UNIVERSITI PUTRA MALAYSIA

PREPARATION AND CHARACTERIZATION OF HYDROXYPROPYLATED SAGO STARCH

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PREPARATION AND CHARACTERIZATION OF HYDROXYPROPYLATED SAGO STARCH

By

MALINI D/O SAILIN @ STALIN

Thesis Submitted in Fulfilment of the Requirement for the Degree of Master of Science in the Faculty of Food Science and Biotechnology, Universiti Putra Malaysia
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THIS THESIS IS SPECIALLY DEDICATED TO MY

BELOVED MOTHER ,

WHOM I SO DEARLY LOVE AND MISS.

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LIST OF ABBREVIATIONS

%	percent
ppm	parts per million
°C	degree celcius
<	less than
>	more than
wt%	weight percent
w/w	weight/ weight
w/v	weight/ volume
v/v	volume / volume
μ	micron
μl	microliter
ml	milliliter
g	gram
μg	microgram
mg	milligram
hr	hour
min	minute (s)
BU	Brabender unit

Abstract of the Thesis Presented to the Senate of Universiti Putra Malaysia in Fulfillment of the Requirements for the Degree of Master of Science

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July 1998

Chairman : Dr. Sharifah Kharidah Syed Muhammad

Faculty : Food Science and Biotechnology

Sago starch was hydroxypropylated with propylene oxide at 40°C in an alkaline medium containing sodium sulphate. In this study, the level of propylene oxide (0-14%), sodium hydroxide (0-2%), sodium sulphate(0-30%), reaction time (8-24 hrs) and reaction temperature (20-50°C) were varied to produce various samples of hydroxypropylated sago starch. The molar substitution (MS), which is the amount of substitution that has occured during hydroxypropylation and the pasting properties were measured for each sample. Increase in the amount of propylene oxide, sodium sulphate and sodium hydroxide, reaction temperature and reaction time progressively increased the molar substitution of the modified

starch. Increase in the amount of propylene oxide from 0% to 14% increased the peak viscosity and the hot paste viscosity. However, the gelatinization temperature, the consistency of the hot paste viscosity after holding at 95°C and the setback value was decreased. Highest molar substitution of 0.41 was observed at 1.5% sodium hydroxide at which the highest peak viscosity and breakdown with the lowest setback value was also observed. The peak viscosity, cold paste viscosity and breakdown was highest at 25% sodium sulphate concentration. The maximum level of hydroxypropylation was observed at 10% propylene oxide, 1.5% sodium hydroxide, 25 % sodium sulphate, at 24 hours reaction time and at 40°C.

In another study, hydroxypropylated sago and corn starch were prepared by reaction with propylene oxide in an alkaline medium containing sodium sulphate at 40°C and its physicochemical characteristics were studied and compared with the native starches. Some of the physicochemical characteristics evaluated were : pasting properties, molar substitution, swelling power and solubility, water holding capacity, gel strength, sediment value, light transmittance, acid and heat stability, starch damage and freeze-thaw stability. In addition, the morphology of the starch granules were also observed.

Hydroxypropylation increased the swelling power and solubility, water holding capacity and freeze-thaw stability of both starches. The swelling power of sago starch increased from 33.69 ± 3.92 % to 60.44 ± 2.72% when it was hydroxypropylated. As for corn starch the swelling power increased three times higher from 8.67 ± 0.056 % for native corn to 24.99 ± 1.039% for hydroxypropylated corn. The water holding capacity of native sago was 11.00 ± 0.12% and it further increased to 17.23 ± 0.25% when it was hydroxypropylated. As described in the literature, it was found that hydroxypropylation increased the freeze-thaw stability of the sago and corn starches. The gel strength of the starches decreased when it was hydroxypropylated and the values were 56.5 ± 2.12%, 11.5 ± 0.71%, 84.5 ± 2.12% and 46 ± 1.42% for native sago, hydroxypropylated sago, native corn and hydroxypropylated corn respectively. The percentage of starch damage was only 0.02% when sago starch was hydroxypropylated but for corn the starch damage was 2.64% when it was hydroxypropylated. The sediment value of native sago (96.25 ± 1.0%), was the highest followed by hydroxypropylated sago starch (94.54 ±0.57%), hydroxypropylated corn starch (67.17 ±0.57%) and native corn starch (27.0 ± 2.6%) respectively. Both starches when hydroxypropylated showed no improvements in their acid and heat stability.

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PENYEDIAN AND SIFAT-SIFAT KANJI SAGO YANG DIHIDROXIPROPILKAN

Oleh

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Kanji sago telah dihidroxipropilkan dengan propilin oksida pada suhu 40°C didalam medium beralkali yang mengandungi nitrium sulfat. Dalam penyelidikan ini, amaun propilin oksida (0-14%), nitrium hidroksida (0-2%), nitrium sulfat (0-30%), masa tindakbalas (8-24 jam) dan suhu tindakbalas (20-50°C) telah di kaji untuk menghasilkan sampel kanji sago terhidroxypropil yang berbagai jenis. Gantian Molar (MS) iaitu amaun gantian yang telah dialami oleh kanji semasa proses hidroxipropil dan sifat 'pasting' telah diukur untuk setiap sampel. Peningkatan amaun propilin oksida, nitrium hidroksida, nitrium sulfat, masa tindakbalas dan suhu tindakbalas telah meningkatkan gantian molar kanji yang

telah ubahsuai. Peningkatan amaun propilin oksida daripada 0% kepada 14% telah meningkatkan puncak pengelatinan dan kelekitan gel panas. Walaubagaimanapun, suhu pengelatinan, konsistensi gel panas selepas 95°C dan nilai penyejukan telah berkurang. Gantian molar yang paling tinggi iaitu 0.41 telah diperhatikan pada 1.5% nitrium hidroksida dan pada masa yang sama puncak kelikatan yang paling tingi dan ketidakstabilan gel serta nilai penyejukan yang paling rendah juga telah diperhatikan. Puncak kelekitan, kelekitan gel sejuk-beku dan ketidakstabilan gel telah diperhatikan paling tinggi pada kepekatan 25% nitrium sulfat. Tahap proses hydroxipropil yang paling maximum diperhatikan pada 10% propilin oksida, 1.5% nitrium hidroksida, 25% nitrium sulfat, pada masa reaksi selama 24 jam dan pada suhu reaksi 40°C.

Dalam penyelidikan yang lain, kanji sago dan jagung terubahsuai telah disediakan dengan propilin oksida, di dalam medium beralkali dengan kehadiran nitrium sulfat pada suhu 40°C dan sifat-sifat kanji tersebut telah dikaji dan dibandingkan dengan kanji jenis asli. Sifat-sifat yang telah dikaji adalah : sifat 'pasting', gantian molar, tahap proses penambahan dan kelarutan butir kanji, tahap proses penyimpanan air, kekuatan gel, nilai sedimentasi, kadar penyerapan cahaya, kestabilan kanji terhadap asid dan suhu panas, kestabilan sejuk-beku cair kanji, kerosakan butir kanji serta morfologi butir kanji.

Proses hydroxipropil telah meningkatkan saiz granul kanji serta kelarutannya, tahap proses pengikatan air dan kestabilan sejuk-beku cair kanji. Tahap proses pengembangan saiz butir kanji telah bertambah dari 33.69 ± 3.92 % ke 60.44 ± 2.72% bila dihidroxipropilkan. Bagi kanji jagung, kadar pengembangan saiz butir kanji meningkat tiga kali lebih tinggi daripada 8.67 ± 0.056 % bagi kanji jagung asli ke 24.99 ± 1.039% bagi kanji jagung yang telah dihydroxipropil. Kadar pengikatan air kanji sago telah bertambah dari 11.00 ± 0.12% kepada 17.23 ± 0.25% bila dihydroxipropil. Sebagaimana yang didapati daripada rujukan, kestabilan sejuk-beku kanji sago dan jagung terhydroxipropilasi telah meningkat berbanding dengan kanji asli. Kekuatan gel telah berkurang dari 56.5 ± 2.12% bagi kanji sago asli ke 11.5 ± 0.71% bagi kanji sago dihydroxipropil dan 84.5 ± 2.12% bagi kanji jagung asli ke 46 ± 1.42% bagi kanji jagung terhydroxipropil. Peratus kerosakan kanji sago apabila dihidroxypropilkan adalah sebanyak 0.02% manakala bagi kanji jagung adalah sebanyak 2.64% bila dihydroxipropilkan. Nilai pemendakan didapati paling tinggi bagi kanji sago asli (96.25 ± 1.0%), diikuti oleh kanji sago dihydroxipropil (94.54 ± 0.57%), kanji jagung dihydroxipropil (67.17 ± 0.57%) dan kanji jagung asli (27.0 ± 2.6%). Kedua -dua kanji sago dan jagung tidak menunjukkan apa-apa perubahan dalam kestabilan asid dan suhu panas bila dihydroxipropilkan.

CHAPTER 1

GENERAL INTRODUCTION

Hydroxypropylation is a stabilisation process, whereby blocking agents are introduced into the starch granules. Hydroxypropylated starches are obtained by etherification of starch with monofunctional reagents such as propylene oxide. During this process the hydroxypropyl groups reacts with the starch granules and binds itself to the starch molecules thus introducing a "blocking action" which hinders the association of the starch molecules.

The introduction of the hydroxypropyl groups weakens the bond strength of the starch molecule, by reducing the tendency for hydrogen bonds to take place inter- or intra- molecularly. Therefore the ability for the starch chains to align closely with one another is reduced. This leads to an increase in the accessibility of the starch granules to water, allowing the starch to remain hydrated with high water binding capacity producing starches with good texture, clarity and stability.

Hydroypropylation can be carried out in an aqueous reaction medium whereby propylene oxide is reacted with the starch granules in the presence of an alkaline metal hydroxide and swelling suppressing salts. The starch slurry is

reacted at a pH of about 10 to 12 for a period of 5 to 24 hours at 35°C to 45°C. This produces starch granules with high integrity and the final product be easily recovered from any unwanted by-products by washing and filtering. or in a non-aqueous reaction medium.

In the non-aqueous reaction, hydroxypropylation is conducted in a limited amount of moisture. Therefore the propylene oxide is directly reacted to the starch granule in the gaseous or liquid state known as the "dry reaction" or the starch is slurried into an organic solvent and reacted with propylene oxide in the presence of an alkaline medium, a process better known as the " organic - liquid slurry reaction ". The advantage of this process is that very high level of substitution can be achieved in a short period of time at a higher temperature.

In the most common procedure, hydroxyropylation is prepared by reacting the granular starch molecules with propylene oxide in the presence of an alkaline medium and swelling suppressing salts. The aqueous starch slurry is first reacted with the alkaline catalyst and the swelling suppressing salts before the addition of propylene oxide. The starch slurry is then reacted at a temperature of about 35°C to 45°C for 24 hours at pH 6.5. The available methods found in the literature can vary in the amount of propylene oxide, sodium sulphate, sodium hydroxide, reaction time and reaction temperature, all depending on the level of hydroxypropyl substitution needed for the end

product (Smolka and Alexander, 1985; Tuschhoff, 1969; Goldstein, 1966; Caldwell and Martin,1957; Hjermstad, 1956; Katt, 1986).

Hydroxypropylated starches exhibit desirable properties highly required in the food and food based industries as well as in the paper and textile industries. The most significant quality of the hydroxyproylated starch when compared to the native starch is that it is freeze-thaw stable with reduced rate of syneresis and retrogradation. This prolongs the shelf-life of the food products. Hydroxypropylation also produces starches with excellent clarity and paste property , better film clarity and decreases the gelling of cooked pastes. The granule size, swelling power, solubility and water binding capacity are also increased with the increase in hydroxypropylation.

The sago palm (*Metroxylon sp*) tree is a native plant of the East Indies, grows wildly in swampy areas and dies immediately after flowering only once. The sago palm industries should be considered economically favourable since it needs no replanting, as sago palm produces basal off-shoots (suckers) with a harvestable period of only about two years (Radley, 1976; Azudin, 1993; Schuiling *et al*., 1993). Sago starch is obtained from sago palm.

The properties of sago starch are comparable to that of potato, corn, cassava and sweet potato starches. Its pasting profile is similar to that of potato starch with a high peak viscosity and a high breakdown. Its amylose content and