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High moisture twin screw extrusion of sago starch. II. Saccharification as influenced by thermomechanical history

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Processing of sago starch in a co-rotating twin screw under high-moisture conditions (34–47% moisture, barrel temperatures 81–147°C and screw speed 315–486 rpm) was investigated as a pre-treatment for subsequent saccharification. Product thermomechanical history was assessed for the various processing conditions. Specific mechanical energy (SME) consumption was in the range 57–131 kWh/kg. Saccharification of the extrudates was independent of the processing variables at a higher enzyme concentration of AMG (0.5 AGU/g). However, when 0.05 AGU/g AMG was used, saccharification was related to the extrusion variables. Despite a poor negative correlation between saccharification and SME ($r = -0.44$), a global trend was observed. Die pressure influenced saccharification ($r = -0.45$) suggesting that a high melt viscosity (as indicated by high die pressure) resulted in a lower percent of saccharification. Additionally water solubility index (WSI) was influenced by SME to a lesser extent. © 1997 Elsevier Science Ltd

INTRODUCTION

Sago starch is an agronomically important indigenous crop of southeast Asia, utilisation of which can provide high yields of starch and lead to conservation of agriculturally marginal areas of land (Oates *et al.*, 1994). Use of sago starch for hydrolysis is currently limited by granular resistance to commercial enzymes and the high paste viscosity of gelatinised starch pastes (Oates *et al.*, 1994). To overcome these limitations and promote sago starch utilisation, there is a need to develop alternative systems.

Product properties depend mostly on the molecular transformations, such as disruption of starch granules, amylose and amylopectin chain splitting or partial depolymerisation (Tayeb *et al.*, 1991). These transformations are generated in the various parts of the extruder by temperature, pressure, shearing and residence time (Tayeb *et al.*, 1991). A complete understanding of the process therefore involves the measurement of these variables, in order to define the 'thermomechanical history' of the product (Tayeb *et al.*, 1991). By relating process parameters to thermomechanical history and then product transformation to thermomechanical history, it is possible to progress toward understanding the effect of process variables on product transformation (Colonna *et al.*, 1989). Development of extrusion-cooking technology requires an understanding of how process variables and their interactions affect the thermomechanical transformation of a feed material (Vainionpää, 1991).

Meuser *et al.* (1984a) used the *System Analytical Model*, to explain how modification of a process parameter can affect product transformation by changing product thermomechanical history during passage through the extruder. Specific mechanical energy (SME) and product temperature at the die were used as intermediate variables between operating conditions and product transformation characteristics. Researchers (Meuser *et al*, 1984a, 1985, 1987; Della Valle *et al.*, 1989) demonstrated using X-ray diffraction studies, gel permeation chromatography, water solubility, intrinsic viscosity and enzy-

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matic susceptibility, that SME input can be related to product transformation. In addition, the system analytical model holds for different screw configurations and for starch materials of complex microstructure (Kirby *et al.*, 1988). Relationship between SME input and saccharification, however, has not been reviewed.

It has been shown for various starch sources, that twin-screw extrusion can be utilised in the pretreatment of starch for subsequent enzymatic saccharification (Linko *et al.*, 1979; Darnoko & Artz, 1988). However, the application of this technology for sago starch has not been documented. This work evaluates the use of thermomechanical extrusion (in a twin-screw extruder) to pretreat sago starch for subsequent saccharification. This present investigation is a continuation of work previously reported (Govindasamy *et al.*, 1996). We have established that gelatinisation which results in various extents of granular structure relaxation was the predominant mechanism when sago starch is processed in a twin-screw extruder (Clextral BC21) under high moisture conditions (34–47%). Product temperature, die pressure and specific mechanical energy (SME) required during extrusion cooking has been computed for the various processing conditions which were selected based on a multifactorial experimental design. These parameters were used as intermediate variables between operating conditions and product transformation characteristics. Possible relations amongst these measurements, the extrusion variables (feed moisture content, screw speed and barrel temperature) and saccharification were examined. Relationships between structural characteristics of the extrudate and extrusion processing variables on susceptibility of the products towards saccharification were described.

MATERIALS AND METHOD

Materials

Sago starch obtained from a commercial producer, PPES Sago Industries (Mukah) Sdn. Bhd. (Sarawak, Malaysia) was used as the feed material for all experiments. Moisture content of the raw material was determined by drying to constant weight in a convection oven at 120°C for 2 h. The moisture content of sago starch was found to be about 13% (wet weight basis; w.b.).

Enzyme preparation

Extrudates were saccharified with *Aspergillus niger* amyloglucosidase (commercially known as AMG 300L) manufactured by Novo Industri A/S bought from Chemcolour Industries (New Zealand) Ltd. The liquid preparation of amyloglucosidase was specified to have an activity of 300 Novo Amyloglucosidase Unit (AGU) where one AGU is the amount of enzyme which hydrolyses 1 μmol maltose/min under Novo's standard conditions (pH 4.3, acetate buffer, 25°C).

Extruder

Experiments were conducted in a co-rotating intermeshing CLEXTRAL BC21 twin-screw extruder (Clextral Co., Firminy, France) as outlined in the previous paper (Govindasamy *et al.*, 1996). Screw configuration was as previously reported.

Extrusion conditions: multifactorial experimental design

In order to assess the effects of the operating parameters on thermomechanical properties and saccharification potentials of the extrudates, a central composite rotatable response surface experimental design (Mullen & Eunis, 1979) based on a three-variable five-level system was carried out (Table 1). Three process variables were selected: M, the total moisture content of the mass feed (%, wet weight basis); T, the barrel temperatures (T_3 and T_4) in zones 3 and 4 (°C); and S, the screw speed (rpm). The other parameters were kept constant: feed-rate at 5.25 kg/h, temperature of the zones 1 and 2 at 40° and 80°C, respectively.

Operating ranges and five standardised levels were selected for each variable (Table 1). Among all possible combinations, 20 extrusion conditions were carried out in a random order (8 factorial points, 6 axial points and 6 replicates of the central point to form a central composite design with α −1.682) to allow the fitting of a second order model. Second order polynomials were computed with a Statgraphics Package (version 6.0, Mannugistics, Inc., Rockville, USA). Three-dimensional surface plots were generated by showing the effects of two process variables, while the other was maintained constant, for each response.

Steady-state operation

Before any change was imposed on the extrusion system, initial steady state conditions were established

Table 1. Levels of independent variables

Variable	Code	Levels				
		$-\alpha$	−1	0	+1	$+\alpha$
(1) Feed moisture (%)	M	34.3	37.0	41.0	45.0	47.4
(2) Barrel temperature (°C)	T	81	95	115	135	149
(3) Screw speed (rpm)	S	315	350	400	450	486

and maintained for 10 min. The system was considered to have attained steady state when all of the measured process variables (torque, die pressure and mass temperature) were not varying by more than ±5%. Upon changing the operating environment, steady state was again established, samples and data collected for 15 min.

Calculations

The total feed rate (F_{RT}) was defined as the sum of the feed rate of the sago starch (F_{Rf}) and the water addition (F_{Rw}) as follows:

$$F_{Rt} = F_{Rf} - F_{Rw} \quad (1)$$

The specific mechanical energy (SME) (in Wh/kg) was calculated using the following formula:

$$\text{SME} = \frac{T\omega}{F_{Rt}} \quad (2)$$

$$= \frac{2\pi\, TS}{60\, F_{Rt}} \quad (3)$$

where ω is the angular velocity (rad/s); T is the torque (Nm); S is the screw speed (rpm); F_{Rt} is the total feed rate (kg/h)

Drying and grinding of samples

Extrudates were dried and ground as previously described (Govindasamy *et al.*, 1996).

Saccharification of extrudates

Extent of saccharification of the extrudates were determined by assaying the glucose released following hydrolysis of the extrudates. Saccharification was then carried out for 8 h in an orbital benchtop shaker (Certomat R M, B. Braun Diessel Biotech Gmbh) in an incubator (Inkubation hood, HK, B. Braun Diessel Biotech Gmbh). The flasks were prepared by dispersing 1 g of each of the samples in 9 ml of 0.1 M acetate buffer, pH 4.5, respectively. Solutions were incubated at 60°C in the shaking incubator. Enzymatic hydrolysis was initiated following the addition of 1 ml of 0.5 AGU/g of amyloglucosidase to the suspensions. After the specified time interval, 1-mL aliquots were withdrawn and added to tubes containing 0.1 ml of chilled 30% TCA, chilled for 30 min and then centrifuged at 10 000 *g* in a microfuge for 15 min at 4°C. Volume of supernatant was determined using a graduated 1 ml syringe fitted with a needle. Glucose content in the supernatant was assayed using the Glucose Diagnostic Kit (Sigma Diagnostics, St. Louis, MO, USA, cat no. 510-A).

RESULTS AND DISCUSSION

Thermomechanical energy

Energy input into the extruder was found to be affected by the processing variables.

Mass temperature (MT)

Product temperature (at the die) was highly dependent ($p < 0.001$) on barrel temperature (Table 2). Change in barrel temperature led to a corresponding equidirectional shift in product temperature. Inclusion of the quadratic term decreases the linear effect of barrel temperature.

Influence of screw speed on mass temperature, was affected by barrel temperature (Fig. 1). At low barrel temperature, increasing screw speed translates into frictional heat as the highly viscous mass is subjected to increasing shear and mixing. Frictional heat is subsequently fed into the mass thereby raising the product temperature slightly.

Frictional effects and mass viscosity are also influenced by feed moisture, lowering of which raises the mass temperature (Table 2). Viscosity of the starch mass, and therefore its ability to dissipate mechanical energy, would increase when the water content is low.

Die pressure

Barrel temperature greatly influences die pressure. Viscosity of molten polymers decreases as barrel temperature increases, resulting in reduction of the die pressure (Fig. 2). Die pressure is related to the melt viscosity at the end of the extruder and has been used in the food industry as a means of extruder control (Davidson, 1991).

Die pressure decreases when water content is increased (Fig. 2). This is due to the decrease in viscosity of molten starch inside the extruder (Fletcher *et al.*, 1984; Della Valle *et al.*, 1987). The reduction was more marked at the lowest barrel temperature (81°C) than at the highest temperature (149°C). Decreasing the water content at the lowest temperature led to a corresponding increase in die pressure. In contrast, there was no appreciable change in the die pressure at the highest temperature.

Molten starch exhibits non-Newtonian shear thinning behaviour (Fletcher *et al.*, 1984; Della Valle *et al.*, 1987). With increasing screw speed, shear rate increases leading to generation of heat which is associated with a consequent temperature rise and decrease in melt viscosity. In such a scenario pressure build-up at the die is reduced (Table 3). Mosso *et al.* (1982) and Fletcher *et al.* (1985) reported that die pressure decreased upon raising the screw speed, but Della Valle *et al.* (1987) noted that die pressure remained stable. The stability is

Table 2. Best selected prediction equations for all dependent variables

Dependent variables	Independent variables	Coefficient	R^{2a} (adjusted)	p-value
Mass temperature	constant	113.903	0.99	0.0000
	M^{***}	−0.992		
	T^{***}	14.576		
	T^{2***}	−2.237		
	TS^{*}	−0.563		
Die pressure	constant	2.245	0.97	0.0000
	M^{***}	−0.481		
	T^{***}	−1.020		
	S^{***}	−0.193		
	T^{2***}	0.202		
	MT^{***}	0.275		
	MS^{*}	0.125		
SME	constant	124.900	0.89	0.0000
	M^{***}	−19.892		
	T^{**}	8.553		
	S^{***}	21.613		
Saccharification	constant	11.112	0.80	0.0000
	M^{***}	3.459		
	M^{2***}	2.218		
	S^{2*}	0.993		

***: $p < 0.001$.
**: $p < 0.01$.
*: $p < 0.05$.
[a] R^2 is adjusted for the degree of freedom.

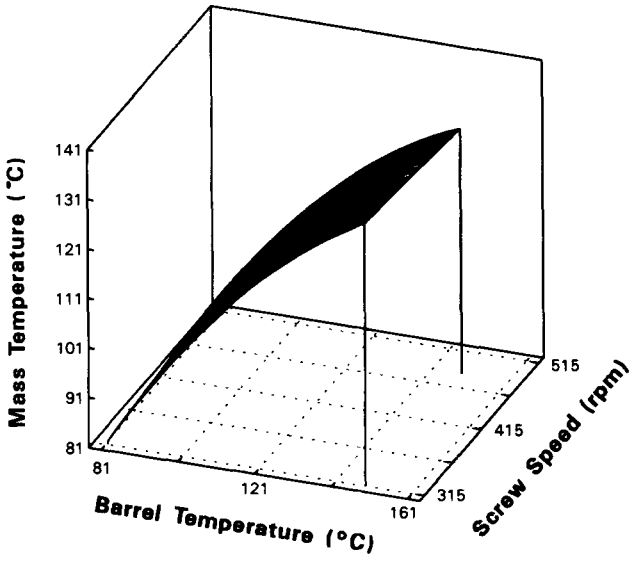

Fig. 1. Influence of barrel temperature and screw speed on mass temperature at screw speed 400 rpm.

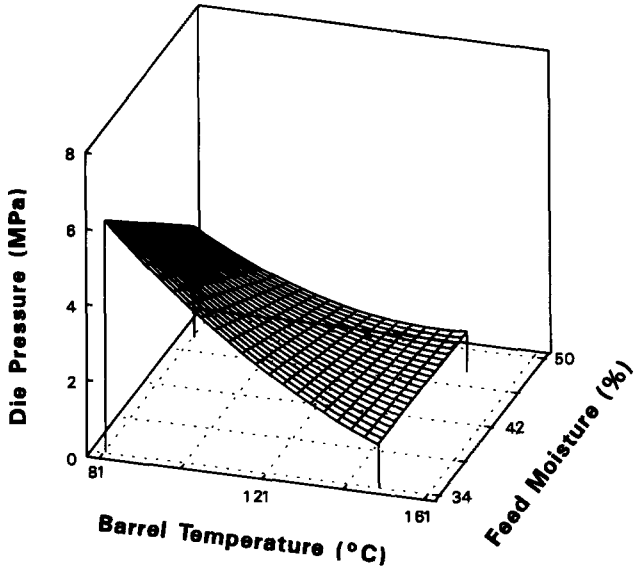

Fig. 2. Influence of barrel temperature and feed moisture on die pressure at screw speed 400 rpm.

attributed to the opposing effect of decreasing viscosity (as a result of increasing screw speed) and increasing mechanical energy input.

Specific mechanical energy (SME)

This study confirms the observations of other investigators (Antila *et al.*, 1983; Linko *et al.*, 1984; Meuser *et al.*, 1984a, 1985; Senouci & Smith, 1986; Mangé & Boissonnat, 1986; Della Valle *et al.*, 1989; Lu *et al.*, 1992) that feed moisture is a key factor in determining flow properties of food dough in extrusion cooking (Table 2). Increased feed moisture decreases the viscosity of a food dough (as indicated by lowered die pressure) and reduces the rotating friction of the screws which is translated into lowered torque (Lu *et al.*, 1992; Grossmann *et al.*, 1988). Lubricating effects of water lowers the SME input. Viscosity of the starch mass and therefore its ability to dissipate mechanical energy decreases when the water content is high.

Barrel temperature exerts a positive effect on SME

Table 3. Correlation coefficients between dependent variables

	MT[a]	Die pressure	SME	DE	WSI[b]	WAI[c]	DG[d]
Die pressure	−0.8470***						
SME	0.2942[ns]	0.0162[ns]					
DE	0.3015[ns]	−0.1099[ns]	0.3885[ns]				
WSI[a]	−0.0364[ns]	0.1436[ns]	0.3999[ns]	0.5684***			
WAI[b]	−0.0660[ns]	0.1340[ns]	0.1957[ns]	0.4048[ns]	0.8853***		
DG[c]	0.3760[ns]	−0.3054[ns]	0.0821[ns]	0.7101***	0.2954[ns]	0.2239[ns]	
Sacch[e]	0.1257[ns]	−0.451*	−0.4377*	0.0291[ns]	0.0163[ns]	0.1414[ns]	0.4233[ns]

***: $p < 0.001$.
**: $p < 0.01$.
*: $p < 0.05$.
[ns]: Not significant.
[a]Mass temperature.
[b]Water Solubility Index.
[c]Water Absorption Index.
[d]Degree of gelatinisation.
[e]Per cent saccharification.

(Table 2). Gelatinisation of the material most likely elevates melt viscosity, causing an initial increase in torque at lower temperatures. Specific mechanical energy was positively correlated with screw speed (Fig. 3) at all temperatures explored affirming the results obtained by other researchers. The influence of screw speed on SME was reported to lead to contradictory results depending on the type of extruder used. Van Zuilichem *et al.* (1983) demonstrated that SME was negatively correlated to screw speed in a single-screw extruder whilst Meuser *et al.* (1982, 1984a, 1985), Fletcher *et al.* (1985) and Della Valle *et al.* (1989) observed a positive correlation in a twin-screw extruder.

Specific mechanical energy consumption ranged between 57 and131 Wh/kg. These values agree well with those reported by Kirby *et al.* (1988) who determined SME values, 61–150 Wh/kg, following extrusion of maize grits with a Barker-Perkins MPF50d twin-screw extruder at a lower feed moisture (18–24%) with a similar screw configuration. Specific mechanical energy consumption for sago starch is lower than that obtained by Vainionpää (1991) for wheat flour (161–368 Wh/kg) using the Creusot-Loire BC-45 cooking extruder. High feed moisture used in the present investigation (34–47%) in comparison to the low moisture used by other researchers would account for the lower SME consumption.

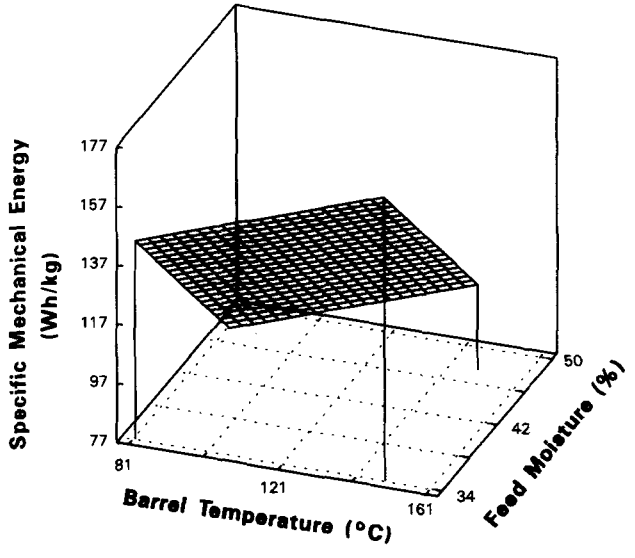

Fig. 3. Influence of barrel temperature and feed moisture on SME required for extruding sago starch at screw speed 400 rpm.

Saccharification

Extent of saccharification

Per cent saccharification of the extrudates ranged from 68 to 79%. Saccharification of the extrudates was independent of the system variables with 0.5 AGU/ml of AMG used for the saccharification as no correlation between the two could be ascertained. Kinetics of the hydrolysis reactions, using the range of enzyme concentrations (Fig. 4), indicated that there were no appreciable difference in the initial rate of hydrolysis.

A high R^2 value was obtained for the model when saccharification was carried out using the lowest AMG concentration (0.05 AGU/g). At high AMG concentration hydrolysis is nearing completion for all the samples and hence no discernible differences can be observed. Conversely, at the lowest enzyme concentration (0.05 AGU/g), AMG level becomes a limiting factor (Fig. 4) thus small structural differences in the substrates would then affect the rate of the reaction.

Feed moisture exerted a predominant effect on subsequent hydrolysis of starch post-extrusion. Despite lower water solubilities of the extrudates, samples extruded at higher moisture content were more easily saccharified (Fig. 5). Low feed moisture content led to

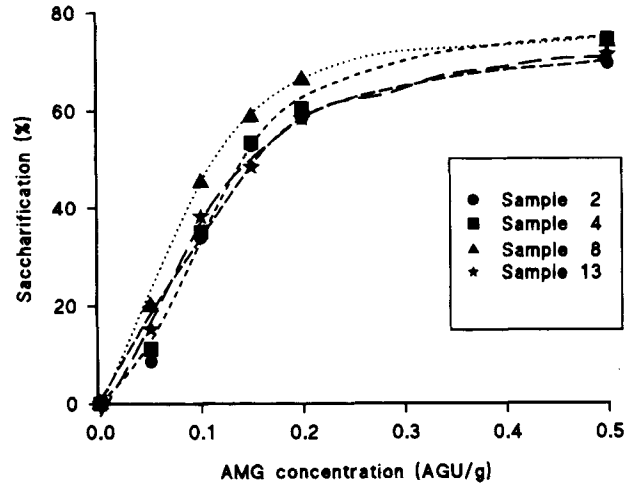

Fig. 4. Effects of AMG concentration on saccharification of sago extrudates.

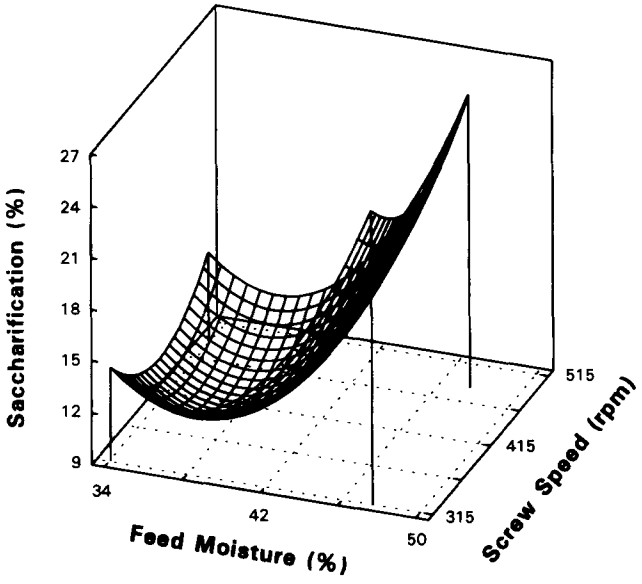

Fig. 5. Influence of feed moisture and screw speed on saccharification of sago extrudates at barrel temperature of 115°C.

extrudates with high water absorption which formed thick pastes and thus thinning of starch paste would be expected to promote saccharification. Samples giving the highest dispersion viscosity tended to absorb water too rapidly, causing clump formation retarding enzyme hydrolysis. Previous work, examining saccharification of sago extrudates, obtained by processing sago starch with a thermostable α-amylase in a Brabender single-screw extruder, suggested that water solubility of these samples was an important criterion for saccharification (Govindasamy *et al.*, 1995).

The quadratic term for screw speed was included in the model and increasing or decreasing the screw speed around 410 rpm led to an elevation in per cent saccharification (Fig. 5).

DE of the saccharified samples

DE values of the samples ranged from 44 to 53 and 93 to 99 after an 8 h treatment with amyloglucosidase (AMG) concentrations of 0.05 and 0.50 AGU/ml, respectively. DE values of the saccharified samples were independent of the extrusion processing variables. Moreover, the highest or the lowest DE values obtained after treating with the different AMG concentrations did not correspond to those samples producing the highest amount of glucose. This may be a reflection of the presence of other oligosaccharides in these samples as DE is an indication of the oligosaccharide profile.

Oligosaccharide spectra (G1–G12) were resolved by HPSEC and the predominant oligosaccharide species in the saccharified samples, apart from glucose, were G4 and G7. Reversion products, such as maltulose and isomaltose were not detected in any of the samples. A likely explanation being that in the present saccharification system, low concentrations of AMG, shorter hydrolysis times and relatively lower concentration (10% compared to 30–40% ds) of substrates were utilised.

Influence of structural characteristics and processing on saccharification

In the absence of a physical model relating processing conditions to product properties, it is only possible to construct statistical models which describe the relationship between such variables. Statistical models have limited value for exploring the underlying mechanisms of a process but such models do offer a means for rationalising large amount of data (Kirby *et al.*, 1988). The model proposed by Meuser *et al.* (1984a, b) enables the variation of water solubility to be understood in terms of SME input and product temperature. This model demonstrates that there is significant changes in process variables, product properties and processing conditions.

Correlation between the different responses were examined (Table 3). Strong negative correlation between mass temperature and die pressure was observed ($r = -0.85$). An increase in the barrel temperature imparted more thermal energy input to the product, thus raising the product temperature. Consequently, viscosity of the food dough decreases which translates into lower die pressure.

Poor negative correlation was found between saccharification and SME ($r = -0.44$) (Table 2). Higher input of mechanical energy leads to formation of the extrudates which were not readily saccharified (Fig. 6). In addition, the model derived for saccharification suggest that extrudates with higher enzyme susceptibility were obtained by processing at higher hydration levels. Enhanced gelatinisation and lower water absorption at the higher hydration levels prob-

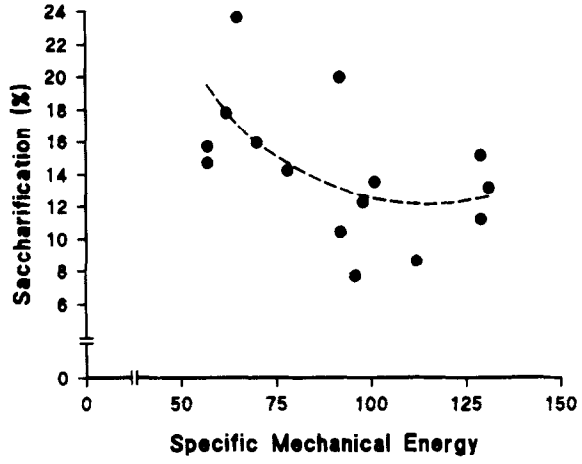

Fig. 6. Effects of SME on saccharification of sago extrudates.

ably contributes to increased enzyme susceptibility. Saccharification and die pressure are weakly correlated ($r = -0.45$). Die pressure is used as an index of melt viscosity (Tadmor & Gogos, 1979). Higher melt viscosity of the extrudates (as indicated by high die pressure), results in a lower percent saccharification. Samples with high melt viscosity form viscous paste at a high solid content, causing problems during saccharification; thus retarding enzyme hydrolysis. Moreover, the high slurry viscosities prevented the use of solid contents greater than 10% (g/100 ml) for the saccharification reaction.

A relationship between WSI and SME is apparent (Fig. 7), though it is only a global trend. This study confirms the observation of Della Valle *et al.* (1989) that WSI increases with SME to a lesser extent. Meuser *et al.* (1982, 1984a, b) and Vergnes *et al.* (1987) demonstrated that WSI is dependent on SME over a wide range of specific energies. The poor relationship observed between SME and WSI may be explained as water solubility is not simply based on any one unique structural parameter, such as intrinsic viscosity, but results from a complex combination of many fundamental phenomenon relating to the organisation of the macromolecules (Della Valle *et al.*, 1989).

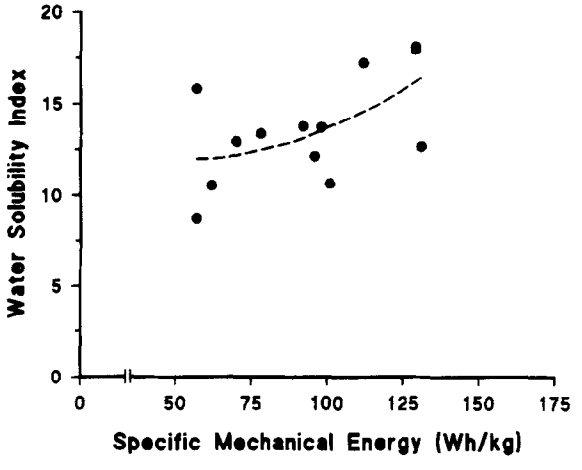

Fig. 7. Effects of SME on water solubility indices of sago extrudates.

CONCLUSION

Low extent of saccharification, 62–80% was obtained when the extrudates were saccharified with 0.5 AGU/ml for only 8 h. However, the high paste viscosity of most of the products precluded the use of solid contents above 10%. During the process of enzymatic starch saccharification, viscosity is critical, since the reaction mixture must be stirred continuously (Darnoko & Artz, 1988). To facilitate hydrolysis of the liquefied starch, the starch suspension should have a low viscosity even at a high solid content (Darnoko & Artz, 1988). Sago products formed from a high viscous mass (as suggested by high die pressure) were poorly saccharified. Such poor enzyme susceptibility is most probably a function of certain structural characteristics that are expressed through both high water absorption and paste viscosity. Die pressure can serve as a useful indicator for subsequent processing of the extrudates as in saccharification.

Despite only a global trend being observed, variations in saccharification with SME input does confirm that the latter determines product transformation that is manifested as its susceptibility towards the saccharifying enzyme. Moisture is a key factor as extruding at high moisture reduces the SME input but the products in turn are more susceptible towards saccharification, rendering the process more economical.

Saccharification and WSI were less influenced by SME and this could be related to both these parameters not being based on a unique structural parameter but results from a complex combination of many fundamental phenomenon.

Nevertheless the saccharification time (8 vs 24 or 65 h) can be reduced using these products compared with those from single-screw system (Govindasamy *et al.*, 1995), the inability to handle higher solid content desirable for subsequent enzymatic processing imposes constraints on the system. The next paper, thus, focuses on the feasibility of combining enzymatic conversion with gelatinisation and thermomechanical liquefaction in the twin-screw extruder by introducing a thermostable α-amylase in its feed stream.

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