

Effect of HPMC on the Quality of Wheat-Free Bread Made from Carob Germ Flour-Starch Mixtures

B.M. Smith, S.R. Bean, T.J. Herald, and F.M. Aramouni

Abstract: Carob germ proteins have been shown to have functional properties similar to wheat gluten enabling formulation and production of yeast leavened gluten-free baked goods from a true dough rather than a stiff batter. The purpose of this research was to optimize the production of wheat-free bread containing carob germ flour, corn starch, NaCl, sucrose, hydroxypropyl methylcellulose (HPMC), and H₂O. A key criterion was to formulate viscoelastic dough similar to wheat dough. To that end, response surface methodology (RSM) was used to determine optimal levels of carob germ flour, H₂O, and HPMC. Components varied as follows: 4.94%–15.05% for carob germ flour, 0.05%–3.75% HPMC, and 65.25%–83.75% H₂O (percents are on a flour basis, where carob germ flour in combination with maize starch equals 100%). Sucrose, NaCl, and yeast were held constant at 2%. Bread parameters evaluated were specific volume and crumb hardness, where the largest specific volume and the lowest value for crumb hardness were considered most desirable. The optimum formula as determined by RSM consisted of 7% carob germ flour, 93% maize starch, 2% HPMC, and 80% H₂O with predicted crumb hardness of ~200 g of force and a specific volume of ~3.5 cm³/g. When proof time was optimized, a specific volume of ~5.6 ml/g and crumb hardness value of ~156 g of force was observed. Carob germ flour may be used as an alternative to wheat flour in formulating viscoelastic dough and high quality gluten-free bread.

Keywords: carob, celiac, dough, gluten-free, wheat-free

Practical Application: Celiac disease affects approximately 1% of the world's population. Sufferers of the disease must consume a gluten-free diet. Currently, gluten-free baked products are made from batters and lack the ability to be made from dough based systems which limits the overall processability and product variety. This research is aimed at the utilization of carob germ protein and its ability to form dough to produce an optimal gluten-free bread formulation. This will help to alleviate problems in processability and product variety associated with gluten-free baked goods.

Introduction

Wheat-free foods developed for people with wheat intolerances are typically of poor quality when compared to their wheat based counterparts. One reason for this may be the lack of a protein network, which gluten provides for wheat products (Schober and others 2008). In wheat products, gluten provides elasticity and extensibility. Elasticity and extensibility are the unique functional attributes that allow for dough formation and gas retention in wheat products. Gluten has also been attributed to soft crumb structures and prolonged freshness of wheat-based foods (Cornish and others 2006). The lack of protein networks may be one contributing factor to the lack of quality and rapid staling as-

sociated with gluten-free foods (Arendt and others 2008; Schober and others 2008).

The formation of dough via gluten networks allows for easier handleability and processing of baked goods. Gluten-free bread products are typically produced from batters resembling that of a traditional cake batter (McCarthy and others 2005; Schober and others 2007, 2008) which limits the types of baked products that can be produced from a batter system. Batter based baked goods can only take the shape of the pans they are baked in, whereas dough on the other can be molded into different shapes resulting in numerous different types of products.

Both carob germ flour and zein have been shown to form viscoelastic dough with properties similar to that of wheat. Zein, however has a glass transition temperature above room temperature which makes bread production somewhat problematic (Mejia and others 2007; Oom and others 2008; Schober and others 2008; 2010; 2011). Carob germ flour is able to form viscoelastic dough when mixed with starch and water at room temperature. Caroubin, the gluten-like proteins found in carob germ flour, were first identified to have gluten-like properties by Bienenstock and others (1935). While caroubin is not the same as wheat gluten, caroubin does function in a similar fashion. Caroubin has been reported to form wheat-like dough due to disulfide bonded high molecular weight proteins (Bengoechea and others 2008; Smith and others

MS 20111499 Submitted 12/15/2011, Accepted 2/15/2012. Authors Smith, Bean, and Herald are with USDA-ARS-CGAHR, 1515 College Ave., Manhattan, KS 66502, U.S.A. Author Aramouni is with Food Science Inst., Kansas State Univ., 216 Call Hall, KSU Manhattan, KS 66506, U.S.A. Direct inquiries to author Bean (E-mail: scott.bean@ars.usda.gov).

Author disclosures: Names are necessary to report factually on available data; however, the U.S. Dept. of Agriculture neither guarantees nor warrants the standard of the product, and use of the name by the U.S. Dept. of Agriculture implies no approval of the product to the exclusion of others that may also be suitable. USDA is an equal opportunity provider and employer.

Journal of Food Science © 2012 Institute of Food Technologists®

No claim to original US government works
doi: 10.1111/j.1750-3841.2012.02739.x
Further reproduction without permission is prohibited

2010). Mixtures of 30% carob germ flour and isolated starches have been used to produce wheat-free breads (Bienstock and others 1935; Smith 2009). Wheat-free breads containing carob germ flour had reduced effects of staling when compared to other gluten-free breads. However, breads made from 30% carob germ flour/70% maize starch mixtures was dense (specific volumes of ~2.5 mL/g) and had high crumb hardness values. This was probably due to the fact that the amount of carob germ flour required to hold gas produced tough dough resulting in lower quality bread. For this reason it was hypothesized that reducing the amount of carob germ flour while adding a hydrocolloid (HPMC) would soften the dough while allowing greater gas retention. This in turn should result in greater bread quality in terms of specific volume and crumb hardness.

Thus, the objectives of this study were to optimize a formula of gluten-free bread containing carob germ flour and HPMC. To accomplish this objective, response surface methodology (RSM) was used to determine which levels of carob germ flour, HPMC, and water produced the highest quality bread. The optimum gluten-free bread formulation was then proofed for varying times to determine the optimum formulation's greatest potential quality.

Materials and Methods

Baking ingredients

Carob germ flour was generously donated by Danisco U.S.A, Inc. (New Century, KS). Unmodified native corn starch was purchased from Bob's Red Mill (Milwaukie, OR). Methocell K4M food grade modified cellulose was kindly donated by The Dow Chemical Company (Midland, MI). Sucrose was a white food grade table sugar purchased from the local grocery store (C&H Sugar Company, Crockett, CA). NaCl was a white noniodized table salt (Morton International, Inc. Chicago, IL). Instant dry yeast was obtained from Fleischmann's Yeast (AB Mauri Food, Inc., Chesterfield, MO).

RSM design

Response surface methodology was used as previously described (McCarthy and others 2005; Schober and others 2005), with modifications to determine the effects of HPMC on carob germ flour in a gluten-free bread system. Ingredient factors carob germ flour, HPMC, and water were used to optimize the gluten-free bread formula. A central composite design was employed using the following ingredient levels; carob germ flour levels were 4.94%–15.05% (starch + carob germ flour = 100% flour), water levels were 65.25%–83.75% (flour basis), and HPMC levels were 0.05%–3.75% (flour basis). This design consisted of 5 levels of each factor and a total of 20 different combinations (Table 1). Carob germ flour, water, and HPMC levels were determined by extensive preliminary research. A key criterion for determining the maximum and minimum values of the factors was the dough's viscoelastic properties. Viscoelastic dough was defined by the ability of the dough to be sheeted using a commercial sheeter (National MFG. Co., Lincoln, NE) with rollers gapped at one-fourth of an inch. The dough was required to produce free-standing bread without the aid of bake pans, and be easily worked by hands (moldable without sticking to hands or other surfaces). Model selection and optimization were performed as described by Schober and others (2005), using carob germ flour, HPMC, and water levels as the factors. Other ingredients in the bread formulation, i.e., salt, sucrose, and yeast were held constant at 2% (flour basis). Statistical analysis of the RSM was completed with Design Expert

6.0.01 (Stat-Ease Corporation, Minneapolis, MN). Model quality is shown in Table 2.

Carob germ flour bread production

Gluten-free bread was produced from 150 g of flour (starch + carob germ flour) by the formula described above. Dry ingredients were blended to homogeneity except for the yeast. Yeast was pre-hydrated for 2 min prior to dough mixing in the amount of 32 °C water needed for bread production. After yeast hydration, the water-yeast mixture was added to the dry ingredients and mixed for 30 s with a 300 W Kitchen Aid Mixer (Ultra Power, St Joseph, MI). The mixer was equipped with a flat beater attachment and dough was mixed on the lowest speed for 30 s. Dough was scraped down from the sides of the mixing bowl after the initial mixing. An additional 2 min of mixing was completed at a mixing speed of 4 s. Dough was then removed from the mixing bowl and hand kneaded for 1 min to remove large pockets of air. A portion of dough was removed equal to 100 g of flour, rounded, and placed in an oiled bake pan. Bake pans were of the same dimensions described by AACCI method 10-10.03 for 100 g loaves (Optimized Straight-Dough Bread-Making Method) (AACCI 2000). Pans containing dough were proofed at 32 °C for 45 min at a relative humidity of 85%. A standardized proof time was chosen over proofing to height due to the extremes in formulations dictated by the RSM design (Table 1). A time of 45 min was determined to be optimum during preliminary research. After proofing, dough was baked at 210 °C for 20 min in a deck oven (1T2, Doyon, Linière, Qc, Canada). Breads were allowed to cool for 2 h prior to analysis.

Table 1—Coded variable levels for carob germ flour, HPMC, and water for the experimental RSM design.

Treatment	Experimental Design		
	Coded Levels ^a		
	Carob Germ Flour	Water	HPMC
1	-1	-1	-1
2	+1	-1	-1
3	-1	+1	-1
4	+1	+1	-1
5	-1	-1	+1
6	+1	-1	+1
7	-1	+1	+1
8	+1	+1	+1
9	0	0	0
10	0	0	0
11	0	0	0
12	0	0	0
13	-1.682	0	0
14	+1.682	0	0
15	0	-1.682	0
16	0	+1.682	0
17	0	0	-1.682
18	0	0	+1.682
19	0	0	0
20	0	0	0

^aCoded levels (flour bases): Carob Germ Flour: -1.682 = 4.94%, -1 = 7%, 0 = 10%, +1 = 13%, +1.682 = 15.05%; Water: -1.682 = 65.25%, -1 = 69%, 0 = 74.5%, +1 = 80%, +1.682 = 83.75%; HPMC: -1.682 = 0.05%, -1 = 0.8%, 0 = 1.9%, +1 = 3%, +1.682 = 3.75%.

Table 2—Model quality of the RSM design.

Parameter	Model Quality			R ²
	Model	SMSS	Lack-of-Fit	
Specific volume (mL/g)	Linear	<i>P</i> < 0.05	<i>P</i> > 0.05	0.76
Hardness (g of force)	Quadratic	<i>P</i> < 0.05	<i>P</i> > 0.05	0.68

Wheat bread production

For comparison to the carob germ flour based bread, wheat bread (100 g loaf) was prepared using the optimized straight dough baking method 10-10.03 (AACCI 2000).

Bread analysis

Bread volumes were measured by rape seed displacement. Specific volume was obtained 2-h postbaking by the equation:

$$\text{Specific Volume} = \frac{\text{Volume of bread loaf}}{\text{weight of bread loaf}} \quad (1)$$

Crumb hardness was determined by texture profile analysis (TPA) as described by Schober and others (2007). TPA was performed with a TA.XT plus (Stable Micro Systems Ltd., Godalming, Surrey, U.K.). A 25 mm diameter cylindrical plastic probe attached to a 30 kg load cell was used. A pretest, test, and posttest speed of 2.0 mm/s was used with a trigger force of 5.0 g to compress the center of the crumb a distance of 40% of the slice thickness (2.5 cm). Rest time between cycles was 5.0 s. Slices were analyzed 2-h postbaking. Lower hardness values are considered more desirable. Bread was sliced to a uniform thickness of 2.5 cm for analysis.

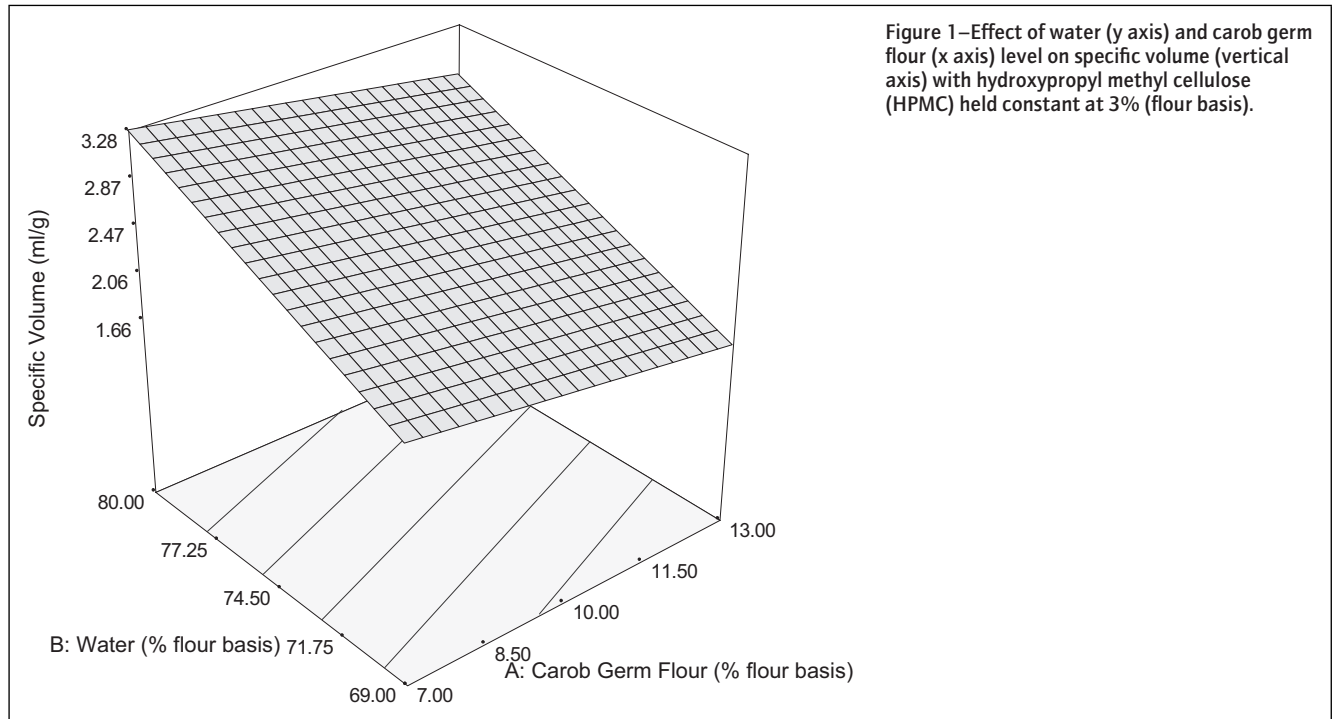


Figure 1—Effect of water (y axis) and carob germ flour (x axis) level on specific volume (vertical axis) with hydroxypropyl methyl cellulose (HPMC) held constant at 3% (flour basis).

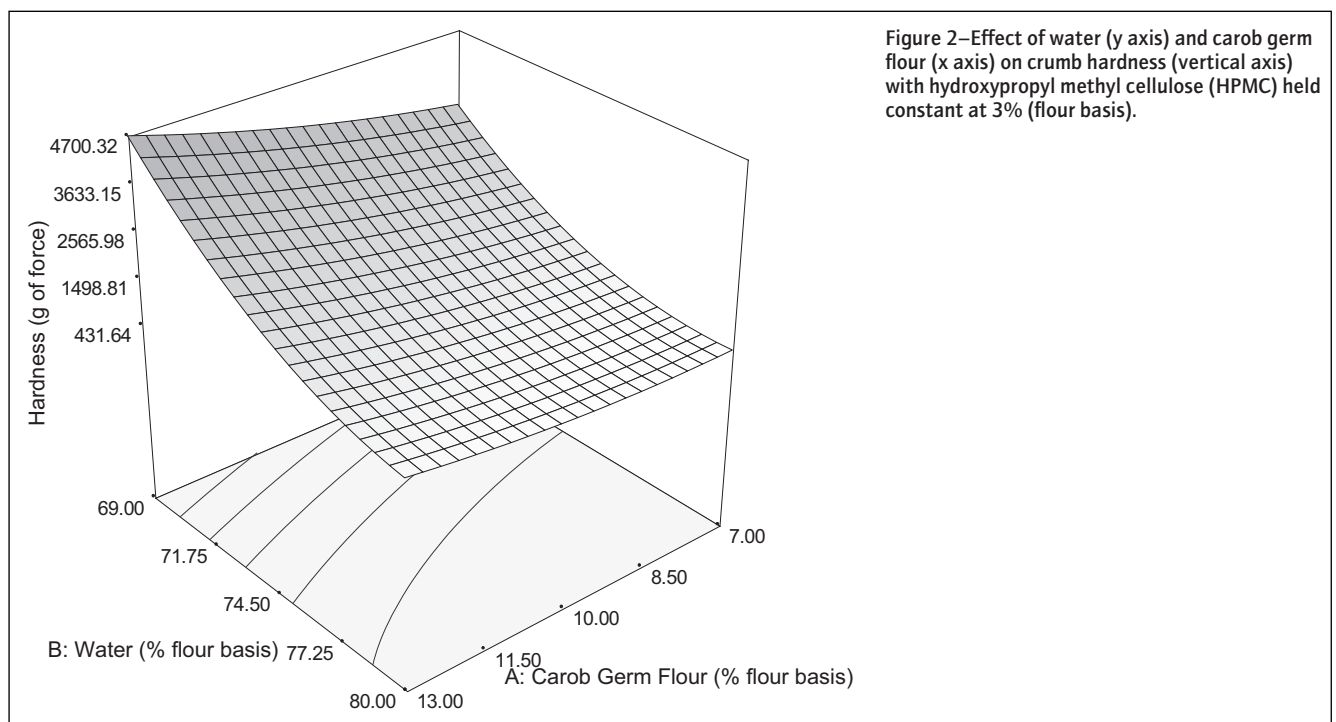


Figure 2—Effect of water (y axis) and carob germ flour (x axis) on crumb hardness (vertical axis) with hydroxypropyl methyl cellulose (HPMC) held constant at 3% (flour basis).

Optimization of proof time

One of the major limitations of the RSM optimization of carob germ flour based gluten-free bread system was the proof time of 45 min for all variable combinations. This was necessary to accommodate for extremes in variable combinations. Therefore, the optimum formulation was produced again under the same conditions covered previously, but with the use of multiple proof times to observe the optimum formulations maximum bread quality potential. Here, proof times of 45, 50, 55, 60, 65, 70, 75, and 80 min were used. Breads were analyzed for specific volume and hardness as mentioned previously. A visual inspection of the crumb was conducted on the breads, crumb failure in the form of voids in the bread was considered unacceptable. The proof times were chosen so that bread would be taken beyond the point of crumb failure. An optimum proof time was selected based on the criterion of the lowest hardness value, highest specific volume, and the absence of crumb failure. Three breads corresponding to each proof time were baked. Analysis of variance was completed with a $P < 0.05$, using Statistical Analysis Software (SAS). A comparison of means was used to determine differences in quality.

Results and Discussion

RSM/bread optimization

One indication of bread quality is specific volume. High-specific volumes are often associated with a softer crumb and higher overall

quality (McCarthy and others 2005). One of the issues associated with gluten-free breads is depreciated specific volumes when compared to similar sized wheat breads. A loaf of wheat bread made by the AACCI method 10-10.03 (Optimized Straight-Dough Bread-Making Method) (AACCI 2000) will generally have specific volumes ranging from ~ 5.5 – 7.0 mL/g depending on the source of wheat. Gluten-free breads typically have a specific volume ranging between ~ 1.5 – 4.0 mL/g (McCarthy and others 2005; Lazaridou and others 2007; Schober and others 2005, 2007; Schober 2009; Smith 2009). Loaf-specific volume clearly increased by increasing water level and decreasing carob germ flour levels (Figure 1). Both factors had a significant ($P < 0.001$) linear effect on specific loaf volume (Figure 1). The effects of HPMC were less clear and were dependent on the amount of carob germ flour and water present in the formulation.

Another indication of bread quality is crumb hardness, where lower hardness values correspond to higher quality bread (McCarthy 2005). For this research the bread quality in terms of crumb hardness followed the same trends as specific volume analysis. Here, hardness values decreased by increasing water level and decreasing carob germ flour levels (Figure 2). Both factors had a significant ($P < 0.001$) quadratic effect.

The predicted optimum values for carob germ flour, water, and HPMC were 7%, 80%, and 3%, respectively. This formulation was predicted to result in bread with a specific volume of 3.46 mL/g and a hardness of 216.53 g. To confirm these

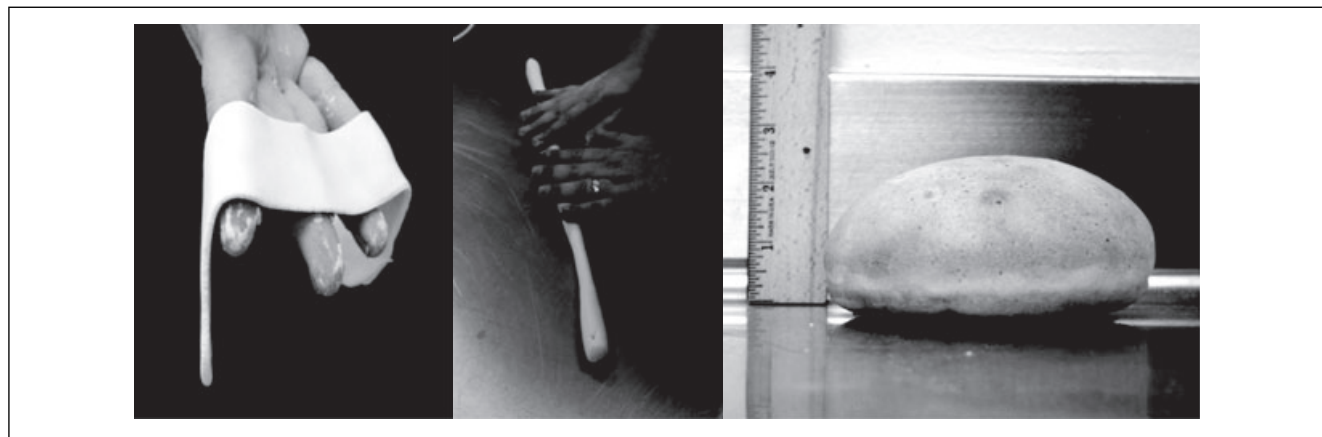


Figure 3—Pictorial representations of dough produced from the optimum formulation sheeted with a dough sheeter gaped at one-fourth of an inch (left), rolled by hand (handleability) (middle), and a free-standing roll produced without the aid of a bake pan (right).

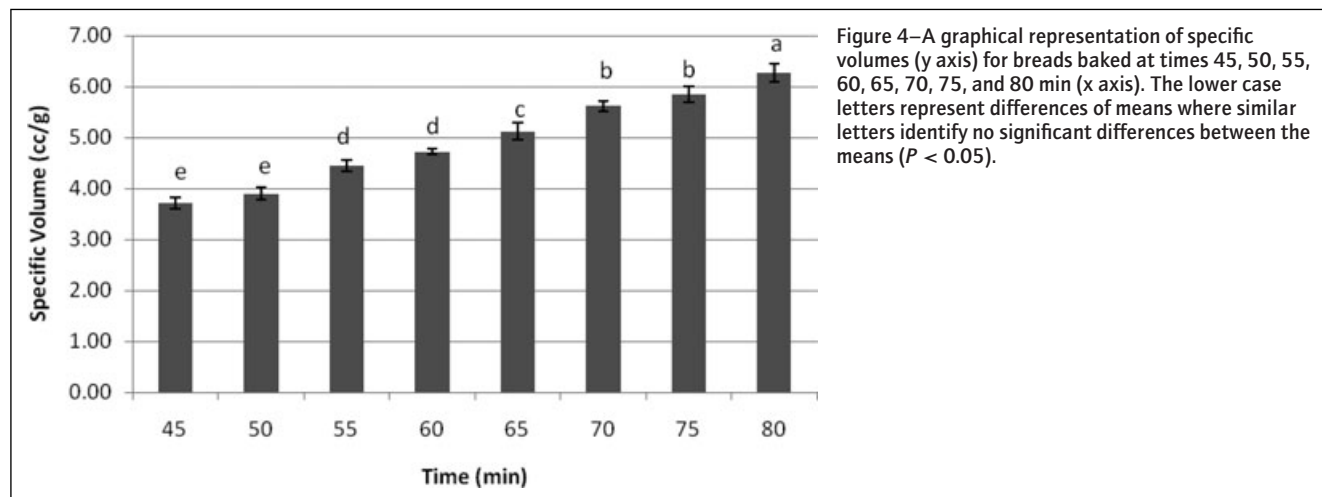


Figure 4—A graphical representation of specific volumes (y axis) for breads baked at times 45, 50, 55, 60, 65, 70, 75, and 80 min (x axis). The lower case letters represent differences of means where similar letters identify no significant differences between the means ($P < 0.05$).

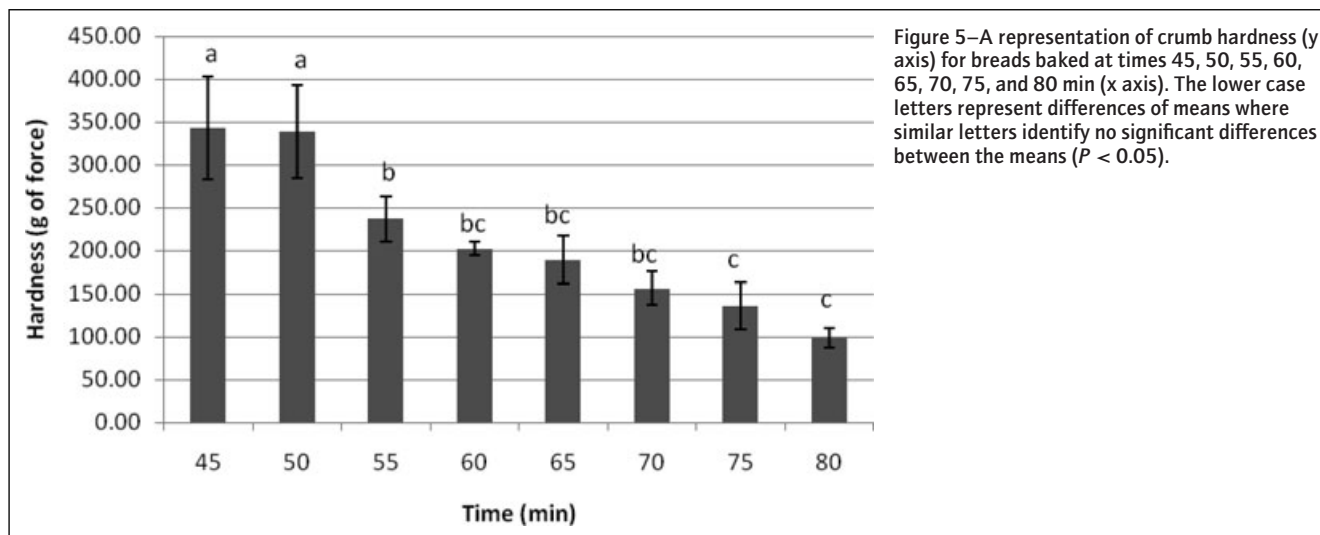


Figure 5—A representation of crumb hardness (y axis) for breads baked at times 45, 50, 55, 60, 65, 70, 75, and 80 min (x axis). The lower case letters represent differences of means where similar letters identify no significant differences between the means ($P < 0.05$).

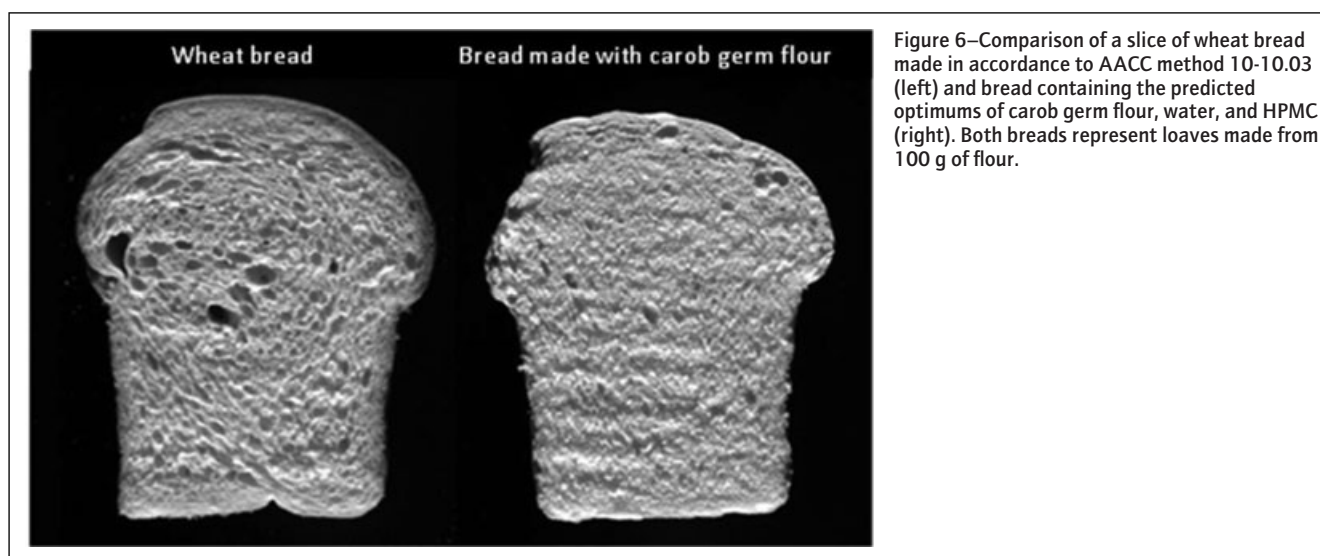


Figure 6—Comparison of a slice of wheat bread made in accordance to AACC method 10-10.03 (left) and bread containing the predicted optimums of carob germ flour, water, and HPMC (right). Both breads represent loaves made from 100 g of flour.

numbers the predicted optimum formulation was baked three times resulting in bread with specific volumes of 3.56 ± 0.12 mL/g and hardness values of 200.28 ± 50 g which confirmed the predicted optimum formulation. The results of the RSM fit well with the initial hypothesis stated that addition of the hydrocolloid HPMC and the reduction in the amount of carob germ flour would result in higher quality bread than that described by Smith (2009). The carob dough produced from the optimum formulation was easily sheeted, able to produce a free-standing roll, and was easily worked by hand (Figure 3). During mixing, dough at this formulation resembled a thick paste that did not easily stick to hands or bench tops. Upon kneading by hand, the dough resembled something similar to wheat dough.

Optimization of proof time

The optimization of proof time showed that bread quality could be improved by increasing the proof time of the optimum formulation determined by RSM. As proof time increased, specific loaf volume increased (Figure 4) and crumb hardness values decreased (Figure 5). The optimum time was determined by the presence or absence of crumb failure, evident by separation of crust and crumb, or large holes in the crumb. A proof time of 70 min the gluten-free breads had no signs of crumb failure or separa-

tion of crust and crumb. At 75 min there was a slight separation of crust and crumb and at a proof time of 80 min there were large holes present (data not shown). A proof time of 70 min under the constraints of this research produced bread with a specific volume of 5.62 ± 0.10 mL/g and a crumb hardness value of 156.25 ± 19.02 g. These values far exceed that of most 1 gluten-free breads (McCarthy and others 2005; Lazaridou and others 2007; Schober and others 2005, 2007; Schober 2009; Smith 2009). In fact the specific volume of ~ 5.6 mL/g and hardness of ~ 156 from the optimized carob germ flour bread were very close to what is typically seen in similar sized wheat breads (Smith 2009). Furthermore, the crumb structure and slice dimensions are very similar to that of a wheat bread baked from a similar sized loaf of wheat flour (Figure 6).

Conclusions

High quality gluten-free bread was produced using carob germ flour and HPMC. To the best of our knowledge this is the first time that values of crumb hardness and specific volume of gluten-free bread have approached quality attributes similar to that of wheat bread. This gluten-free bread formulation is unique in that a true dough was formed. The ability to make gluten-free breads from true dough will provide the means to diversify gluten-free products

by allowing for divergence away from the traditional constraints of batter based gluten-free breads.

References

- AACCI. 2000. AACC methods 10-10.03 (Optimized Straight-Dough Bread-Making Method). In Approved methods of American Association of Cereal Chemists. 10th ed. ST. Paul, MN: AACC International. Available from: <http://methods.aaccnet.org/cite.aspx>. Accessed May 14, 2012.
- Arendt EK, Morrissey A, Moore MM, Dal Bello F. 2008. Gluten-free breads. Gluten-free cereal products and beverages. New York: Elsevier Inc. 311 p.
- Bengoechea C, Romero A, Villanueva A, Moreno G, Alaiz M, Millan F, Guerro A, Puppo MC. 2008. Composition and structure of carob (*Ceratonia siliqua* L.) germ proteins. Food chem 107(2):675-83.
- Bienenstock M, Csaski L, Pless J, Sagi A, Sagi E. 1935. Manufacture of Mill Products for alimentary purposes and of paste foods and bake products from such milled products. U.S. patent 2,025,705.
- Cornish GB, Bekes F, Eagles HA, Payne PI. 2006. Gliadin and Glutenin, the unique balance of wheat quality: prediction of dough properties for bread wheats. St. Paul, Minn.: AACC International. 280 p.
- Mejia CD, Mauer LJ, Hamaker BR. 2007. Similarities and differences in secondary structure of viscoelastic polymers of maize α -zein and wheat gluten proteins. J Cereal Sci 45(3):353-9.
- Lazaridou A, Duta D, Papageorgiou M, Belc N, Biliaderis. 2007. Effects of hydrocolloids on dough rheology and bread quality parameters in gluten-free formulations. J Food Eng 79(3):1033-47.
- McCarthy DF, Gallagher E, Gormley TR, Schober TJ, Arendt EK. 2005. Application of response surface methodology in the development of gluten-free bread. Cereal Chem 82(5): 609-15.
- Oom A, Pettersson A, Taylor JRN, Stading M. 2008. Rheological properties of kafirin and zein prolamins. J Cereal Sci 47(1):109-16.
- Schober T. 2009. Manufacture of gluten-free specialty breads and confectionery products. In: Gallagher E, editor. Gluten-free food science and technology. Iowa: Wiley-Blackwell. p 130-80.
- Schober T, Bean S, Boyle D, Park A. 2008. Improved viscoelastic zein-starch doughs for leavened gluten-free breads: their rheology and microstructure. J Cereal Sci 48(3):755-67.
- Schober T, Bean S, Boyle D. 2007. Gluten-free sorghum bread improved by sourdough fermentation: biochemical, rheological, and microstructural background. J Agric Food Chem 55(13):5137-46.
- Schober T, Messerschmidt M, Bean S, Park S, Arendt E. 2005. Gluten-free bread from sorghum: quality differences among hybrids. Cereal Chem 82(4):394-404.
- Schober T, Moreau R, Bean S, Boyle D. 2010. Removal of surface lipids improves the functionality of commercial zein in viscoelastic zein-starch dough for gluten-free breadmaking. J Cereal Sci 52(3):417-25.
- Schober TJ, Bean SR, Michael T, Smith BM, Ioerger BP. 2011. Impact of different isolation procedures on the functionality of zein and kafirin. J Cereal Chem 54(2):241-9.
- Smith BM. 2009. Characterization and functionality of carob germ proteins. [MS thesis]. Manhattan, KS: Kansas State Univ. 89 p. Available from: <http://krex.k-state.edu>.
- Smith BM, Bean SR, Schober TJ, Tilley M, Herald TJ, Aramouni FM. 2010. Composition and molecular weight distribution of carob germ protein fractions. J Agric Food Chem 58(13):7794-800.