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Effects of phosphate salts on extrusion behaviour of rice

Narpinder Singh[a,*], Kulwinder Kaur[a], Baljeet Singh[b], Kashmira S. Sekhon[b]

[a]*Department of Food Science and Technology, Guru Nanak Dev University, Amritsar 143005, India*
[b]*Department of Food Science and Technology, Punjab Agricultural University Ludhiana 141004, India*

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Abstract

A study on the effect of addition of Na_2HPO_4, and NaH_2PO_4 with a change of process variables, on the extrusion behaviour of rice grits, was made. The extruder die pressure and specific energy consumption (SEC) and extrudate properties such as expansion, density, water absorption and water solubility indices, aqueous dispersion viscosity, before and after cooking, and shear-thinning index were analysed. Second order polynomials were used to model extruder parameter and product characteristics. Addition of NaH_2PO_4 to rice grits decreased die pressure, SEC of extruder and expansion of extrudates, and increased water absorption and solubility indices and aqueous dispersion viscosities of extrudates. Na_2HPO_4 also showed a similar effect on die pressure, SEC of extruder and expansion of extrudates whereas the reverse was observed for water absorption and solubility indices and aqueous dispersion viscosities of extrudates.

Keywords: Extrusion; Rice; Phosphate salts; WSI; WAI

1. Introduction

Extrusion cooking, a high temperature short time process with advantage of high versatility, is widely used to produce modified starches, ready-to-eat cereals, texturized vegetable protein, chewing gums, confectionary items, croûtons and pet foods (Harper, 1981, 1989; Frame, 1994; Smith & Singh, 1996). During extrusion cooking starch granules gelatinize with loss of crystalline structure and disruption of granules (Colonna, Tayeb, & Mercier, 1989). Variations in extrusion conditions of temperature, moisture content and emulsifiers have been reported to have a significant effect on the crystallinity and polymorphism of material extruded (Cairns, Morris, Singh, & Smith, 1997). Expansion of extrudates has been reported to be influenced by extrusion temperature, moisture content, screw speed, screw configuration and die geometry (Mercier & Feillet, 1975; Colonna et al., 1989; Chinnaswamy & Hanna, 1988a; Kirby, Ollett, Parker, & Smith, 1988; Singh, Sekhon, & Nagi, 1994; Singh, Singh, Sandhu, Bawa, & Sekhon, 1996). The effects of different ingredients such as sugars, wheat germ oil, bran, emulsifiers, sodium bicarbonates and sodium chloride have been extensively studied (Lai, Guetzlaff, & Hoseney, 1989; Chinnaswamy & Hanna, 1988b; Hsieh, Peng, & Huff, 1990; Fan, Mitchell, & Blanshard, 1996; Sekhon, Dhillon, Singh, & Singh, 1997; Singh & Smith, 1997; Singh, Smith, & Frame, 1998).

Extrusion cooking can be advantageously used to improve the qualities of products and produce modified starches which provide functional attributes for food applications that native starches normally cannot provide (Kim & Rottier, 1980; Singh, Bawa, & Sekhon, 1995). Starch phosphates, an example of modified starch, are suitable for use as thickeners in different food products such as gravies, cream soups, sauces, oriental foods and baby foods (Rutenberg & Solarek, 1984). These starches thicken food products without forming gels. Starch phosphate dispersions have clarity, high viscosity, a long cohesive texture and stability to retrogradation (Hamilton & Paschall, 1967). Starch phosphates are conventionally produced through the reaction of starch with salts or ortho-, meta-, pyro-, and tripolyphosphoric acids and phosphorus oxychloride (Paschall, 1964; Nierle, 1969; Whistler & Towle, 1969; Bergthaller, 1971). The properties of starch phosphates have been reported to depend upon degree of substitution, starch type, reaction time and temperature (Kerr & Cleveland, 1957, 1960; Rutenberg & Solarek, 1984). Efforts have also been made to replace the conventional process for the production of starch phosphates with an

* Corresponding author.

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extrusion process (Chang & Lii, 1992). The objective of our investigation was to study the effect of adding chemical substances such as of sodium dihydrogen orthophosphate (NaH_2PO_4) and di-sodium hydrogen orthophosphate dihydrate (Na_2HPO_4) on extrusion behaviour of rice grits.

2. Materials and methods

2.1. Materials

Broken rice was procured from a local market. Sodium dihydrogen orthophosphate (NaH_2PO_4) and di-sodium hydrogen orthophosphate dihydrate (Na_2HPO_4) of analytical grade were used.

2.2. Experimental design

The second order polynomials were computed by stepwise regression using Minitab statistical software (Minitab Inc., USA). Feed moisture, die temperature and sodium dihydrogen orthophosphate/di-sodium hydrogen orthophosphate dihydrate were used as independent variables. These variables had values of X_1 (die temperature), 125°, 150°, 175°; X_2 (feed moisture), 20, 25, 30 and X_3 (sodium dihydrogen orthophosphate or di-sodium hydrogen orthophosphate dihydrate), 5, 10, 15. The polynomials were fitted to measure dependent variables (yi), such as die pressure, specific energy consumption (SEC), expansion, density, water absorption index (WAI), water solubility index (WSI), aqueous dispersion viscosity (20 rpm) and paste shear-thinning index. The equation used was of the form described earlier (Singh & Smith, 1997).

2.3. Preparation of samples

Broken rice was ground to pass through a 20 mesh sieve. The moisture content of rice grits was adjusted to the desired moisture content by spraying a calculated amount of distilled water and mixing continuously in a Hobart mixer (Model N-50). The samples were packed in polyethylene bags and kept in the refrigerator overnight to equilibrate the moisture. To see the effect of chemical substances, 5, 10 and 15 g of sodium dihydrogen orthophosphate/di-sodium hydrogen orthophosphate dihydrate per 100 g of rice grits were used.

2.4. Extrusion cooking

Extrusion cooking was carried out in a single screw extruder (Model-2003, C. W. Brabender, Hackensack, NJ, USA) with 1.9 cm barrel diameter and 20:1 barrel length and diameter ratio using a 4 mm diameter die. The feed and compression zone temperature was maintained at 70 and 125°C, respectively, while die zone temperature was varied from 125 to 175°C. The extruder was run at a constant speed of 100 rpm. The speed of the feeding screw was kept constant at 100 rpm.

Extrusion pressure was measured using a Dynisco (Dynisco Ltd. 0-5000 psi) pressure transducer in the die just before the orifice. Readings were recorded every 10 s for at least 5 min under steady conditions of pressure, which were generally achieved after about 5 min. Specific energy consumption was calculated using the expression (Mason & Hoseney, 1986):

$$\text{SEC (Wh kg}^{-1}) = (\text{Amperes} \times \text{Volts})/(\text{kg h}^{-1}\text{ throughput}).$$

2.5. Extrudate characteristics

The diameter of extrudates was measured as a mean of 10 random measurements using a vernier calliper. WAI and WSI were determined in triplicate by the method of Anderson, Conway, Pfeifer, & Griffin (1969a, b). The extrudates were milled to a mean particle size of approximately 180–250 μm. A 2.5 g sample was dispersed in 25 g of distilled water, using a glass rod to break up any lumps. After stirring for 30 min the dispersions were rinsed into tared centrifuge tubes, made up to 32.5 g and centrifuged at 3000 *g* for 10 min. The supernatant was decanted for determination of its solids content and the sediment was weighed. WSI and WAI were determined using the expression:

$$\text{WAI} = \text{weight of sediment/weight of dry solids}$$

$$\text{WSI (\%)} = \text{weight of dissolved solids in supernatant} \times 100/\text{weight of dry solids}$$

To determine the apparent viscosity, the extrudates were ground to pass through a 60 μ mesh sieve. The ground extrudates (8 g) samples were mixed with 80 ml of distilled water and kept for 1 h at 30°C with stirring at 15 min intervals. Aqueous dispersion viscosity (η) was measured with a Brookfield viscometer (Brookfield Engineering Inc., USA) at 2 and 20 rpm using T-bar spindle (No C). Shear-thinning index was calculated by dividing apparent viscosity measured at 2 rpm with that measured at 20 rpm. The samples were then cooked in a water bath at 80°C for 1 h and again measured for apparent dispersion viscosity (η_{80}) at 20 rpm. All viscosity measurements, before and after cooking at 80°C, were made at 30°C. The viscosities of dispersion measured at 20 rpm before and after cooking at 80°C were termed as η and η_{80}, respectively.

3. Results and discussion

The second-order polynomials were computed for the extruder parameter and product characteristics using actual variables and the equations tabulated are reported in Tables 1 and 2. All the models correlate well with the measured data and were statistically significant. R^2 values for different models ranged from 81 to 97 which represents the proportion of variability in the data accounted for by the model (Montgomery, 1984).

3.1. Die pressure

Statistical data in Tables 3 and 4 show the variables that had a significant effect on the die pressure of the extruder. The regression models for die pressure reported in Tables 1 and 2 correlate well with the measured data with R^2 values from 94 to 96. Temperature, feed moisture and phosphate salt concentration had a significant effect on the die pressure of the extruder. Temperature and feed moisture content in interaction with phosphate salts also showed a significant effect on die pressure of the extruder (Fig. 1). Die pressure decreased with the increase in moisture content and temperature. These results are in agreement with earlier reported findings (Fletcher, Richmond, & Smith, 1985; Kirby et al., 1988; Singh & Smith, 1997). NaH_2PO_4 concentration showed greater effect than Na_2HPO_4, as revealed by comparision of the coefficients. Die pressure progressively decreased with the increase in both the phosphate salts which may be attributed to a decrease in dough mass viscosity. A lower dough mass viscosity may result from a higher dough mass temperature from an increased heat conduction rate with the addition of phosphate salts according to the Poiseuille equation (Martelli, 1983)

$$DP = Q \times \mu / K_f$$

where DP is die pressure, Q is feed rate, μ is dough viscosity and K_f is die conductance. Gerkens and d'Arnaud (1963) and Chinnaswamy and Hanna (1988b) hypothesise that heat conduction from the barrel to starch paste during extrusion-cooking would be greater when a metallic salt such as NaCl is present in the system, which perhaps decreases the viscosity and hence die pressure.

Table 1
Coefficients of regression models for dependent variables

Term	Die pressure	SEC	Expansion	WSI	WAI	η	STI	η_{80}
Constant	38933	1973	22.2379	25.33	9.2005	519.5	3.39177	1408.9
X_1	−294.6	−5.43	−0.0571	−0.004	−0.0107	0.034	0.00395	−2.27
X_2	−431.6	−68.8	−0.6394	0.040	−0.2355	−7.265	0.2207	−46.6
X_3	−910.5	−34.5	−0.3896	−0.322	0.0649	2.02	0.5602	−5.47
X_1^2	0.6	0	0.0001	−0.0002	0.0001	−0.001	0.00008	0.00
X_2^2	−4.5	0.65	0.0078	−0.01	0.0045	0.072	0.00117	0.56
X_3^2	6.4	0.17	−0.005	0.0038	−0.0023	−0.006	−0.0004	−0.07
$X_1 \times X_2$	2.1	0.13	0.0004	−0.0009	−0.0005	0.014	−0.0008	0.09
$X_1 \times X_3$	2.1	−0.05	0	0.0006	0.0001	−0.007	−0.0001	0.04
$X_2 \times X_3$	15.3	0.89	0.0119	−0.01274	−0.0003	0.015	−0.0006	0.08
R^2	94.8	92.8	97	94.9	92.7	97.1	94.5	92.7

X_1 = temperature; X_2 = feed moisture; X_3 = NaH_2PO_4.

Table 2
Coefficients of regression models for dependent variables

Term	Die pressure	SEC	Expansion	WSI	WAI	η	STI	η_{80}
Constant	48718	2343	22.9308	−21.66	6.6947	529.7	−0.893	1523.4
X_1	−291	−2.6	−0.0054	0.29	−0.004	0.39	0.0663	−8.27
X_2	−1218	−115	−0.973	2.09	−0.038	−10.31	0.0158	−21.64
X_3	−787	−15.4	−0.3185	0.23	−0.078	−7.96	−0.1662	−15.12
X_1^2	1	0	−0.0001	0	0.0001	−0.00	−0.0002	0.03
X_2^2	9	1.5	0.0138	−0.04	0.0031	0.09	−0.0008	0.31
X_3^2	3	−0.3	−0.0094	0	−0.004	0.04	−0.0006	0.56
$X_1 \times X_2$	3	0.1	0.0005	0	−0.002	0.03	−0.0001	0.00
$X_1 \times X_3$	2	0	0.0004	0	0.0003	0.04	0.0005	0.04
$X_2 \times X_3$	11	0.4	0.0094	−0.01	−0.002	−0.02	0.0024	−0.33
R^2	96.4	94.9	96.5	95.3	88.6	97.4	81.1	87.0

X_1 = temperature; X_2 = feed moisture; X_3 = Na_2HPO_4.

Table 3
T-ratios for the extrusion and product parameters in the response surface regression

Term	DP	SEC	Expansion	WSI	WAI	η	STI	η_{80}
X_1	−4.12****	ns	ns	ns	ns	ns	ns	ns
X_2	ns	−2.31*	−3.57**	ns	−1.66*	−4.8****	ns	−5.62****
X_3	−7.43****	−2.95**	−5.52****	2.5**	ns	3.39***	2.55**	−1.67*
X_1^2	2.73**	ns	ns	ns	ns	ns	1.87*	ns
X_2^2	ns	ns	2.38*	−1.69*	1.72*	2.58**	ns	3.7***
X_3^2	2.37*	ns	−3.20**	1.38*	−1.88*	ns	ns	ns
$X_1 \times X_2$	2.65**	1.72*	ns	ns	−1.36*	3.70***	−5.59****	4.12****
$X_1 \times X_3$	3.53***	ns	ns	ns	ns	−2.37*	ns	2.85***
$X_2 \times X_3$	5.19****	3.16**	7.00****	−4.18****	ns	ns	ns	ns

X_1 = temperature; X_2 = feed moisture; X_3 = NaH_2PO_4.
****$p \leq 0.0002$; ***$p \leq 0.002$; **$p \leq 0.02$; *$p \leq 0.2$; ns = non-significant.

Table 4
T-ratios for the extrusion and product parameters in the response surface regression

Term	DP	SEC	Expansion	WSI	WAI	η	STI	η_{80}
X_1	−4.45****	ns	ns	2.7**	ns	ns	2.18*	−1.55*
X_2	−4.28****	−4.94****	−5.05****	4.4****	ns	−3.52***	ns	ns
X_3	−7.02****	−1.68*	−4.20****	ns	ns	−6.90****	−3.19**	−1.65
X_1^2	2.77**	ns	ns	−2.33*	1.4*	ns	−2.0*	1.81*
X_2^2	1.66*	3.52***	3.89***	−4.16****	ns	1.68*	ns	ns
X_3^2	ns	−1.55*	−5.62****	ns	−2.37*	1.67*	ns	2.8**
$X_1 \times X_2$	3.62**	2.46*	ns	3.33**	−3.31**	3.62***	ns	ns
$X_1 \times X_3$	4.29****	ns	ns	ns	ns	6.35****	2.19*	ns
$X_2 \times X_3$	4.19****	1.83*	5.17****	1.94*	ns	ns	ns	−1.5*

X_1 = temperature; X_2 = feed moisture; X_3 = Na_2HPO_4.
****$p \leq 0.0002$; ***$p \leq 0.002$; **$p \leq 0.02$; *$p \leq 0.2$; ns = non-significant.

3.2. SEC

The statistical data in Tables 3 and 4 show a highly significant effect of phosphate salts on SEC of the extruder. The regression models in Table 1 show that NaH_2PO_4 had a highly significant effect followed by feed moisture. Table 2 reveals feed moisture as a prominent factor followed by Na_2HPO_4 in affecting SEC of the extruder. NaH_2PO_4 in interaction with feed moisture shows a highly significant effect on SEC. The effects of feed moisture and temperature on SEC for rice grits with and without NaH_2PO_4 are illustrated in Fig. 2. The SEC values varied from 290 to 562 Wh kg^{-1} with the change of feed moisture and temperature, comparable with values reported earlier (Singh et al., 1996) for rice–potato grits extrusion using the same extruder. SEC decreased with the increase in moisture content and temperature. Addition of NaH_2PO_4 as well as Na_2HPO_4 also decreased SEC of the extruder. The changes brought about in SEC may be attributed to the reduction in viscosity of molten rice starch. Similar effects of increasing feed moisture and temperature during extrusion of different cereals with twin and single screw extruders have been reported previously (Antila, Seiler, & Linko, 1983; Kirby et al., 1988; Singh et al., 1994, 1997).

3.3. Expansion

The statistical analysis in Tables 3 and 4 reveals that both NaH_2PO_4 and Na_2HPO_4 concentrations had the most pronounced effects on the expansion of extrudates both in linear and squared terms followed by feed moisture content. Both salts in interaction with moisture also showed significant effects on expansion of extrudates. The effects of feed moisture and temperature on expansion of rice grits extruded with and without NaH_2PO_4 are presented in Fig. 3. Expansion progressively decreased with increased concentration of both salts and feed moisture content. The coefficients of salts revealed that NaH_2PO_4 had a greater effect than Na_2HPO_4. A number of studies have reported an inverse relationship between feed moisture and expansion of extrudates from different materials (Faubion & Hoseney, 1982; Bhattacharya & Hanna, 1987; Fletcher, McMaster, Richmond, & Smith, 1984; Singh et al., 1996; Singh & Smith, 1997). The changes brought about by phosphate salts may be attributed to altered viscoelastic properties of the extrusion-cooked starch. Chinnaswamy and Hanna (1990) reported that the apparent viscosity of the extrusion-cooked starch or flour affected expansion more than did the extrusion pressure.

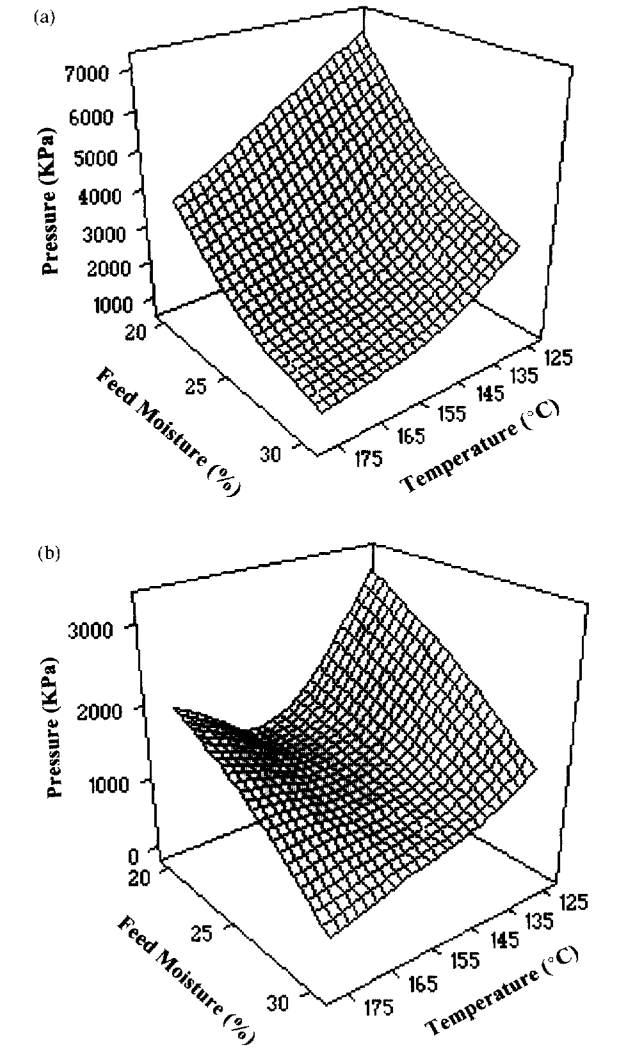

Fig. 1. Pressure as a function of moisture and temperature for (a) rice grits and (b) rice grits + 15% NaH_2PO_4.

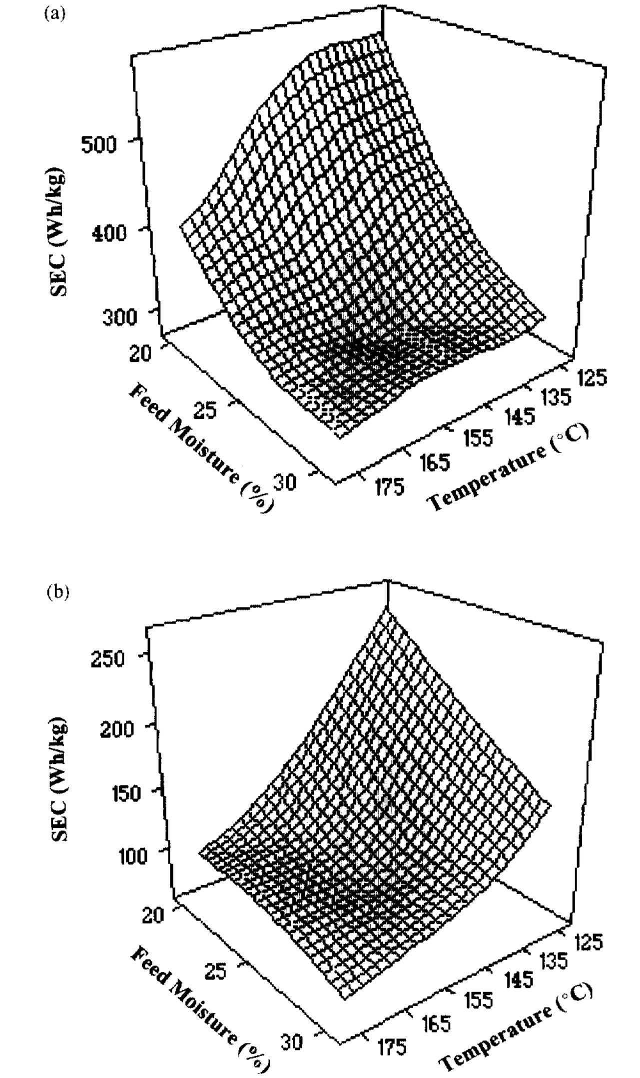

Fig. 2. SEC as a function of moisture and temperature for (a) rice grits and (b) rice grits + 15% NaH_2PO_4.

3.4. WSI

Among the various extrusion process variables, statistical data (Tables 3 and 4) and the correlation coefficients of the regression models showed that feed moisture had a significant and dominating effect on WSI both in linear and squared terms (Table 2). Addition of NaH_2PO_4 also showed a significant effect on WSI (Table 1). WSI increased with the increase in concentration of NaH_2PO_4 and decreased with Na_2HPO_4. The negative interaction between feed moisture and NaH_2PO_4 showed highly significant effects on WSI, indicating an increase in WSI with an increase in NaH_2PO_4 and decrease in feed moisture. Salay and Ciacco (1990) reported that the WSI of starch phosphated through the extrusion process is independent of the presence of sodium tripolyphosphate. WSI increased with the decrease in feed moisture content, which may be attributed to higher degradation of starch, which corresponds to a higher SEC. Similar effects of decreasing feed moisture on WSI have been reported previously for starch, maize grits and wheat (Kirby et al., 1988; Singh & Smith, 1997; Singh et al., 1997). The importance of SME in starch solubilisation has been demonstrated in a number of studies. Kirby et al. (1988) reported a linear increase in WSI in the extrusion of maize grits using an APV Bakers MPF-50 extruder. Meuser, Pfaller, and Van Lengerich (1987) related WSI to SME and product temperature using a Contima 37 Werner and Pfleiderer twin-screw extruder.

3.5. WAI

The statistical data presented in Table 3 show that feed moisture had a significant effect on WAI of extrudates, both in linear and squared terms. Both NaH_2PO_4 and Na_2HPO_4 had significant effect on WAI

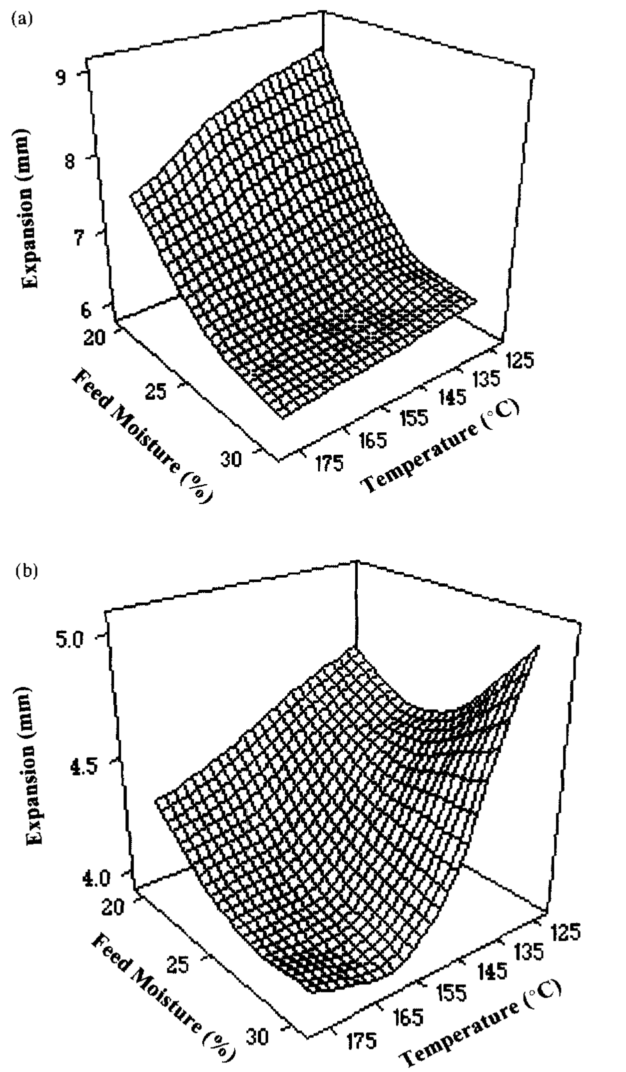

Fig. 3. Expansion as a function of moisture and temperature for (a) rice grits and (b) rice grits + 15% NaH_2PO_4.

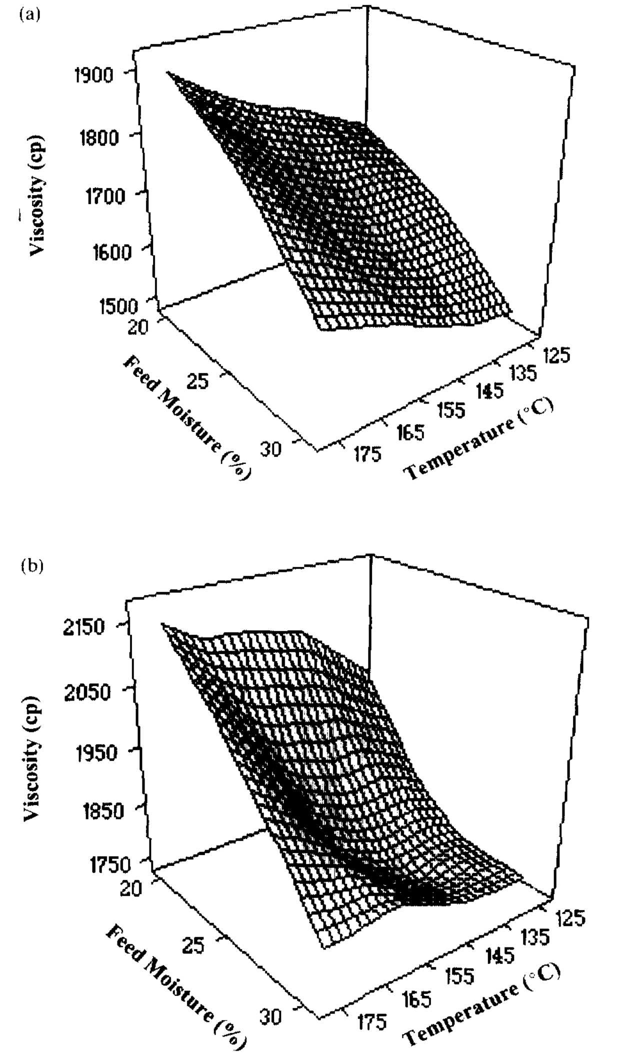

Fig. 4. Viscosity as a function of moisture and temperature for (a) rice grits and (b) rice grits + 15% NaH_2PO_4.

of extrudates in squared terms only. An increase in temperature and decrease in feed moisture increased WAI. WAI decreased with addition of NaH_2PO_4 and increased with Na_2HPO_4. Interestingly, changes in WAI brought about with the addition of both the salts were more pronounced at lower feed moisture. Increase in WAI of extrudates extruded at 125°C and 20% moisture with the addition of NaH_2PO_4 at 5, 10 and 15% was 15.2, 15.5 and 16.5%, respectively, over the corresponding increase of 3.6, 6.5 and 9.0% for those extruded at 125°C and 30% moisture. These changes in extrudate properties by moisture variation may be attributed to variation in starch degradation. Paschall (1964) reported that, for efficient phosphation of starch with orthophosphate salts, some starch hydrolysis is required by reducing the pH. The feed moisture interacted significantly with temperature in affecting the WAI. The intensity of increase in WAI with the increase in temperature decreased with the increase in feed moisture. WAI of extrusion cooked cereals has been reported by several workers to depend upon severity of extrusion conditions. A maximum water absorption at a barrel temperature of 170°C and extrusion moisture content of 14 and 25% has been reported earlier (Anderson et al., 1969b). Mercier and Feillet (1975) observed maximum WAI in the region of 170–200°C at a moisture content of 18%.

3.6. Viscosity

The statistical data in Tables 3 and 4 show a highly significant effect of phosphate salts and feed moisture on the aqueous dispersion viscosity, η, of extrudates measured at 30°C. Aqueous dispersion viscosity decreased with the addition of NaH_2PO_4 and increased with Na_2HPO_4. Viscosity of aqueous dispersion decreased with the increase in rotational speed of the spindle which indicates shear-thinning behaviour of the dispersion. Aqueous dispersion viscosities of extrudates increased with the decrease in feed moisture which may be attributed to an increase in damaged starch due to higher mechanical energy consumption (Davidson, Paton, Diosady, & Rudin, 1984; Fletcher et al., 1985). Shear-thinning index, an indicator of shear thinning over the range of 2–20 rpm, showed that shear thinning increased with the increase in NaH_2PO_4 and decreased with Na_2HPO_4. Aqueous dispersion viscosity after cooking (η_{80}) increased. Fig. 4 shows the effect of feed moisture and temperature on aqueous dispersion viscosity of extrudates extruded with and without NaH_2PO_4 measured at 2 rpm. Both salts had a similar effect on η_{80} as observed for η. The response surface regression in Table 3 reveals that feed moisture and NaH_2PO_4 had a significant affect on aqueous dispersion viscosity after cooking (η_{80}); however, feed moisture shows a significant effect both in linear and squared terms. Temperature interacted significantly with moisture and NaH_2PO_4 in affecting η_{80}. Chang and Lii (1992) reported that starch phosphates, produced through conventional and extrusion processes using sodium tripolyphosphate, had higher viscosities, measured with a Brabender Amylograph, than native starch.

4. Conclusion

The effect of adding NaH_2PO_4 and Na_2HPO_4, with changes in feed moisture and temperature, on extrusion behaviour of rice grits, was studied using response surface methodology. The high correlation of the models showed that second order polynomials can be used to study the effects of phosphate salts, feed moisture and temperature on the extrusion behaviour and product characteristics of rice grits. The models developed could be used as a tool to model functional properties, such as WSI, WAI and viscosity, of rice grits for different food applications. Additional studies are needed to investigate the effect of phosphate salts on extrusion behaviour of starch under rigorous shear-extrusion conditions.

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