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A comparative account of conditions of synthesis of hydroxypropyl derivative from corn and amaranth starch

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Abstract

Conditions for the preparation of hydroxypropyl derivatives of corn and small sized (1–2 μm) waxy amaranth starch were compared. The synthesis was followed in terms of molar substitution (MS). The parameters optimized included propylene oxide concentration, reaction time, starch:water ratio and the quantity of alkali required in the process. The two starches differed considerably, and were unique in their own respect. The optimization conditions of one starch type cannot be extended to another. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Hydroxypropyl derivative; Corn starch; Amaranth starch

1. Introduction

The reaction of starch with etherifying reagent, propylene oxide, results in the introduction of hydroxypropyl group onto the polymeric chain of starch. The alignment of polymers that causes a change in the structure of the food product, leading to an opaque, gelled, and/or chunky texture with “weeping” of liquid from the gel. This is termed as retrogradation, and is undesirable in many food applications (Osman, 1967). Etherification process is mainly done to inhibit retrogradation (Dias, Tekchandani & Mehta, 1997). The reactive nature of propylene oxide is due to its highly strained three-membered epoxide ring. Bond angles in the ring average 60° resulting in a very unstable (reactive) molecule.

In substitution reactions by etherification, the starch molecule should first be activated to make the O–H bond nucleophilic and to facilitate the formation of starch–O^-. Alkaline reagents in this regard are excellent as catalysts. This is followed by reaction of starch–O^- and propylene oxide which results in bimolecular substitution producing hydroxypropyl starch (Tuschhoff, 1987). The efficiency of hydroxypropylation is greatly influenced by the reagents used. Etherification occurs mainly in the amorphous region of the starch granule. It is reported to affect the conformation of amylose molecules, and holes are known to appear at the surface of granule (Zhou, Zhang & Fan, 1991). The reaction efficiency is defined as the percentage of the reagent reacted or substituted upon starch. The remaining reagent is consumed to form by-products. The efficiency depends upon the diffusion or penetration of alkali catalyst and etherifying agent into starch granules and the chances of collisions of the starch alcoholate nucleophile with the propylene oxide molecule. The elevated temperature of reaction helps in diffusion of alkaline catalyst and penetration of etherifying reagent more readily into the reaction point inside the starch granule and thus economises the reagent consumption.

Preparation of hydroxypropyl starch from a variety of cereal starch sources like rice (Islam & Azemi, 1997; Seow & Thevamalar, 1993; Yeh & Yeh, 1993), wheat (Wootton & Haryadi, 1992; Wootton & Mahdar, 1993; Wootton, Kesavamoorthy & Azami, 1985), maize (Azemi & Wootton, 1994; Wootton & Haryadi, 1992; Wootton & Manatsathit, 1983), tuber starch sources like potato (Lammers, Stanhuis & Beenackers, 1993; Leegwater & Luten, 1971; McHale, 1988; Perera & Hoover, 1998) and legume starch sources e.g. field pea (Hoover, Hannonz & Sosulski, 1988) has been reported. A number of patented processes have been developed for the preparation of low-substituted hydroxyalkyl starch ethers in aqueous phase. High levels of substitution can be obtained in granular starch by using non-aqueous media (Hjermstad & Martin, 1964; Kesler & Hjermstad, 1958) or in dry conditions (Kesler & Hjermstad, 1958).

Alkaline-catalyzed reactions of cellulose or starch with alkylene oxides had been known for many years. Kesler and Hjermstad (1950) first showed that, under carefully

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regulated conditions, a reaction could be effected between starch and alkylene oxide in a aqueous slurry system while keeping the starch granule intact. These authors patented a process for the preparation of hydroxyalkyl starch ethers of low substitution on the basis of propylene oxide reaction. In this modification, reaction is made by reacting a water suspension of starch at high pH with propylene oxide. The hydrophilic hydroxypropyl groups decreases the gelatinization temperature, and since the reaction requires higher alkalinity, swelling inhibiting salts (Na_2SO_4, for example) are added to starch before propylene oxide (Tsuzuki, 1968). The reaction takes place in aqueous phase as long as molar substitution (MS) is less. As the level of hydroxyalkylation increases, more salt is required, and for $MS > 0.1$, the product becomes difficult to purify. This is due to the swelling of the granules when the salt is washed out. The real technological breakthrough for hydroxypropyl starch came with the discovery that the starch can be reacted while maintaining its native granule form (Tuschhoff, 1987). Hydroxypropyl starch with maintenance of granular structure and better homogenity using a lower amount of alkali can only be prepared by complete gelatinization of aqueous starch slurry and feeding the gelatinized mass into a reactor (Lammers, Balt, Stanhuis, & Beenackers, 1996). Recently, with the advancement of extruder technology, interest in the chemical derivatization of gelatinized starch has increased (Lammers et al., 1993).

Molar substitution (MS) takes into account the number of moles of substituting groups introduced per anhydroglucose unit. This is applicable for polymeric substituents (Rutenberg & Solarek, 1984). The MS (Azemi & Wootton, 1984; Hoover et al., 1988; Kim, Harmannson & Erickson, 1992; Wootton & Manatsathit, 1983, 1984), average molecular weight (Rutenberg & Solarek, 1984) and distribution of substituent (Azemi & Wootton, 1994; Wootton & Haryadi, 1992) determine the properties of hydroxypropyl starch (HPS), provided the starch source (guiding the shape, size and amylose–amylopectin ratio) is the same. Thus, permutation and combination of the reaction parameters can yield different varieties of HPS. The Food and Drug Administration (FDA) limit of MS for HPS is 0.2 (Dias et al., 1997).

The main reaction parameters which influence the MS of HPS are reagent concentration, starch:water ratio, duration of reaction and alkali concentration (Wootton & Manatsathit, 1983). Proportion of amylose and amylopectin, and intragranular arrangement are also additional factors determining mainly substituent distribution (Wootton et al., 1985).

Earlier work from our laboratory has explored the possibility of using waxy starch from *Amaranthus paniculatas* Linn seeds (Rajgeera) for preparation of useful starch derivatives. In continuation, the present work was planned to look for the possibility of hydroxypropylation of this starch in comparison to the hydroxypropyl derivative of conventionally used corn starch.

2. Materials and methods

2.1. Materials

Corn starch obtained from M/s Raptakos Brett & Co. Ltd, Thane and 60 mesh amaranth starch isolated in the laboratory by alkali steeping method (Yanez & Walker, 1986) from *A. paniculatus* Linn (Rajgeera) was used in the present work. All other reagents used in this work were of analytical grade.

2.2. Methods

2.2.1. Effect of process parameters on hydroxypropylation of starches

Hydroxypropylation procedure was based on earlier literature reports (Hoover et al., 1988; Leegwater & Luten, 1971; McHale, 1988; Wootton & Mahdar, 1993; Wootton & Manatsathit, 1983) available on the preparation of HPS. Commercial aqueous slurry reaction was carried out in a sealed reactor with rapid agitation after adding the required quantities of sodium sulphate and sodium hydroxide at 40°C for varying time periods. The protocol followed in this work (Fig. 1) was similar to that of Wootton and Manatsathit (1983) with some minor modifications.

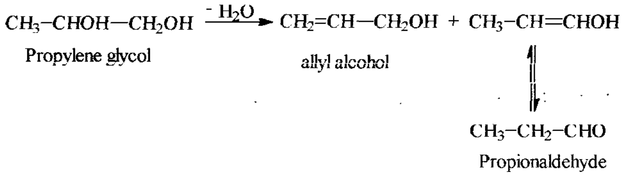
A three-neck conical flask immersed in a water bath was used as the static mixer reactor and mechanical stirring was adopted instead of shaking the water-bath. Process parameters like propylene oxide concentration, starch:water ratio, duration of reaction and alkali concentration were studied with respect to their MS. The variation of the process parameters during the optimization of the hydroxypropylation process was carried out as shown in Tables 1 and 2. The range of these parameters was selected on the basis of the literature reports and initial trials.

For amaranth starch, the range of some parameters was changed during the optimization process. Immense difficulties were encountered in washing hydroxypropylated amaranth starch (HPSA). Unlike hydroxypropylated corn starch (HPSC), the product could not be separated only by repeated settling and decanting. This could be due to the waxy nature of amaranth starch. Repeated centrifugation was carried out for amaranth starch to remove impurities.

2.2.2. Determination of molar substitution of HPSC and HPSA

The spectrophotometric determination of hydroxypropyl group using pure propylene glycol was followed to determine the molar substitution. The method is based on the principles given by Jones and Riddick (1957) to determine propylene glycol and polyoxypropylene.

The method involves hydrolysis of the hydroxypropyl group to propylene glycol which in turn is dehydrated to propionaldehyde and the enolic form of allyl alcohol.



$$CH_3\text{-}CHOH\text{—}CH_2OH \xrightarrow{-H_2O} CH_2\text{=}CH\text{—}CH_2OH + CH_3\text{-}CH\text{=}CHOH \rightleftharpoons CH_3\text{-}CH_2\text{-}CHO$$

These products are measured spectrophotometrically at 590 nm after they are reacted with ninhydrin to form a purple colour. The procedure is as follows:

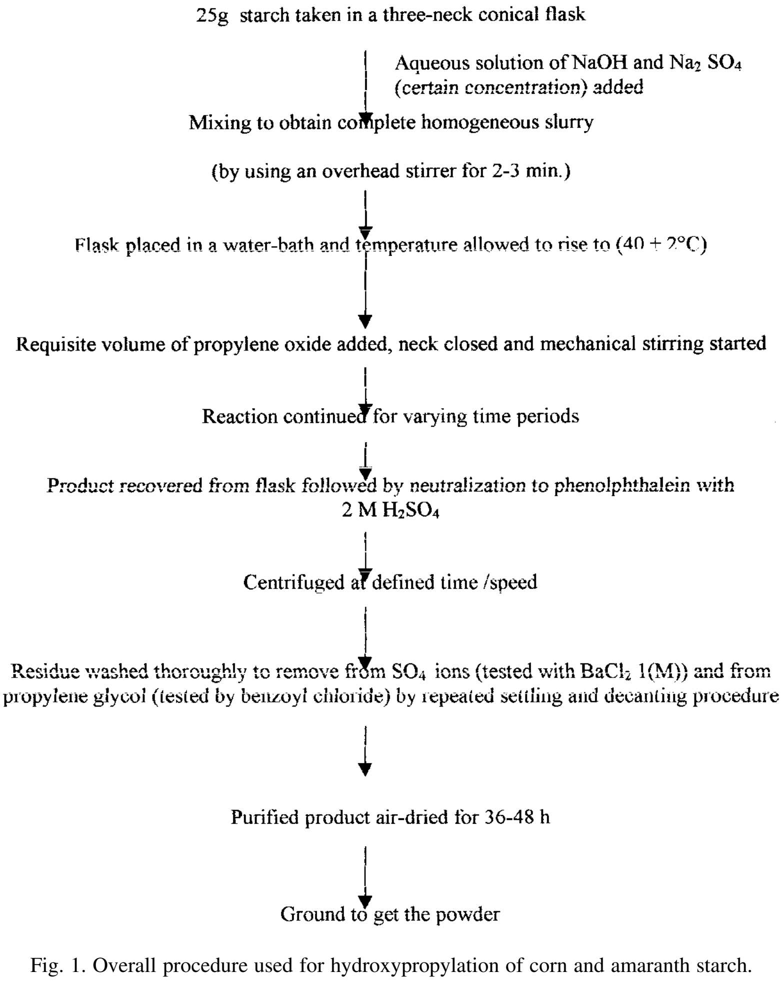
(a) *Sample preparation*: known weight of HPS sample (0.05–0.1 g) were weighted into a 100 ml volumetric flask. 25 ml of 2 M H_2SO_4 was added to it. The flask was then placed in a boiling water bath and was heated until the samples dissolved. It was then cooled to ambient temperature and diluted to 100 ml with water.

(b) *Analysis*: 0.5 ml aliquot of the solutions for different HPS samples were transferred into 25 ml graduated test-tube. Conc. H_2SO_4 (96%) (4 ml) was added drop-wise, immersing the graduated test-tube in cold water and mixed well. Tubes were then placed in a boiling water bath for exactly 34 min and transferred immediately to an ice bath. 0.3 ml of ninhydrin reagent (3% solution of 1,2,3-triketohydrindene crystals in a 5% aqueous sodium bisulphite solution (Johnson, 1969) was then added to the chilled solution and it was shaken well. Then they were placed in a 25°C water bath for 100 min. The tubes were then taken out from the water bath and volume made to 12.5 ml with conc. H_2SO_4. Absorbance for each tube was then measured at 590 nm using the unmodified starch as the reference.

(c) *Prepartion of standard curve*: a calibration curve with 0.5 ml aliquots of standard aqueous solutions containing 10, 20, 30, 40 and 50 μg of propylene glycol/ml was also prepared. Stock solutions containing the above concentrations of propylene glycol were prepared in 100 ml volumetric flasks. Of these standards were taken and assayed as described above.

From the standard graph of concentration of propylene glycol vs. absorbance, the concentration of propylene glycol produced from HP group of HPS is known. The concentration of propylene glycol was then converted to HP group equivalent from which MS was calculated according to the formula (Rutenberg & Solarek, 1984):

$$\mathrm{MS} = 162W/100M - (M - 1)W$$



25g starch taken in a three-neck conical flask

Aqueous solution of NaOH and Na_2SO_4 (certain concentration) added

Mixing to obtain complete homogeneous slurry

(by using an overhead stirrer for 2-3 min.)

Flask placed in a water-bath and temperature allowed to rise to (40 ± 2°C)

Requisite volume of propylene oxide added, neck closed and mechanical stirring started

Reaction continued for varying time periods

Product recovered from flask followed by neutralization to phenolphthalein with 2 M H_2SO_4

Centrifuged at defined time /speed

Residue washed thoroughly to remove from SO_4 ions (tested with $BaCl_2$ 1(M)) and from propylene glycol (tested by benzoyl chloride) by repeated settling and decanting procedure

Purified product air-dried for 36-48 h

Ground to get the powder

Fig. 1. Overall procedure used for hydroxypropylation of corn and amaranth starch.

Table 1
Optimization process for hydroxypropyl corn starch

Starch (g)	Volume of propylene oxide (ml)	Starch:water (g:ml)	Quantity of Na_2SO_4 (g)	Quantity of NaOH (g)	Temperature (°C)	Time (h)
25	1	25:30	3.75	0.36	40	8
	2					
	3					
	4					
	5					
	6					
25	6	25:30	3.75	0.36	40	8
						12
						16
						20
						24
25	6	25:30	3.75	0.36	40	12
		25:35				
		25:40				
		25:45				
25	6	25:35	3.75	0.30	40	12
				0.36		
				0.42		
				0.48		
				0.56		
				0.63		

where W is the percentage by weight of substituent, and M is the molecular weight of the monomeric units of the polymeric substituent.

For propylene-oxide treated starch: $W = \text{HP}$ group equivalent in 100 mg of dry starch; $M =$ molecular weight of $C_3H_6O = 58$. So

$$\text{MS} = 162W/5800 - 57W$$

3. Results and discussion

The optimization process of hydroxypropylation was achieved by varying the process parameters. On the basis of the literature reported so far (Leegwater & Luten, 1971; Wootton & Manatsathit, 1983), the levels of process parameters were chosen. The optimization process began by varying only one parameter at a time, keeping others

Table 2
Optimization process for hydroxypropyl amaranth starch

Starch (g)	Volume of propylene oxide (ml)	Starch:water (g:ml)	Quantity of Na_2SO_4 (g)	Quantity of NaOH (g)	Temperature (°C)	Time (h)
25	1	25:40	0.36	3.75	40	8
	2					
	3					
	4					
	5					
	6					
25	6	25:30	0.36	3.75	40	8
		25:35				
		25:40				
		25:45				
		25:50				
		25:60				
25	6	25:45	0.30	3.75	40	8
			0.36			
			0.42			
			0.48			
			0.56			
			0.63			
25	6	25:45	0.63	3.75	40	4
						8
						12
						16
						20
						24

Table 3
Effect of propylene oxide concentration on molar substitution (mean ± SD of three determinations) of hydroxypropyl corn (other conditions for corn work are detailed in Table 1) and amaranth starch (other conditions for amaranth work are detailed in Table 2)

Volume of propylene oxide added in 25 g dry starch (ml)	MS of hydroxypropyl corn starch (HPSC)	MS of hydroxypropyl amaranth starch (HPSA)
1.0	0.025 ± 0.001	0.022 ± 0.001
2.0	0.027 ± 0.009	0.034 ± 0.010
3.0	0.037 ± 0.047	0.049 ± 0.003
4.0	0.056 ± 0.063	0.057 ± 0.007
5.0	0.063 ± 0.080	0.085 ± 0.009
6.0	0.007 ± 0.010	0.094 ± 0.005

constant. Hydroxypropyl derivatives so obtained were analysed in order to determine the MS. The parameter tested, which resulted in the highest MS, was kept fixed for the next optimization process. A number of analytical methods for determining hydroxyalkyl groups in starch can be found in the literature. The methods of Lortz (1956); Morgan (1946) are modifications of the classical Zeisel method in which hydroiodic acid is used to decompose ether into an alkyl iodide and alkene. Johnson (1969) reported a spectrophotometric method for determining the HP group in starch.

Different sets of optimization conditions used for HPSC and HPSA are shown in Tables 1 and 2, respectively. Initially, the effect of propylene oxide in the concentration range of 4–24% (v/w) of starch on the MS of HPSC and HPSA was observed. As shown in Table 3, for both the starches, 24% propylene oxide gave a maximum MS of 0.077 for HPSC, and 0.094 for HPSA. This is probably due to the greater availability of propylene oxide at higher concentrations in the proximity of starch granules. The findings are well supported by the reports in the literature (Wootton & Manatsathit, 1983). At the same concentration of propylene oxide, MS was found higher for amaranth starch than corn starch. It may be due to the greater swelling of amaranth starch granules (attributed to its waxy nature) which enables it to remain more dispersible in suspension. This in turn favours greater diffusion of etherifying agent in the interior of the amaranth starch granules compared to that of corn starch.

Table 4
Effect of reaction time on molar substitution MS (mean ± SD of three determinations) of hydroxypropyl corn starch (other conditions for corn work are detailed in Table 1)

Reaction time (h)	Molar substitution of hydroxypropyl corn starch (HPSC)
8	0.077 ± 0.010
12	0.097 ± 0.003
16	0.099 ± 0.012
20	0.100 ± 0.015
24	0.098 ± 0.005

All the available literature on corn starch hydroxypropylation (Hoover et al., 1988; McHale, 1988; Wootton & Mahdar, 1993; Wootton & Manatsathit, 1983) recommend a longer reaction duration (24 h). Since the reaction was continued for 8 h only, hydroxypropyl derivatives of lower MS were obtained. Hence in order to increase the MS of HPSC, the next parameter chosen was the duration of the reaction. These results are shown in Table 4. Since the MS of HPSA was considerably higher than HPSC after 8 h reaction (Table 3), this parameter was optimized initially for corn starch.

The MS of HPSC increased significantly only in the first incremental step from 8 to 12 h after which it remained almost constant. Greater contact time with continuous agitation probably led to efficient absorption or diffusion of etherifying agent into starch granules, which increased the chances of collisions between the starch nucleophile and propylene oxide, which induces a higher bimolecular reaction rate. However, after 12 h no noticeable change in MS was observed. It implies that a 12 h continuous mechanical agitation accomplishes almost complete diffusion within the starch granule. Other workers had used shaking water-bath reaction where a maximum MS was achieved after 24 h (Wootton & Manatsathit, 1983).

MS of HPSC produced with 24% propylene oxide after 12 h mechanical stirring was found comparable with that of amaranth starch produced with the same per cent of propylene oxide after 8 h stirring. The next parameter chosen for optimization for HPSC and HPSA was the starch:water ratio. Data obtained with this parameter as a variable are shown in Table 5.

Slurry concentration, guided by the starch:water ratio affects the reaction rate significantly as shown by changing MS of both HPSC and HPSA. For corn starch, MS decreased significantly with increase in volume of water up to 45 ml. Hence water level was not increased any further. For amaranth starch, the reaction was carried out up to a starch:water ratio of 25:60, which gave the lowest MS. The maximum lower limit of starch:water ratio chosen for corn and amaranth starch was 25:30 and 25:40, respectively, as below this volume, the starch slurry became a thick compact mass which was difficult to stir mechanically. This limiting volume was more for amaranth starch than corn due to its higher swelling power and waxy nature.

A starch:water ratio of 25:35 for corn starch and 25:45 for amaranth starch gave the highest MS, and which decreased on either side of these values. The above observation signifies the role of water in aqueous slurry reactions. Water acts as a transport vector for catalyst and reagent into the starch granule. As starch granules swell in a definite volume of water, the diffusion or absorption of catalyst and etherifying agents inside the starch granules is facilitated. But, when volume of water is more, reagent in the aqueous starch slurry gets diluted, and therefore the availability of

Table 5
Effect of starch:water ratio on molar substitution MS (mean ± SD of three determinations) of hydroxypropyl corn (other conditions for corn work are as per Table 1) and amaranth starch (other conditions for amaranth work are as per Table 2)

Starch:water ratio (g/ml)	Molar substitution of hydroxypropyl corn starch (HPSC)	Molar substitution of hydroxypropyl amaranth starch (HPSA)
25:30	0.097 ± 0.003	–
25:35	0.113 ± 0.022	–
25:40	0.082 ± 0.021	0.094 ± 0.005
25:45	0.089 ± 0.006	0.1003 ± 0.003
25:50	–	0.072 ± 0.004
25:60	–	0.063 ± 0.009

propylene oxide surrounding starch granules becomes less compared with the availability of this reagent surrounding water molecule. So, the competitive reaction of propylene oxide with water leading to the side product propylene glycol mainly occurs as reflected by decreasing MS values.

The effect of amount of alkali required was also studied. Since, NaOH was added in a definite quantity (mass) together with Na_2SO_4, the optimization study was carried out with respect to the quantity of NaOH. As the granular structure of starch was retained even after adding the NaOH and Na_2SO_4 solution, this solution provided the aqueous phase of the reaction to produce suitable slurry for mechanical stirring. The optimization with HPSC and HPSA using the quantity of NaOH is shown in Table 6.

Some observations were made when the amount of alkali was increased. For both corn and amaranth starch, NaOH quantity in the range of 0.30– − 0.48 g, had not shown any significant effect on MS, but above this range there was an increase in MS. For a 12 h run of corn starch, from 0.30 to 0.48 g, starch paste was suitable for mechanical stirring. But with 0.56 and 0.63 g and after about 6 h for 0.63 g NaOH, respectively). In both cases, centrifugation (5000 rpm) for 50 min was sufficient for proper separation of the starch granules. For a 8 h run of amaranth starch, a slurry suitable for mechanical stirring was obtained in between the range of 0.30–0.56 g NaOH. But with 0.63 g NaOH after about 5 h, it formed a very thick slurry that was difficult to rotate. In the purification step, 40–50 min at 5000 rpm was sufficient for separation of starch granules from the slurry made from 0.30 to 0.56 g NaOH. However, with 0.63 g NaOH, 8000 rpm/50 min was needed for proper separation. Another significant observation was that for corn starch, as there was no trace of gelatinization of starch observed after drying up to 0.56 g NaOH, but with 0.63 g NaOH, some gelatinization in the starch was obtained after air-drying. For amaranth starch, 0.56 and 0.63 g NaOH produced a significant amount of gelatinized starch after air-drying.

Table 6
Effect of quantity of alkali on molar substitution (mean ± SD of three determinations) of hydroxypropyl corn (other conditions for corn work are as per Table 1) and amaranth (other conditions for amaranth work are as per Table 2) starch

Quantity of alkali (g)	Molar substitution of hydroxypropyl corn starch (HPSC)	Molar substitution of hydroxypropyl amaranth starch (HPSA)
0.30	0.106 ± 0.003	0.097 ± 0.038
0.36	0.113 ± 0.022	0.100 ± 0.003
0.42	0.105 ± 0.020	0.092 ± 0.007
0.48	0.118 ± 0.001	0.114 ± 0.005
0.56	0.134 ± 0.002	0.140 ± 0.001
0.63	0.133 ± 0.010	0.142 ± 0.010

Table 7
Effect of reaction time on molar substitution of HPSA (values are Mean ± SD of three determinations; other conditions were as per Table 2)

Reaction time (h)	Molar substitution of hydroxypropyl amaranth starch (HPSA)
4	0.114 ± 0.006
8	0.142 ± 0.003
12	0.148 ± 0.002
16	0.150 ± 0.010
20	–
24	–

The observed change in MS with the amount of alkali can be explained by the following mechanism: alkali catalyses the hydrolysis of 1,2-propylene oxide which leads to the formation of propane 1,2-diol (bi-product). This reaction competes with the catalysis of starch within the NaOH range of 0.30–0.48 g. Hence, an increase in NaOH within this range did not change the MS. Beyond 0.48 g of NaOH, MS of both HPSC and HPSA was found to increase suggesting the catalytic effect of NaOH on the hydroxypropylation reaction. As the swelling power of amaranth starch is high compared to corn starch, repeated centrifugation to wash out the sulphate salts, renders the starch granule to be in a more swelled condition compared to the corn starch. Difficulties in settling which were observed were overcome by increasing the speed and time of centrifugation.

Waxy amaranth starch has a lower gelatinization temperature compared to corn starch (Lorenz, 1981; Zobel, 1984). In alkaline conditions and after incorporation of the hydroxypropyl group, this temperature is lowered further which results in the production of totally gelatinized HPS.

As the duration of the reaction is the most vital parameter to economize any reaction process, the next and the last parameter chosen for the production of HPSA was reaction time. The change in MS by prolonging the duration is tabulated in Table 7. In the course of 12 and 16 h reaction, a thick paste was formed almost immediately which was difficult to stir. In addition, a completely gelatinized mass was

Table 8
Conditions optimized for preparation of hydroxypropyl starch from corn and amaranth samples

Sample	Volume of propylene oxide (ml)	Starch:water ratio (g/ml)	Quantity of alkali (g)	Reaction time (h)	Molar substitution (MS)
Corn starch	6.0	25:35	0.56	12	0.133[a]
Amaranth starch	6.0	25:45	0.63	8	0.142[b]

[a] Partially gelatinized.

obtained after purification and drying. Hence, the reaction trials for 20 and 24 h duration was discarded.

Comparing the results of time parameter with corn starch, it was observed that for both the cases, there was no significant change in MS after 12 h for corn starch and 8 h for amaranth starch. Moreover, after 8 h, HPSA also lost its granular integrity. Corn starch, however, still maintained its granular integrity. This implies that the higher swelling power and lower gelatinization temperature of amaranth starch granules compared to that of corn starch help it to attain a maximum MS within 8 h and simultaneously convert it to pregelatinized starch when longer duration reaction was undertaken. It can be concluded that optimized time of hydroxypropylation in this mechanical stirring arrangement was 8 h for amaranth starch and 12 h for corn starch. Another interesting factor is that in both the cases (corn and amaranth), optimum time was less than the 24 h required in gyratory shaking water bath arrangement. It may be due to some potential advantages of a static mixer reactor such as good plug flow characteristics, good radial mixing and uniform distribution of substrate and reagent achieved at low shear rate.

The optimized conditions for achieving maximum MS for HPSC and HPSA from the present set of trials is summarized in Table 8.

4. Conclusion

Native starches differ in their morphological, physicochemical and functional properties. These differences are further magnified during chemical modification, in this instance, hydroxypropylation. The results obtained from this study suggest that each starch type is unique and needs to be treated as such. Optimization differs from one starch type to another and it would be fallacious to extend the optimization conditions of one starch type to another.

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