analyzer (Mettler Toledo, HG53, USA). Extent of hydroxypropylation was measured according to Ratnayake and Jackson [12].

### 2.4. Pasting Properties, Thermal Properties and Freeze-Thaw Stability

Pasting properties of starch was investigated by a Rapid Visco Analyzer (RVA) (Newport Scientific, Model 4) interfaced with a personal computer equipped with Thermocline Windows software version 3 (TCW3). Gelatinization of starch was determined using a DSC (Differential Scanning Colorimeter – Perkin Elmer, Diamond DSC, USA) equipped with a thermal analysis data system (Pyris Manager). Indium was used to calibrate the DSC. Measurements were made on starch:water (1:4) (w/w). The samples were scanned from 30°C to 100°C at 10°C/minute. An empty pan was used as the reference for all measurements. The freeze-thaw stability of starch was investigated by slight modification of reported method [13, 14] by subjecting the samples to five freeze-thaw cycles (24 hrs at -20$^{o}$C 2 hrs at ambient temperature).

### 2.5. Statistical Analysis

Response Surface Methodology was used to design experiment, model and optimized selected response variables. The statistical software package (Design-Expert ver 6.0, Stat-Ease Inc., Minneapolis, USA) was used for regression analysis of experimental data and to plot response surface. Experimental data were fitted to the second-order polynomial model and regression coefficients obtained. The model was simplified by dropping terms which were not statistically significant ($p>0.05$) by analysis of variance (ANOVA). The response surface and contour plots were generated by holding a variable constant in the second-order polynomial model.

## 3. Results and Discussion

### 3.1. Sample Yield and Moisture Content

Dried banana flour recovered from fresh Saba banana pulp was 39.145 ± 0.007%. Meanwhile, the starch that was extracted from the banana flour was 48.07 ± 0.01%. The yield obtained after hydroxypropylation was only 2.7-3% due to the lost during modification and drying. The moisture content of Saba banana starch was 11.4 ± 0.1%, whereas the moisture content of hydroxypropylated banana starches ranged between 7.3 - 10.8 %.

### 3.2. Molar Substitution

The molar substitution (MS) of hydroxypropylated samples fell between 0.059 – 0.148. The pH, propylene oxide and temperature were found to increase the MS in a linear manner ($p<0.05$) with propylene oxide exerted the most pronounced effect (Fig. 1). Higher concentration of propylene oxide resulted greater rate of collision between the starch alkoxide and the reagent in the proximity of starch granule [3] that caused higher degree of substitution. Whereas increase in temperature and pH induced the starch granule to swell more, exposing more hydroxyl groups in starch to be more accessible to base catalyzes reactions [15]. Alkaline treatment could induce swelling by ionizing starch hydroxyl groups at higher pH [16], which is essential for the substitution reaction to take place in granular starch. The reaction efficiency of hydroxypropylation depends on the diffusion or penetration of the alkaline catalyst and the etherifying agent into the starch granules and the probability of reactivity between the starch alcoholate nucleophile and the propylene oxide molecule [17].

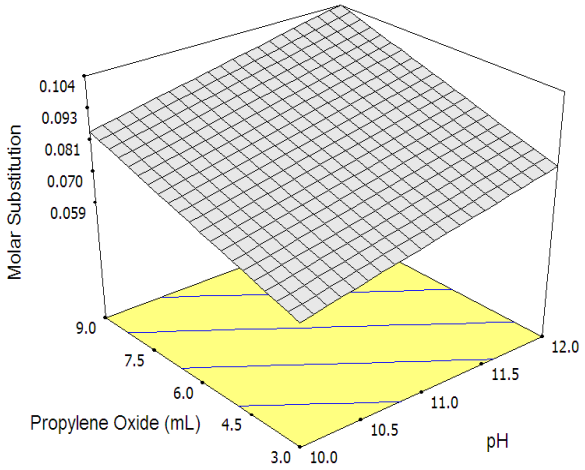


Fig. 1: Response surface plot for molar substitution at 40°C.

## 3.3. Pasting Properties

Table 1 shows that pasting temperature of hydroxypropylated banana starch decreased linearly with increasing amount of propylene oxide ($p<0.01$). Pasting temperature of starch samples was also found negatively correlated with MS (r=-0.727**), meaning the higher MS, the lower pasting temperature. Hydroxypropylated starch is hydrophilic in nature and this facilitates penetration of water into the starch granules during gelatinization [3]. Results also show that the three variables studied have greater influence on the setback of banana starch ($R^2$=0.97), whereby starch retrogradation tendency decreased linearly with pH and propylene oxide and increased quadratically with temperature ($p<0.01$). The bulky hydroxypropyl groups introduced during the modification prevented the structural realignment of leached amylose molecules after gelatinization [9], thus minimized the retrogradation. Various studies reported decrease of setback in hydroxypropylated starch with increasing of MS [3, 14, 18]. However, only weak correlation was found between these two variables in this study (r=-0.556**). Peak time was not affected by the independent variables ($p>0.05$).

Table 1: Results of analysis of variance (ANOVA) for pasting properties of hydroxypropylated Saba banana starch

| Factor | Pasting and Thermal Parameters | | | | | |
|---|---|---|---|---|---|---|
| | Pasting Temperature (°C) | Peak Viscosity (cP) | Setback (cP) | Onset Temperature (°C) | Peak Temperature (°C) | $\Delta H$ (J/g) |
| Intercept | 78.24* | 4695.01 | 992.62** | 69.64* | 72.93* | 1.28 |
| Linear | | | | | | |
| A | -0.76 | -263.23 | -339.04** | -0.26 | -0.40 | -0.29 |
| B | -1.77** | 348.06* | -484.13** | -1.73** | -1.72** | -0.32* |
| C | -0.17 | -165.48 | 65.06 | 0.29 | 0.007 | 0.33 |
| Quadratic | | | | | | |
| $A^2$ | - | -399.63* | 89.81* | 1.08* | 0.94* | 0.002 |
| $B^2$ | - | 134.64 | 122.57** | -0.06 | -0.46 | 0.09 |
| $C^2$ | - | -97.11 | 201.82** | 0.37 | 0.46 | 0.73** |
| Interaction | | | | | | |
| AB | - | 238.42 | -5.67 | -0.74 | -0.75 | 0.26 |
| AC | - | 41.00 | 153.33** | 0.59 | 0.40 | 0.14 |
| BC | - | -50.33 | -192.58** | -0.39 | -0.43 | 0.21 |
| $R^2$ | 0.6182 | 0.6786 | 0.9739 | 0.7623 | 0.7694 | 0.7934 |

* Significant at $p<0.05$; ** significant at $p<0.01$
A – pH; B – amount of propylene oxide; C – temperature

## 3.4. Thermal Properties

The quadratic model was found to best fit the data obtained for onset temperature ($T_o$), peak temperature ($T_p$) and enthalpy of gelatinization of modified samples (Table 1). The endset temperature was not affected by the independent variables (data not shown). When higher amount of propylene oxide was used in the

modification reaction, both $T_o$ and $T_p$ were reduced. On the other hand, these temperatures dropped when the medium of reaction was increased from pH10, and gradually increased from pH11 to pH12 (figure not shown). In agreement with previously reported data, the $T_o$ and $T_p$ were negatively correlated to MS (r=-0.622** and r=-0.713** respectively). The addition of hydroxyrpopyl groups on starch polymer backbone allowed higher flexibility and thus led to lower melting temperature [1]. The disruption of hydrogen bonds between starch chains in the amorphous regions during modification could most probably contributed to lowering of gelatinization temperature [14]. Enthalpy of gelatinization ($\Delta H$) of hydroxypropylated banana starch was also significantly affected by the quantity of propylene oxide and temperature used during modification. Generally modified samples exhibited lower $\Delta H$ than native starch due to loss of crystallinity [14] by hydroxypropylation.

### 3.5. Freeze-thaw Stability

Among the independent variables, the increase of propylene oxide during hydroxypropylation was evident to substantially improve the freeze-thaw stability of Saba banana starch (data not shown). Native starch reported 21.3% and 23.5% or syneresis in the first and fifth cycle respectively. Whilt the most stable hydroxypropylated sample exhibited negligible syneresis in the first cycle and only 3.6% syneresis in the fifth cycle. Other variables were also significantly affected the freeze-thaw stability of the sample. Starch gel syneresis during the freeze-thaw cycles was reduced by increasing pH and propylene oxide ($p<0.01$) but increased with temperature ($p<0.05$). Freeze-thaw stability data was well correlated with values of setback (r=0.925**).

### 3.6. Optimization

To optimize the hydroxypropylation of Saba banana starch, four responses with desirable criteria were chosen to be limiting factor. MS was selected with the intention to achieve the highest possible value; while peak viscosity was set to be higher than the native counterpart i.e. 5000 cP (which is a normal characteristic for hydroxypropylated starch). The values for setback and syneresis (freeze-thaw stability) were set to attain the lowest possible value. Based on the numerical method, the optimum condition to prepared hydroxypropylated Saba banana starch with desirable properties was identified to be at pH12 and 42.5$^{o}$C using 9 ml (15% d.w.b starch) of propylene oxide.

## 4. Conclusion

Among three variables investigated, quantity of propylene oxide used in the reaction condition exerted the most pronounced effect on hydroxypropylation of Saba banana starch as compared to reaction pH and temperature. Hydroxypropylation improved the freeze-thaw stability and tendency for retrogradation of Saba banana starch, besides lowered the pasting, gelatinization temperature and enthalpy. Within the error of this experiment, the optimum condition to hydroxypropylated Saba banana was predicted and yet to be validated in future research.

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