Effect of Extrusion Cooking on Functional Properties and *in vitro* Starch Digestibility of Barley-Based Extrudates from Fruit and Vegetable By-Products

A. ALTAN, K.L. MCCARTHY, AND M. MASKAN

ABSTRACT: Barley flour and barley flour–pomace (tomato, grape) blends were extruded through a co-rotating twin-screw extruder. The aim of the present study was to investigate the effects of die temperature, screw speed, and pomace level on water absorption index (WAI), water solubility index (WSI), degree of starch gelatinization, and *in vitro* starch digestibility using a response surface methodology. The selected extrudate samples were examined further using differential scanning calorimetry (DSC) and polarized light microscopy, respectively. The WAI of barley–pomace extrudates was affected by increasing pomace level. Temperature had significant effect on all types of extrudate but screw speed had significant linear effect only on barley and barley–grape pomace extrudates on degree of starch gelatinization. Although no gelatinization peak was detected, an endotherm was observed on all selected extrudates. In general, extrusion cooking significantly increased *in vitro* starch digestibility of extrudates. However, increasing level of both tomato and grape pomace led to reduction in starch digestibility.

Keywords: barley, by-product, digestibility, extrusion

Introduction

Extrusion cooking is one of processing method due to its lower processing cost when compared to other usual cooking and forming processing methods and continuous processing capability that has been used to modify the functional properties, such as paste viscosity, water solubility, and water absorption of cereal flours and starches and digestible characteristic of cereal grain. Water absorption has been generally attributed to the dispersion of starch in excess water, and the dispersion is increased by the degree of starch damage due to gelatinization and extrusion-induced fragmentation, that is, molecular weight reduction of amylose and amylopectin molecules (Rayas-Duarte and others 1998). Water solubility index, often used as an indicator of degradation of molecular components, measures the degree of starch conversion during extrusion, which is the amount of soluble polysaccharide released from the starch component after extrusion (Ding and others 2005). Raw food ingredients undergo many order–disorder transitions, such as starch gelatinization, protein denaturation, and complex formation between lipids and amylose during extrusion, and are finally shaped at the extruder die. These molecular transformations convert food material into viscoelastic dough under the presence of heat, moisture, and shear (Lai and Kokini 1991). Processes involving high pressure-temperature and high shear have been known to cause partial or complete destruction of crystalline structure of starch, and considerable macro-molecular degradation (Guha and Ali 2002). Continuous high-temperature short-time extrusion cooking induces starch gelatinization, in part explained by mechanistic pressure that destroys the barrier formed by fibers and facilitates the accessibility to enzymatic activity. However, in some cases, when extrusion occurs in extreme conditions, some starch modifications altering their digestibility may also occur (Mercier and others 1980). Starch gelatinization is an important phenomenon occurring in various food processing operations because it provides unique textural and structural characteristics for the products. Therefore, the evaluation of degree of gelatinization is required during processing of starchy food. On the other hand, degree of gelatinization is an important factor in the rate of starch digestion in the thin intestine determining the glycemic response, since cooking food increases the susceptibility to enzymatic hydrolysis considerably (Holm and others 1988). The rate of starch digestion and absorption is a determinant of metabolic response to a starchy meal. There is evidence that slowly digested and absorbed carbohydrates are favorable for dietary management of metabolic disorders such as diabetes. The incorporation of dietary fiber in snacks has received increased attention in recent years due to its role in health and nutrition. Especially, researchers have focused on the use of by-products of fruits and vegetables for fiber supplementation and thereby evaluated them as a potential fiber source in the enrichment of foods (Altan and others 2008a; Yağcı and Göğüş 2008). There is need for research on how fiber affects functional and digestive properties of snacks developed by incorporation of by-products.

Therefore, the objective of this study was to investigate the effect of the extrusion variables such as die temperature, screw speed, and pomace level on water absorption and solubility indices (WAI and WSI), degree of starch gelatinization using amylose–iodine complexing method, differential scanning calorimetry (DSC) and birefringence and on *in vitro* starch digestibility of extrudates produced from barley, barley–tomato pomace, and barley–grape pomace blends, respectively.

MS 20080622 Submitted 8/15/2008, Accepted 11/19/2008. *Authors Altan and Maskan are with the Dept. of Food Engineering, Univ. of Gaziantep, Gaziantep, TR-27310, Turkey. Authors Altan and McCarthy are with the Dept. of Food Science and Technology, One Shields Ave., Univ. of California, Davis, Davis, CA 95616, U.S.A. Direct inquiries to author Altan (E-mail: altan@gantep.edu.tr).*

doi: 10.1111/j.1750-3841.2009.01051.x

Materials and Methods

Raw materials

Barley flour was purchased from Bob's Red Mill Natural Foods (Milwaukie, Oreg., U.S.A.). Average grain size varied between 125 and 420 μm. Tomato pomace was donated by ConAgra Foods from the paste line in tomato processing plant located in Oakdale (Calif., U.S.A.) as tomato-processing by-product. The tomato pomace, dried at 50 °C overnight in a forced-air drier (Model # R-4, Commercial Dehydrator System Inc., Eugene, Oreg., U.S.A.), was coarsely ground and passed on sieve with mesh size of 833 μm. Thompson seedless grape pomace was provided by Dept. of Viticulture and Enology, UC Davis pilot plant (Univ. of California, Davis, Calif., U.S.A.). Grape pomace was frozen as sheet in a blast freezer (Model FB27-5-5 ST S, Conrad, Mich., U.S.A.) at −63.9 °C for freeze drying. The pomace was freeze-dried (Model 50-SRC-5, Virtis, Gardiner, N.Y., U.S.A.) at 8 Pa pressure for 72 h. The condenser temperature was approximately −40 °C. Both the sieved tomato pomace and freeze-dried grape pomace were finely ground, sieved through a 250-μm screen and stored in polyethylene bags at −20 °C until used.

Sample preparation

The barley flour samples were conditioned to 21.97% ± 0.48% (wb) while the blends of barley flour–tomato pomace and barley flour–grape pomace samples were conditioned to 21.84% ± 0.26% and 21.66% ± 0.49% (wb) moisture by spraying with a calculated amount of water and mixing continuously at medium speed in a mixer (Model F-30T, Blakeslee, Chicago, Ill., U.S.A.). Blends were prepared by mixing barley flour and tomato pomace and grape pomace in the ratios of 100:0, 98:2, 94:6, 90:10, and 87.27:12.73 on a dry-weight basis. The level of moisture content was chosen according to preliminary tests and to ensure smooth operation of the laboratory-scale extruder. The samples were put in buckets and stored at 4 °C overnight. The feed material was then allowed 3 h to equilibrate at room temperature prior to extrusion. Moisture content of samples was determined by a halogen moisture analyzer (Model HR83 and HR83P, Mettler-Toledo GmbH, Greifensee, Switzerland) at 105 °C.

Extrusion cooking

The extrusion was carried out on a laboratory-scale corotating twin-screw extruder (MPC/V-30 model, APV, Staffordshire, England), equipped with a computer control and data acquisition system and a System9000 torque rheometer (Haake Buchler, Paramus, N.J., U.S.A.). The extruder had a barrel diameter of 30 mm and its length to diameter ratio (L/D) of 13:1 and had a slit die (Haake Buchler) of 1.47 × 20 × 150 mm. The MPC/V-30 had a clamshell barrel consisting of 3 independent zones and transition section temperatures controlled by electrical heating and compressed air cooling. The barrel zone temperatures were set constant at 30, 60, and 100 °C; temperature of the transition section between the barrel and the die was set at 130 °C throughout the experiments. The die temperature was changed according to the experimental design. The extruder screw speed was in the range of 140 to 210 rpm and 133 to 217 rpm for extrusion of barley flour and barley flour–pomaces, respectively. The screws were composed of screw elements and lope-shaped paddles, which could be assembled on the hexagon-shaped shafts to give different screw configurations. The screw configuration used is shown in Figure 1. It had had 3 pieces of 1.5 D twin lead feed screws, two 1 D twin lead feed screws, 9 kneading elements oriented at 30° feed forward, one 1 D single lead feed screw followed by 9 kneading elements oriented at 30° feed forward and 1 D discharge screw. Barley flour and barley flour–pomace blends were fed into extruder with a K-tron Type T-20 twin-screw volumetric feeder (K-Tron Corp., Pitman, N.J., U.S.A.) at a rate of 2.1 ± 0.014 kg/h. Extrudate was collected when the operation condition was at steady state identified by torque values that varied less than 5%. The samples were dried at 52 °C overnight in a forced-air drier (Model # R-4, Commercial Dehydrator System Inc.). The final dried samples contained a maximum of 5.7% (wb) moisture. Dried samples were stored in polyethylene bags at room temperature and used for further analysis.

Experimental design and data analysis

The central composite design for 2 independent variables was performed for barley flour and 3 independent variables for barley flour–tomato pomace and barley flour–grape pomace. The independent variables considered were die temperature (X_1) and screw speed (X_2) for barley flour but die temperature (X_1), screw speed (X_2), and pomace level (X_3) for barley flour–tomato pomace and barley flour–grape pomace. The independent variables and variation levels are shown in Table 1 and 2. The levels of each variable were established according to literature data and preliminary trials for suitable extrusion cooking. The outline of experimental design with the coded and actual levels for extrusion of barley

Table 1 — Process variables used in the central composite design for 2 independent variables for barley flour.

		Variable level codes				
	Code	−1.414	−1	0	1	1.414
Die temperature (°C)	X_1	136	140	150	160	164
Screw speed (rpm)	X_2	140	150	175	200	210

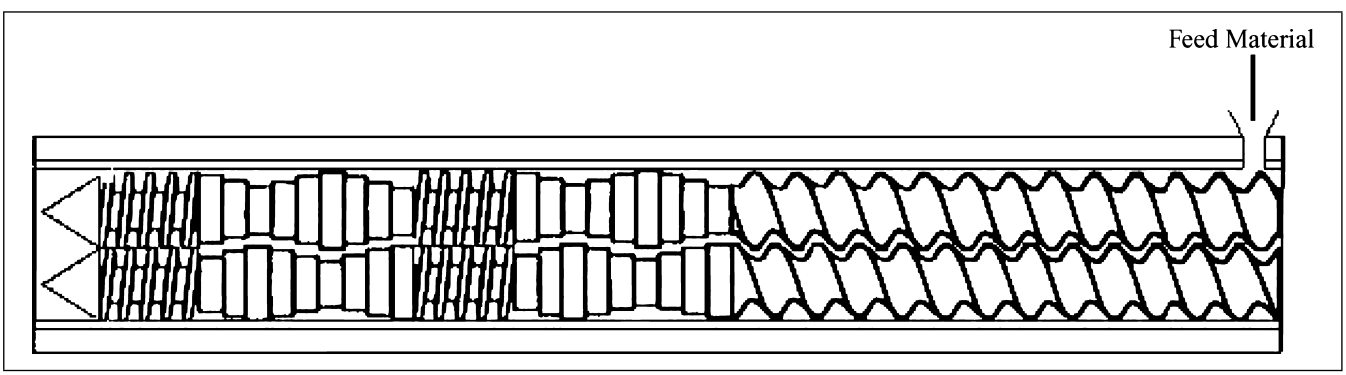

Figure 1 — Schematic representation of screw configuration.

flour and barley flour–pomace blends was given elsewhere (Altan and others 2008a, 2008b). Dependent variables were water absorption and solubility indices, *in vitro* starch digestibility, and degree of starch gelatinization as product responses. Response surface methodology was applied for experimental data using a commercial statistical package, Design-Expert version 6.0.6 (Statease Inc., Minneapolis, Minn., U.S.A.) for the generation of response surface plots. The same software was used for statistical analysis of experimental data. The results were analyzed by a multiple linear regression method, which describes the effects of variables in 1st order, a 2-factor interaction (2FI) and 2nd order polynomial models. Experimental data were fitted to the selected models and regression coefficients obtained. Statistical significance of the terms in the regression equation was examined by analysis of variance (ANOVA) for each response. To evaluate the goodness of the models, coefficient of determination (R^2), *F*-values, the derived *P* values, and coefficient of variance (*CV*) were determined. The lack-of-fit term was also used to judge adequacy of model fit. A Pearson's correlation matrix between WAI, WSI, degree of starch gelatinization, and *in vitro* starch digestibility was carried out using SPSS 11.0 (SPSS Inc., Chicago, Ill., U.S.A.) in order to determine correlation coefficients between parameters. Duncan's multiple range test was performed for gelatinization transition and amylose–lipid complex transition data obtained from DSC to determine differences between blends and extrudates.

Chemical analysis

Analyses of proximates, dietary fiber, and starch of the barley were performed by Silliker, Inc. (Modesto, Calif., U.S.A.). The moisture content, ash, protein (Kjeldahl, protein factor: 6.25) and starch (Ewers starch) were determined according to approved methods described in AOAC (AOAC 1995). The carbohydrate content was calculated by difference.

Water absorption and solubility indices

The WAI is the weight of gel obtained per gram of dry ground sample. The ground extrudate was suspended in water at room temperature. After standing for 10 min, gently stirred during this period, samples were centrifuged for 15 min at 1000 × *g* (Allegra™ 6 Centrifuge, Beckman Coulter Inc., Palo Alto, Calif., U.S.A.). The supernatant was decanted into a tared aluminum pan. The WAI was calculated as the weight of sediment obtained after removal of the supernatant per unit weight of original solids as dry basis. The WSI is the percentage of dry matter recovered after the supernatant is evaporated from the water absorption determination. The supernatant was dried in a vacuum oven at 84.4 °C and 20 to 24 mmHg gauge pressure for 24 h and weighed. The WSI was the weight of dry solids in the supernatant expressed as a percentage of the original weight of sample on dry basis (Jin and others 1995). WAI and WSI determinations were replicated 4 times.

Table 2—Process variables used in the central composite design for 3 independent variables for barley flour–tomato pomace and barley flour–grape pomace blends.

		Variable level codes				
	Code	−1.682	−1	0	1	1.682
Die temperature (°C)	X_1	133	140	150	160	167
Screw speed (rpm)	X_2	133	150	175	200	217
Pomace level (%)	X_3	0	2	6	10	12.7

Degree of starch gelatinization (amylose–iodine complex formation)

The degree of starch gelatinization (DG) in extrudates was determined according to the method of Wootton and Chaudhry (1980) as modified by Ibanoglu and others (1996). A ground sample (2 g, db) was dispersed in 100 mL of distilled water by mixing on a laboratory stirrer for 2 min at room temperature. The resulting suspension was then centrifuged at 1500 × *g* for 10 min and 1 mL iodine solution (4% KI, 1% I_2) was added to 1 mL of the aliquot of supernatant to form a blue complex with the dissolved amylose present in the sample and made up to 10 mL with distilled water. The absorbance (A_1) was then measured at 600 nm using a spectrophotometer (Lambda 25 UV/VIS Spectrometer, Perkin Elmer, Shelton, Conn., U.S.A.) against a reference solution containing all reagents except extrudate sample. Two grams of unextruded barley flour–tomato pomace blends was heated and brought to boiling in water with gentle stirring, held for 5 min boiling and made up to 100 mL with distilled water. Starch in boiled unextruded blends was accepted as 100% gelatinized. The 100% gelatinized starch was treated with iodine and its absorbance (A_2) was measured as described previously. The extent of starch gelatinization in extruded samples was calculated as follows:

$$\text{Degree of starch gelatinization (\%)} = \frac{A_1}{A_2} \times 100 \qquad (1)$$

Measurements of starch gelatinization by DSC

Gelatinization of barley flour, barley flour–pomace blends (100:0, 98:2, 94:6, 90:10, and 87.3:12.7 flour to pomace ratio on a dry base) and selected extrudates were analyzed using DSC (DSC-6, PerkinElmer, The Netherlands). Selection of extrudates was based on the extreme and moderate conditions (pomace level, die temperature, screw speed) of extrusion of barley flour and barley flour–pomace blends. The extrudates were ground and sieved through a 250-μm screen. Ground samples of about 10 mg (db) were weighed on aluminum pans and 25 μL of distilled water was added using a micro-syringe. The sample pans were sealed and allowed to equilibrate overnight in a refrigerator. Samples were heated at the rate of 5 °C/min from 5 to 150 °C with nitrogen flushing (40 cm^3/min). A sealed empty pan was used as a reference. Gelatinization onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), and the enthalpy (ΔH) of the endotherm for gelatinization and the peak melting temperature of the amylose–lipid complex (T_{pcx}) and the enthalpy of melting of the amylose–lipid complex (ΔH_{cx}) were measured and calculated using Pyris software, version 7.0 (PerkinElmer Life and Analytical Sciences, Shelton, Conn., U.S.A.).

Birefringence measurements

A polarized light microscope (Model BX 51/52-P, Olympus, Japan) equipped with a 100-W halogen light source connected to a camera (Pixera, Model PVC 100C, Pixera Corp., Los Gatos, Calif., U.S.A.) and a computer was used to examine birefringence on barley flour and extrudate samples. The extrudates were ground and passed through a 125-μm screen. Before observation, samples were covered by a droplet of glycerol/water (20:20) solution and cover glass on microscope slide and observed at a magnification of 20× under a polarized light microscope. Two suspensions were prepared and analyzed for each sample. Pictures from different locations on the slide were taken randomly both under normal and polarized light. Maltese cross still present was evaluated as ungelatinized starch granules.

Starch digestibility

In vitro starch digestibility (SD) of raw materials and extrudates was determined according to the method of Onyango and others (2004a). Five milligrams of sample of extrudate were dissolved in 1 mL of 0.2 M phosphate buffer (pH 6.9). A stock solution of α-amylase was prepared by mixing 20 mg of porcine pancreatic α-amylase (No A-6255, Sigma-Aldrich Inc., St. Louis, Mo., U.S.A.) with 50 mL of same buffer. Half a milliliter of α-amylase solution was added to the sample suspension and incubated at 37 °C for 2 h on an incubator with shaking (Model INNOVA 40R, New Brunswick Scientific, Edison, N.J., U.S.A.). After incubation period, 1 mL of 3-5 dinitrosalicyclic acid was immediately added and the mixture was heated for 5 min in a boiling water bath to inactivate α-amylase. Samples were withdrawn and cooled. Then, the solution was made up to 25 mL with distilled water and filtered prior to measurement of absorbance at 510 nm using a Lambda 25 UV-visible spectrophotometer (PerkinElmer). A blank for each sample was prepared by the same manner. But in this case, the samples were incubated first and 3-5 dinitrosalicyclic acid was added before addition of the enzyme solution. Maltose monohydrate was used as the standard and a standard curve was prepared using solutions containing known concentrations of maltose monohydrate (10 to 160 μg/mL). *In vitro* starch digestibility of samples was expressed as milligrams maltose per gram sample (db). All the experiments were conducted at least in duplicate.

Results and Discussion

The chemical composition of the raw materials (db) is given in Table 3. Barley, tomato pomace, and grape pomace contain more than 82% carbohydrate and significant amount of fiber. Carbohydrate content of barley was primarily starch (80% of total carbohydrate) and fiber while of tomato pomace was fiber and sugar and of grape pomace was mostly sugar. Fat content of tomato pomace was the highest due to seeds when compared to barley and grape pomace. Protein content varied between 6.9% and 10.3% for raw materials.

Table 3—Chemical composition of raw materials (%, db).

Raw material	Ash	Carbohydrate[a]	Fat	Protein	Starch	Fiber
Barley flour	1.7	85.7	2.3	10.3	68.4	16.2
Tomato pomace	2.8	82.7	4.8	9.7	0.8	52.8
Grape pomace	4.1	86.6	2.4	6.9	0.0	12.3

[a]Percent carbohydrate is obtained by difference.

Water absorption index

Table 4 shows the regression equations generated for WAI with coded levels of independent variables for barley–tomato pomace and barley–grape pomace extrudates. No significant model was found for the WAI of barley extrudates. The lack-of-fit was found to be significant ($P < 0.05$) for the WAI of barley–grape pomace extrudates with low coefficient of variation ($CV = 2.33\%$). The coefficient of determination (R^2) for the WAI of barley–grape pomace extrudates was 0.739. Statistical analysis showed that grape pomace level had significant effect on the WAI of barley–grape pomace extrudates but the effect of temperature was not significant ($P > 0.05$) (Table 4). The WAI of barley–grape pomace extrudates was significantly affected by interaction of screw speed and grape pomace level ($P < 0.05$). The effect of screw speed on WAI of barley–tomato pomace extrudates was not significant ($P > 0.05$).

The measured WAI of barley extrudates ranged between 6.42 and 7.26 g gel/g dry sample. The independent process variables (temperature and screw speed) did not affect significantly ($P > 0.05$) WAI of barley flour extrudates. The WAI of barley–tomato pomace and barley–grape pomace extrudates changed from 6.10 to 7.03 (Altan and others 2008a) and 5.85 to 6.97 g gel/g dry sample for the various extrusion conditions studied. The relationship between process variables and WAI of barley–tomato pomace was published elsewhere (Altan and others 2008a). The study revealed that WAI decreased with increasing both die temperature and tomato pomace level. They attributed this change to decomposition, degradation, or dextrinization of starch as temperature increased and relative decrease in starch content due to addition of pomace and competition of absorption of water between pomace and available starch. Similar trends were observed with respect to WAI of barley–grape pomace extrudate. Effect of pomace level and screw speed on WAI of barley–grape pomace extrudates is shown in Figure 2. Increasing screw speed at low grape pomace level decreased WAI of barley–grape pomace extrudates but at high-pomace level, increasing screw speed led to rise in WAI. This indicated that the effect of screw speed was dependent on grape pomace level. The decrease in WAI with increase in the screw speed at low pomace level was probably due to starch degradation or dextrinization under high-shear conditions. However, the increase of WAI at high-pomace level suggested that there might take place some structural modification of grape pomace components with increasing screw speed. The increased specific mechanical energy by increasing screw speed could probably induce a more open structure of fiber allowing more water to enter into contact with hydrophilic groups. It could be expected that more undamaged polymer chains and a greater availability of hydrophilic groups, which could bind more water resulted in higher values of WAI

Table 4—Regression equations (based on coded data) for the predicted models representing the relationships between the dependent and independent variables.

Response	Model	R^2
WAI_T^a	$6.54 - 0.12X_1 - 0.18X_3$	0.557
WAI_G	$6.37 - 0.19X_3 + 0.18X_2X_3$	0.739
WSI_B	$8.74 - 0.51X_1 + 0.95X_2 - 0.98X_1^2$	0.872
WSI_T^a	$9.66 - 1.15X_1 + 1.03X_2 + 0.98X_3$	0.831
WSI_G	$10.80 - 0.69X_1 + 1.49X_3 + 0.68X_3^2$	0.865
DG_B	$86.09 - 2.98X_1 + 4.17X_2 - 4.44X_2^1$	0.860
DG_T	$95.79 - 4.99X_1 - 4.41X_1^2 - 5.51X_2^3 + 6.03X_1X_2 - 6.81X_1X_3$	0.780
DG_G	$90.77 - 3.52X_1 + 4.29X_2 - 5.30X_1^2$	0.751
SD_T	$448.56 - 27.06X_1 - 23.94X_3 - 21.66X_1^2 + 23.24X_1X_3$	0.883
SD_G	$378.95 - 26.05X_3 + 28.37X_1^2 + 20.08X_3^2$	0.782

[a]From Altan and others (2008a).
B = barley extrudate; T = barley–tomato pomace extrudate; G = barley–grape pomace extrudate.
X_1 = die temperature (°C); X_2 = screw speed (rpm); X_3 = pomace level (%).

under low shear conditions (Jin and others 1995; Guha and others 1997).

Water solubility index

The relationship between WSI and independent variables obtained from regression analysis is expressed in Table 4. The lack-of-fit was not significant ($P > 0.05$) for WSI of barley and barley–grape pomace extrudates, respectively. The coefficients of determination of the predicted models for WSI of barley and barley–grape pomace extrudates were 0.872 and 0.865, respectively. The negative linear and quadratic effects of temperature had significant effect ($P < 0.05$) on WSI of barley extrudates while linear term of temperature only was significant ($P < 0.05$) for WSI of barley–grape pomace extrudates. The significant positive linear effect of screw speed on WSI was obtained for barley extrudates, whereas it was not significant for barley–grape pomace extrudates at $P > 0.05$. The linear and quadratic terms of pomace level were significantly affected WSI of barley–grape pomace extrudates ($P < 0.05$).

The values of WSI varied from 6.27% to 9.67% for barley extrudates while it ranged from 7.08% to 12.99% (Altan and others 2008a) and 7.85% to 15.79% for barley–tomato pomace and barley–grape pomace extrudates, respectively. WSI of barley extrudates first increased with increase in temperature up to 150 °C and then decreased (Figure 3). Increasing temperature would increase the degree of starch gelatinization that could increase the amount of soluble starch resulting in an increase in WSI (Ding and others 2005). An increase in the amount of dextrinized starch during extrusion cooking may also result in an increase in WSI. The reduction in WSI with further increasing temperature could be due to molecular interactions between degraded starch, protein, fiber, and lipid components. These interactions may increase molecular weight of complex formed, causing decrease in the solubility index. Similar behavior was observed for WSI of yam extrudates studied by Sebio and Chang (2000). However, WSI of barley–tomato pomace previously published by Altan and others (2008a) and barley–grape pomace extrudates decreased with increasing temperature, which is in agreement with study of Gutkoski and El-Dash (1999) in extruded oat products.

The WSI increased significantly ($P < 0.05$) with increasing screw speed for barley extrudates (Figure 3) but screw speed was not significantly affected WSI of barley–grape pomace extrudates. The higher WSI of extrudate with increasing screw speed may be related to increasing specific mechanical energy with screw speed. The high mechanical shear caused breakdown of macromolecules to small molecules with higher solubility. The increase in WSI with increasing screw speed was consistent with the results reported by other researchers (Guha and others 1997; Sebio and Chang 2000; Doğan and Karwe 2003).

Increasing level of pomace raised WSI of barley–tomato pomace (Altan and others 2008a) and barley–grape pomace extrudates. This may be related to the modification of fiber, coming from pomace, on extrusion causing increase in WSI (Hashimoto and Grossmann 2003). It could also be attributed to the presence of compounds having a low molecular weight and therefore, the presence of soluble material in pomace may cause increase in WSI of extrudates. Jin and others (1995) observed an increase in WSI of cornmeal extrudates as fiber content increased from 0% to 20%. The highest value of WSI of barley–grape pomace extrudates was found at the highest level of grape pomace (12.7%). This result may be related to availability of more sugar in the system due to incorporation of sugar supplied with grape pomace in addition to the fiber content. Onyango and others (2004b) suggested that an increase in WSI with increasing sugar concentration was a sign of increased solubilization of starch. An increase in WSI coincides with the decrease in WAI for barley–grape pomace extrudates, which was proved by a negative correlation between WSI and WAI ($R = -0.511$, $P < 0.05$). This agrees well with the result of Badrie and Mellowes (1991) where they found a negative correlation between WSI and WAI for cassava extrudates. Similar correlation was not observed for barley extrudates and barley–tomato pomace extrudates in this study.

Degree of starch gelatinization

The models developed for the degree of starch gelatinization of barley and barley–pomace extrudates as functions of coded independent variables are presented in Table 4. The coefficients of determination (R^2) for the degree of starch gelatinization of barley, barley–tomato pomace, and barley–grape pomace extrudates were 0.860, 0.780, and 0.751, respectively. The lack-of-fit was found to be nonsignificant ($P > 0.05$) for the degree of starch gelatinization of barley and barley–tomato pomace extrudates, significant ($P < 0.05$) for barley–grape pomace extrudates. Although the lack-of-fit was significant for grape pomace extrudates, the *CV* was low (6.55%). Temperature had significant ($P < 0.05$) both linear and quadratic

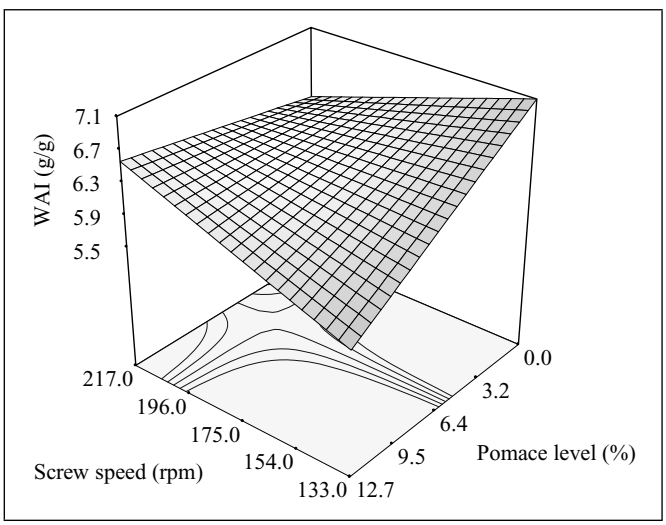

Figure 2—Response surface plot for the effect of pomace level and screw speed on WAI of barley–grape pomace extrudates at a temperature of 150 °C.

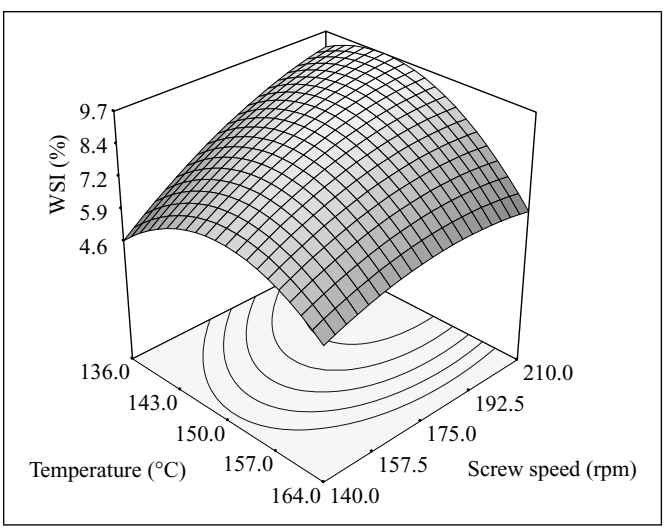

Figure 3—Response surface plot for the effect of screw speed and temperature on WSI of barley extrudates.

effects on all types of extrudate while screw speed had significant ($P < 0.05$) linear effect on barley and barley–grape pomace extrudates on the degree of starch gelatinization. The interactions of temperature with screw speed and pomace level on the degree of starch gelatinization were found to be significant ($P < 0.05$) only for barley–tomato pomace extrudates.

The influence of temperature and screw speed on the extent of gelatinization determined by iodine complexing method for barley extrudates is shown in Figure 4. The degree of starch gelatinization of barley extrudates increased until 150 °C, but a decrease was observed by further increasing temperature. One of the possible reasons for reduction in gelatinization may be the choice of screw profile yielding a higher extent of degradation, probably because of mechanical shear associated with the profile used. This may also be due to a reduced swelling on account of the formation of resistant starch, starch–lipid complexes, starch–protein complexes, or even retrograded amylose (Guha and others 1998).

An increase in screw speed resulted in increase in the degree of starch gelatinization of barley extrudates (Figure 4) as well as barley–grape pomace extrudates (Table 4). Although higher screw speeds reduce residence time, increasing screw speed from 140 to 210 rpm increased the degree of starch gelatinization of extrudates. At higher screw speeds, the shearing action probably predominates over residence time and, thus, enhances gelatinization. The results are in agreement with the findings of Guha and others (1998) and Doğan and Karwe (2003) that observed an increase in degree of gelatinization with an increase in screw speed during extrusion of rice and quinoa extrudates.

The effect of temperature on the degree of starch gelatinization for barley–pomace blends extrudates was similar to that of barley extrudates. At low-screw speed, the increase in temperature decreased the degree of starch gelatinization while at high-screw speed, the increase in temperature resulted in an increase in the degree of starch gelatinization of barley–tomato pomace extrudates. A higher screw speed would generate a higher friction and, therefore, a higher energy input into the material and hence a higher degree of starch gelatinization at the end of barrel even though the residence time of the material was shorter (Lin and others 1997). The shear force, which physically tears apart starch granules during extrusion and allows faster transfer of water into the interior starch molecules and would affect the degree of starch gelatinization (Burros and others 1987). Increasing temperature decreased degree of starch gelatinization as pomace level changed from 2% to 12.7% (Figure 5A). The reduction in the degree of starch gelatinization when pomace level was increased can be attributed to increasing fiber content coming from tomato pomace. The nonstarch polysaccharides have the capacity to hydrate and consequently to compete for and restrict the plasticizer and hence the gelatinization process by increasing the melt viscosity and reducing the availability of water for the gelatinization process (Yanniotis and others 2007). Surprisingly, grape pomace level did not affect the degree of starch gelatinization of barley–grape pomace extrudates (Figure 5B). This, maybe, comes from difference in fiber content between tomato and grape pomaces (Table 3).

The degree of starch gelatinization was correlated ($R = 0.788$, $P < 0.05$) with WSI of barley extrudates. Gomez and Aguilera (1983) found that degree of gelatinization correlated very well with WSI ($R = 0.963$), indicating that in the case of extruded products degree of gelatinization could be considered as an indicator of the extent of starch degradation rather than as an index of gelatinization.

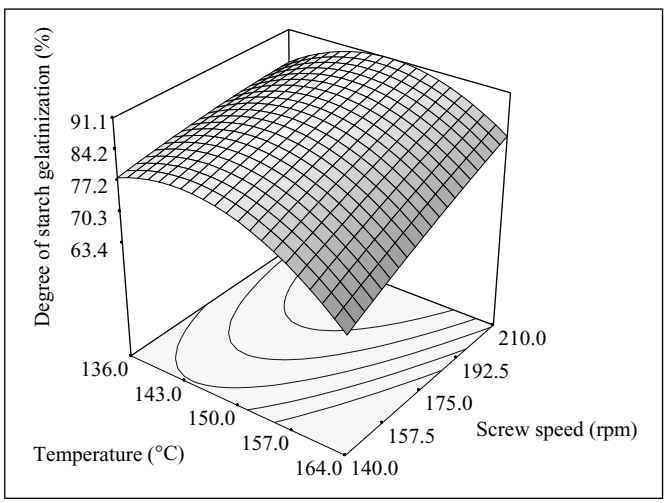

Figure 4—Response surface plot for the effect of screw speed and temperature on the degree of starch gelatinization (%) of barley flour extrudates.

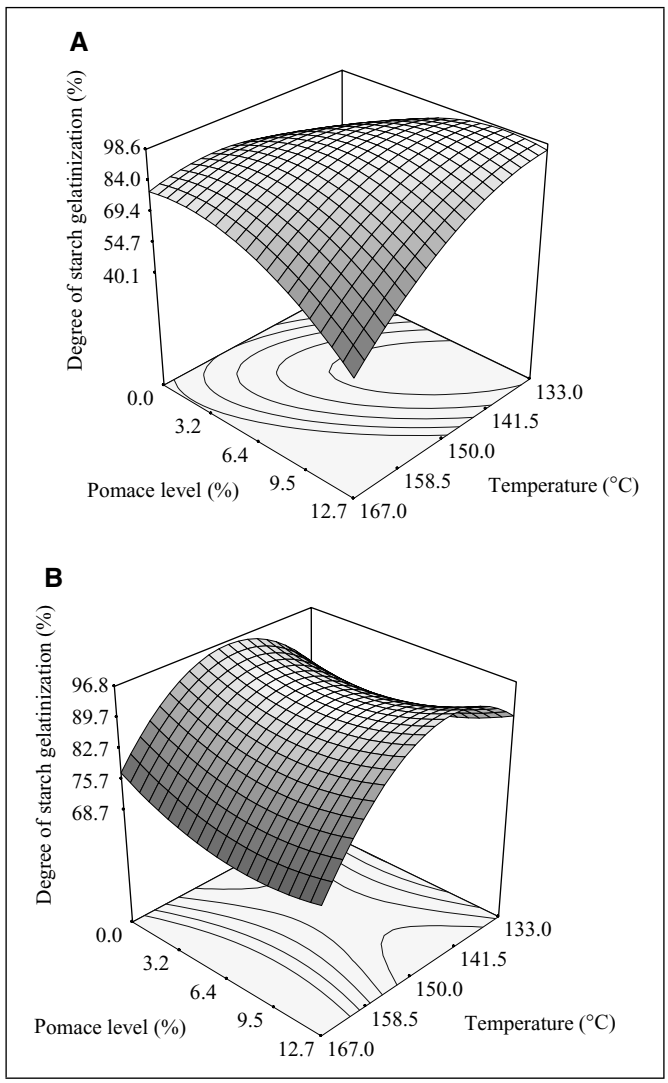

Figure 5—Response surface plot for the effect of temperature and pomace level on the degree of starch gelatinization of (A) barley–tomato pomace extrudates, (B) barley–grape pomace extrudates at screw speed of 175 rpm.

DSC and polarized light microscopy

Gelatinization properties of barley flour and barley flour–pomace blends evaluated by DSC are presented in Table 5. Gelatinization temperature (T_p) of barley flour was found to be 68.5 °C. The T_p values of barley flour–pomace blends varied within a narrow range 67.2 to 69.6 °C when compared to that of barley flour. Björck and others (1990) reported that gelatinization temperature of 5 different barley samples varied between 62 and 69 °C. There was apparently little effect of the addition of tomato and grape pomaces on the peak temperatures (T_p) (Table 5). However, the enthalpy of gelatinization (ΔH_g) tended to decrease when pomace was added. There was a significant ($P < 0.05$) difference between the enthalpy of gelatinization of barley flour and barley flour–pomace blends. Similar results were observed by Cleary and Brennan (2006) in β-glucan enriched pasta. As mentioned previously, certain polysaccharides may restrict the swelling of starch granules and consequently restrict gelatinization of starch resulting in an increase in gelatinization temperature and a decrease in enthalpy due to immobilization of water.

The amylose–lipid complex melting peak temperature (T_{pcx}) of barley flour was 101.9 °C while barley flour–pomace blends were in the range from 93.3 to 96.4 °C (Table 5). Björck and others (1990) found T_{pcx} value between 93.7 and 105.5 °C for different types of barley samples.

Table 6 also shows transition peak temperature (T_{pcx}) and enthalpy (ΔH_{cx}) of amylose–lipid complex for some selected barley and barley–pomace extrudates. The extrudates produced at low and high temperatures and screw speeds as well as at high-pomace level (12.7%) for barley and barley–pomace blends were selected. Barley flour had endothermic gelatinization peak at 68.5 °C. No peak was detected for barley flour extrudates indicating 100% gelatinization. However, iodine complexing method revealed that the degree of gelatinization of barley flour extrudates is not more than 90% (Figure 4). This result was similar to the studies of Gomez and Aguilera (1984). Gomez and Aguilera (1984) found no peak in the temperature range of 25 to 115 °C for extrudate samples and postulated that the amount of native starch left in extruded samples is minimal and undetectable by the DSC procedure. Chanvrier and others (2007) observed no residual gelatinization enthalpy by DSC for wholemeal products after extrusion at 110 °C. However, they found that there was still some cystallinity left as detected by X-ray diffraction, which was not measurable by DSC, although no Maltese cross typical of native starch granules within the samples observed by polarized microscopy. Although no gelatinization peak was detected, an endotherm was observed on all selected barley extrudates at 84 to 90.9 °C while 80.7 to 88.4 °C and 89 to 90.1 °C, which was attributed to amylose–lipid complexes, for barley–tomato pomace and barley–grape pomace extrudates. It has been reported that cereal starches containing natural fatty acids and amylose form an amylose–lipid complex when extruded (Mercier and others 1980). Figure 6 displays the typical birefringence pattern observed in barley flour. The process of gelatinization leads to loss of birefringence and hence a loss of the Maltese cross pattern depicted in Figure 6. The results obtained through measurements of iodine complexing method indicated that there was still an ungelatinized starch granule although no gelatinization peak was observed by DSC. This was confirmed by microscopic examination of the sample, which revealed the existence of Maltese cross in barley, barley–tomato pomace, and barley–grape pomace extrudates.

In vitro starch digestibility

The regression equations for the relationship between *in vitro* starch digestibility (SD) and independent variables of temperature and tomato and grape pomace levels obtained in terms of coded variables are presented in Table 4. The coefficients of determination (R^2) were 0.883 and 0.782 for barley–tomato pomace

Table 6—Thermal behavior of barley flour extrudates and barley–pomace blends extrudates.*

	Amylose–lipid complex transition	
Samples	T_{pcx}(°C)	ΔH_{cx}(J/g)
Barley extrudate		
136 °C/175 rpm	84.0[a]	3.14[a]
150 °C/140 rpm	84.7[a]	2.42[a]
150 °C/210 rpm	86.9[b]	1.97[a]
164 °C/175 rpm	90.9[c]	2.36[a]
Barley–tomato pomace extrudate		
133 °C/175 rpm/6%	80.7[a]	0.85[a]
150 °C/133 rpm/6%	84.6[b]	0.97[a]
150 °C/175 rpm/12.7%	86.9[c]	2.02[a]
167 °C/175 rpm/6%	88.4[c]	1.34[a]
Barley–grape pomace extrudate		
133 °C/175 rpm/6%	89.0[a]	1.79[a]
150 °C/133 rpm/6%	89.8[a]	3.22[a]
150 °C/175 rpm/12.7%	90.1[a]	1.92[a]
150 °C/217 rpm/6%	89.4[a]	2.33[a]
167 °C/175 rpm/6%	89.4[a]	2.58[a]

*Within columns, means with same superscript are not significantly different ($P > 0.05$).
T_{pcx} and ΔH_{cx} represent the peak melting temperature of the amylose–lipid complex and the enthalpy of melting of the amylose–lipid complex.

Table 5—Gelatinization characteristics of barley flour and barley flour–pomace blends.*

	Gelatinization transition				Amylose–lipid complex transition	
Samples	T_o(°C)	T_p(°C)	T_c(°C)	ΔH_g(J/g)	T_{pcx}(°C)	ΔH_{cx}(J/g)
Barley flour	62.4[abc]	68.5[abc]	79.5[c]	6.9[a]	101.9[d]	0.96[a]
Blends						
BF–TP (2%)	62.4[abc]	68.5[abc]	77.6[abc]	4.8[b]	93.3[a]	1.46[a]
BF–TP (6%)	61.1[a]	67.3[ab]	77.5[ab]	5.0[b]	95.9[bc]	2.18[a]
BF–TP (10%)	62.5[abc]	67.8[abc]	76.5[a]	4.2[b]	95.4[bc]	1.84[a]
BF–TP (12.7%)	61.4[ab]	67.2[a]	77.3[ab]	4.1[b]	95.3[bc]	2.19[a]
BF–GP (2%)	62.7[abcd]	68.5[abc]	77.7[abc]	4.2[b]	94.2[ab]	1.70[a]
BF–GP (6%)	63.1[bcd]	68.4[abc]	77.8[abc]	4.9[b]	96.4[c]	1.72[a]
BF–GP (10%)	63.6[cd]	69.2[bc]	79.1[bc]	4.5[b]	95.8[bc]	1.81[a]
BF–GP (12.7%)	64.4[a]	69.6[c]	77.8[abc]	3.8[b]	95.7[bc]	1.65[a]

BF = barley flour; TP = tomato pomace; GP = grape pomace.
*Within columns, means with same superscript are not significantly different ($P > 0.05$).
T_o, T_p, T_c, and ΔH_g represent the onset, peak, conclusion, and enthalpy of gelatinization.
T_{pcx} and ΔH_{cx} represent the peak melting temperature of the amylose–lipid complex and the enthalpy of melting of the amylose–lipid complex.

and barley–grape pomace extrudates with a low value of coefficient of variation (4.49% and 6.82%) of the predicted model. However, the lack-of-fit was significant ($P < 0.05$) for model of barley–tomato pomace extrudate. Linear effect of temperature and tomato pomace level as well as the quadratic effect of temperature were found to significantly influence *in vitro* starch digestibility of barley–tomato pomace extrudates at $P < 0.05$. The interaction term between temperature and tomato pomace level was also significant ($P < 0.05$) for barley–tomato pomace extrudates. Both the quadratic effects of temperature and grape pomace level in addition to linear effect of pomace level were significant ($P < 0.05$) on *in vitro* digestibility for barley–grape pomace extrudates. Screw speed had no significant effect on starch digestibility of barley–pomace extrudates.

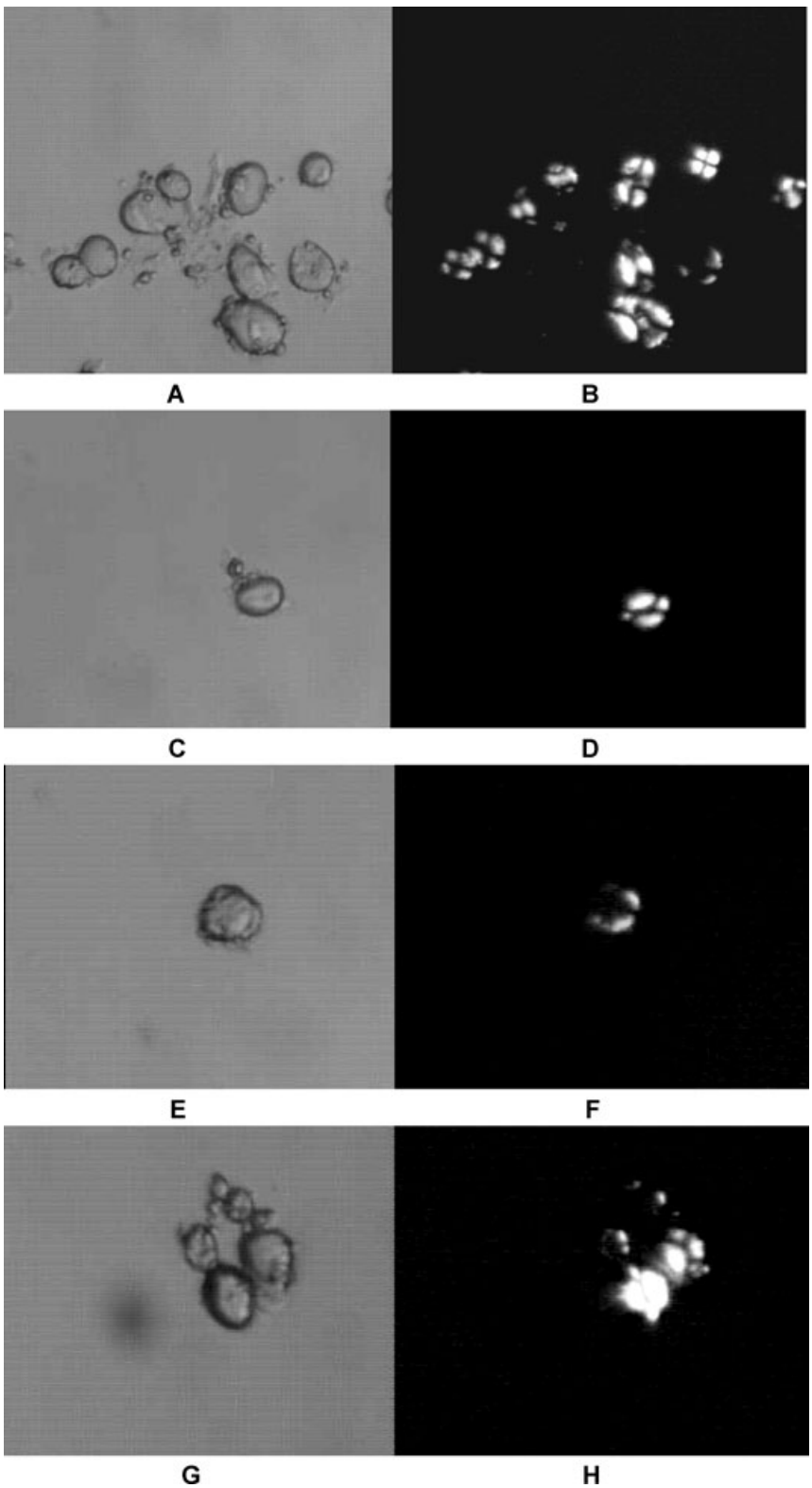

Figure 6—Images of barley flour under bright field (A) and polarized light (B); barley extrudate produced at 164 °C and 175 rpm screw speed under bright field (C) and polarized light (D); barley–tomato pomace extrudate produced at 160 °C, 150 rpm screw speed, and 2% tomato pomace under bright field (E) and polarized light (F); barley–grape pomace extrudate produced at 167 °C, 175 rpm screw speed, and 6% grape pomace under bright field (G) and polarized light (H).

There was no significant model that fit *in vitro* starch digestibility of barley extrudates. The starch digestibility of barley flour was 169.5 mg maltose/g dry sample. Those of barley extrudates varied between 447.2 and 560.6 mg maltose/g dry sample. It was in the range 313.3 to 501.8 and 360.7 to 509.4 mg maltose/g dry sample for barley–tomato pomace and barley–grape pomace extrudates, respectively. Extrusion cooking significantly increased the *in vitro* digestibility of barley starch, which is in agreement with those of other researchers (Alonso and others 2000). They found that extrusion treatment significantly increased the *in vitro* digestibility of pea starch. This may be explained in such a way that the increased shearing action develops heat through dissipation of mechanical energy and causes loss of structural integrity and increases enzyme susceptibility.

Changes in *in vitro* starch digestibility of barley–tomato pomace and barley–grape pomace extrudates, as a function of temperature and pomace level, are given in Figure 7A and 7B, respectively. Starch digestibility of barley flour–tomato pomace extrudates decreased as temperature increased. Low value of starch digestibility for barley–tomato pomace extrudates was obtained at about 167 °C, 175 rpm screw speed, and 6% tomato pomace level. The reduction of digestibility by increasing temperature was attributed to retrogradation or reassociation of gelatinized starch or formation of amylose–lipid complex, starch–protein complex, or starch and thus these complexes caused to reduce the susceptibility of starch to enzyme hydrolysis (Guha and others 1997). It is known from DSC results that there was amylose–lipid complex in extrudates and this may be partly explained the reduction in digestibility. The amylose–lipid complex was observed from DSC measurements at 80.7 to 88.4 °C for barley–tomato pomace extrudates while 89 to 90.1 °C for barley–grape pomace extrudates (Table 6). Hagenimana and others (2006) suggested that any lipid-amylose complexes formed during the extrusion process observed at 103 °C might have played an important role in delaying starch hydrolysis. Temperature decreased both starch digestibility and gelatinization of barley–tomato pomace extrudates. The availability of the starch granules to digestive enzymes increases to different levels with increasing degree of gelatinization. Increasing temperature decreased *in vitro* starch digestibility of barley–grape pomace extrudates up to 155 °C extrusion temperature then increased (Figure 7B). This may be attributed to disruption of amylose–lipid complexes, which have been shown to become dissociated at high temperatures and become more susceptible to enzymic degradation (Björck and others 1984). Increasing level of both tomato and grape pomace led to reduction in starch digestibility (Figure 7A and 7B). It may be due to fiber in pomaces which tends to reduce starch digestibility by trapping starch granules within a viscous protein–fiber–starch network. Another possible reason may be the limitation of water availability as a consequence of soluble nonstarch polysaccharide hydration can restrict gelatinization of starch and hence reduce hydrolysis by α-amylase (Tester and Sommerville 2003). Other than fiber, an increase in pomace level (Table 3) may cause increase in protein and lipid content of extrudates and therefore decreased digestibility of extrudates. The presence of protein bodies around starch granules may restrict granule swelling and starch gelatinization and hence, reduces the susceptibility to enzymatic attack (Aarathi and others 2003). The interaction of temperature and tomato pomace was also significantly ($P < 0.05$) affected *in vitro* starch digestibility of barley–tomato pomace extrudates. High value of starch digestibility was obtained at 140 °C and 2% tomato pomace level, whereas extrusion at 160 °C and 10% pomace level resulted in low value of *in vitro* starch digestibility for barley–tomato pomace extrudates (Figure 7A).

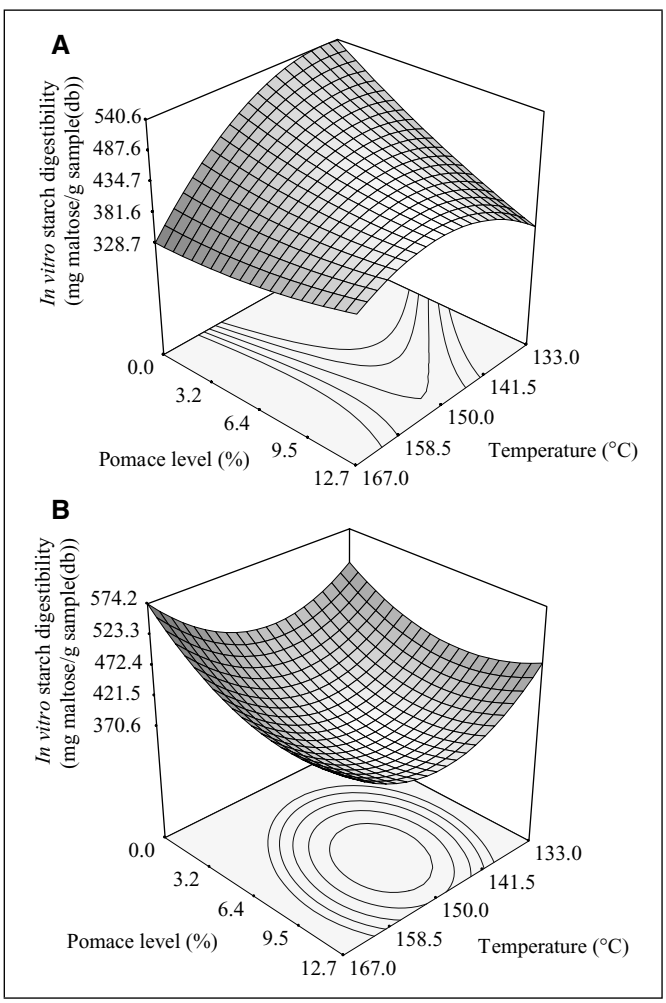

Figure 7 — Response surface plot for the effect of temperature and pomace level on the *in vitro* starch digestibility of (A) barley–tomato pomace extrudates, (B) barley–grape pomace extrudates at screw speed of 175 rpm.

Conclusions

The WSI of barley extrudates was affected by both die temperature and screw speed while die temperature and grape pomace level had a significant effect on the WSI of barley–grape pomace extrudates. Die temperature and screw speed were the most important variables affecting gelatinization of barley and barley–pomace extrudates. The effect of pomace level on degree of gelatinization was dependent on temperature for barley–tomato pomace extrudates. Amylose–lipid complex formation was observed from DSC on all selected barley extrudates at 84 to 90.9 °C while 80.7 to 88.4 °C and 89 to 90.1 °C for barley–tomato pomace and barley–grape pomace extrudates. Extrusion process increased digestibility of extrudates but the incorporation of both tomato and grape pomace caused a decrease in the digestibility of samples.

Acknowledgment

This research project was supported by the Univ. of Gaziantep, Scientific Research Projects Governing Unit (Turkey), and Center for Advanced Materials, Methods and Processing, supporting the mission of the Robert Mondavi Inst. for Wine and Food Science, Univ. of California, Davis.

References

Aarathi A, Urooj A, Puttaraj S. 2003. *In vitro* starch digestibility and nutritionally important starch fractions in cereals and their mixtures. Starch/Stärke 55: 94–9.

Alonso R, Grant G, Dewey P, Marzo F. 2000. Nutritional assessment *in vitro* and *in vivo* of raw and extruded peas (*Pisum sativum* L.). J Agric Food Chem 48: 2286–90.

Altan A, McCarthy KL, Maskan M. 2008a. Evaluation of snack foods from barley–tomato pomace blends by extrusion processing. J Food Eng 84:231–42.

Altan A, McCarthy KL, Maskan M. 2008b. Extrusion cooking of barley flour and process parameter optimization by using response surface methodology. J Sci Food Agric 88:1648–59.

AOAC. 1995. Official methods of analysis of the AOAC. 16th ed. Washington, D.C.: Assn. of Official Analytical Chemists.

Badrie N, Mellowes WA. 1991. Effect of extrusion variables on cassava extrudates. J Food Sci 56:1334–7.

Björck I, Asp NG, Birkhed D, Eliasson AC, Sjoberg LB, Lundquist I. 1984. I. Effects of processing on starch availability *in vitro* and *in vivo*. II. Drum drying of wheat flour. J Cereal Sci 2:165–78.

Björck I, Eliasson AC, Drews A, Gudmundson M, Karlsson R. 1990. Some nutritional properties of starch and dietary fiber in barley genotypes containing different levels of amylose. Cereal Chem 67:327–33.

Burros BC, Young LA, Carroad PA. 1987. Kinetics of corn meal gelatinization at high temperature and low moisture. J Food Sci 52:1372–80.

Chanvrier H, Appelqvist IAM, Bird AR, Gilbert E, Htoon A, Li Z, Lillford PJ, Lopez-Rubio A, Morell MK, Topping DL. 2007. Processing of novel elevated amylose wheats: functional properties and starch digestibility of extruded products. J Agric Food Chem 55:10248–57.

Cleary L, Brennan C. 2006. The influence of a (1→3)(1→4)-β-D-glucan rich fraction from barley on the physico-chemical properties and *in vitro* reducing sugars release of durum wheat pasta. Int J Food Sci Tech 41:910–8.

Ding QB, Ainsworth P, Tucker G, Marson H. 2005. The effect of extrusion conditions on the physicochemical properties and sensory characteristics of rice-expanded snacks. J Food Eng 66:283–9.

Doğan H, Karwe MV. 2003. Physicochemical properties of quinoa extrudates. Food Sci Tech Int 9:101–14.

Gomez MH, Aguilera JM. 1983. Changes in the starch fraction during extrusion-cooking of corn. J Food Sci 48:378–81.

Gomez MH, Aguilera JM. 1984. A physicochemical model for extrusion of corn starch. J Food Sci 49:40–3, 63.

Guha M, Ali SZ. 2002. Molecular degradation of starch during extrusion cooking of rice. Int J Food Properties 5:509–21.

Guha M, Ali SZ, Bhattacharya S. 1997. Twin-screw extrusion of rice flour without die: effect of barrel temperature and screw speed on extrusion and extrudate characteristics. J Food Eng 32:251–67.

Guha M, Ali SZ, Bhattacharya S. 1998. Effect of barrel temperature and screw speed on rapid viscoanalyser pasting behaviour of rice extrudate. Int J Food Sci Tech 33:259–66.

Gutkoski LC, El-Dash AA. 1999. Effect of extrusion process variables on physical and chemical properties of extruded oat products. Plant Foods Human Nutr 54:315–25.

Hagenimana A, Ding X, Fang T. 2006. Evaluation of rice flour modified by extrusion cooking. J Cereal Sci 43:38–46.

Hashimoto JM, Grossmann MVE. 2003. Effects of extrusion conditions on quality of cassava bran/cassava starch extrudates. Int J Food Sci Tech 38:511–7.

Holm J, Lundquist MD, Björck I, Eliasson AC, Asp NG. 1988. Degree of starch gelatinization, digestion rate of starch *in vitro*, and metabolic response in rats. A J Clin Nutr 47:1010–6.

Ibanoglu S, Ainsworth P, Hayes GD. 1996. Extrusion of tarhana: effect of operating variables on starch gelatinization. Food Chem 57:541–4.

Jin Z, Hsieh F, Huff HE. 1995. Effects of soy fiber, salt, sugar, and screw speed on physical properties and microstructure of corn meal extrudate. J Cereal Sci 22:185–94.

Lai LS, Kokini JL. 1991. Physicochemical changes and rheological properties of starch during extrusion (A Review). Biotechnol Progress 7:251–66.

Lin S, Hsieh F, Huff HE. 1997. Effects of lipids and processing conditions on degree of starch gelatinization of extruded dry pet foods. Lebens Wiss Tech 30:754–61.

Mercier C, Charbonniere R, Grebaut J, de la Gueriviere JF. 1980. Formation of amylose–lipid complexes by twin-screw extrusion cooking of manioc starch. Cereal Chem 57:4–9.

Onyango C, Noetzold H, Bley T, Henle T. 2004a. Proximate composition and digestibility of fermented and extruded uji from maize–finger millet blend. Lebens Wiss Tech 37:827–32.

Onyango C, Henle T, Ziems A, Hofmann T, Bley T. 2004b. Effect of extrusion variables on fermented maize-finger millet blend in the production of uji. Lebens Wiss Tech 37:409–15.

Rayas-Duarte P, Majewska K, Doetkott C. 1998. Effect of extrusion process parameters on the quality of buckwheat flour mixes. Cereal Chem 75:338–45.

Sebio L, Chang YK. 2000. Effects of selected process parameters in extrusion of yam flour (*Dioscorea rotundata*) on physicochemical properties of extrudates. Nahrung 44:96–100.

Tester RF, Sommerville MD. 2003. The effects of non-starch polysaccharides on extent of gelatinisation, swelling and a-amylase hydrolysis of maize and wheat starches. Food Hydrocolloids 17:41–54.

Wootton M, Chaudhry MA. 1980. Gelatinization and *in vitro* digestibility of starch in baked foods. J Food Sci 45:1783–4.

Yağcı S, Göğüş F. 2008. Response surface methodology for evaluation of physical and functional properties of extruded snack foods developed from food-by-products. J Food Eng 86:122–32.

Yanniotis S, Petraki A, Soumpasi E. 2007. Effect of pectin and wheat fibers on quality attributes of extruded cornstarch. J Food Eng 80:594–9.