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Research Article

Optimisation of Malting Parameters for Quinoa and Barley: Application of Response Surface Methodology

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Quinoa (*Chenopodium quinoa* Willd) is a nutritious pseudocereal that is more stress-tolerant compared with traditional cereals. It is an excellent example of a climate-smart crop that is more resilient to climate change compared with barley. The purpose of the study was to investigate the optimum malting conditions required to produce quinoa malt using barley as a control. Response surface methodology (RSM) was used to investigate the influence of the two malting parameters steeping time and germination time on Brix (wort extract), diastatic power (DP), and free amino nitrogen (FAN) of the malt. The temperature was set at 15°C during the steeping process. Steeping time ranging from 12 to 48 hours and germination time ranging from 24 to 96 hours were designed using a central composite design (CCD). The kilning temperature for all malts was 65°C. For quinoa malt, there was a notable weak positive correlation between germination time and Brix ($r = +0.119$). However, there was a strong positive correlation between steeping time and diastatic power ($r = +0.893$). A similar trend was noted for barley with a weak positive correlation between germination time and Brix ($r = +0.142$). A strong positive correlation was also recorded between steeping time and diastatic power ($r = +0.897$) during the malting of barley. There was a relatively stronger correlation between steeping time and FAN ($r = +0.895$) than germination time and FAN ($r = +0.275$) in quinoa malt. The optimum values for the malting of barley were 47.68 hrs steeping time and 82.55 hrs germination time with a desirability value of 1.00. The responses for the optimised barley malt were 8.25°Bx, 162.28 mg/L, and 271.69°L for Brix, FAN, and diastatic power, respectively. To produce quinoa malt with Brix, FAN, and diastatic power of 8.37°Bx, 165.60 mg/L, and 275.86°L, respectively, malting conditions of 47.69 hrs steeping time and 95.81 hrs germination time are required. It was noted that quinoa is a very good candidate for producing high-quality malt for the brewing process.

1. Introduction

Barley (*Hordeum vulgare* L) is the primary cereal used in the production of malt in the world. It is a monocotyledon that belongs to the grass family Poaceae [1]. The major use of barley malt is in the brewing and distilling industries, with a lesser amount utilized in food products [2]. The quality of the beer and the cost-effectiveness of the brewing process are influenced by the chemical composition, brewing techniques, and technological indices of the barley malt. The barley malt quality then becomes critical in determining the quality of the manufactured products [3]. Whilst barley is an important source of enzymes and fermentable sugars used by yeasts in brewing, alternative cereals prove to be more economic, with an added advantage of sustainability [1].

Malting is the controlled germination of cereals, causing biochemical changes within the grain, followed by kilning. Steeping increases the moisture content from 12 to at least 40%, whilst kilning ensures product stability [4]. Mashing manipulates temperature profiles, interspersed with rest periods to provide optimum conditions for enzyme catalysis. The process of mashing breaks down complex nutrient

components (e.g., starch) from the grain by enzymatic hydrolysis, resulting in simple fermentable molecules (e.g., sugars and amino acids) [5].

Malting quality is an important parameter for barley grain used in the brewing process [6]. Important variables in determining the malt quality include extract, viscosity, diastatic power, Kolbach index, free amino nitrogen, wort β-glucan content, and soluble protein [6, 7]. The ability to hydrolyse starch to simple sugar during the germination of barley is the diastatic power. The enzymes that contribute to this malt diastatic system include α-amylase, β-amylase, limit dextrinase, and α-glucosidase. The diastatic power is directly proportional to the yield and quality of beer brewing [7]. The solubility and filtration speed of the malt wort are represented by viscosity, with a low viscosity indicating high-quality malt [6]. FAN measures the nitrogenous compounds in the wort that can be utilised by yeast during fermentation [8]. The level of FAN is determined primarily by the enzyme carboxypeptidase, a very heat-resistant enzyme that is present in abundant quantities in most malts.

Quinoa (*Chenopodium quinoa* Willd) is a pseudocereal that has been cultivated for thousands of years and has been rediscovered as a super grain for its health-promoting benefits [9]. It is a climate-smart crop, adapted to low rainfall, high temperatures, and different soil conditions. Consumers are becoming more health-conscious with a preference for functional foods. There is a public interest in the replacement of common cereal grains (maize, wheat) with more nutritious grains such as quinoa [10]. Quinoa seeds reveal a total absence of gluten and high levels of fatty acids, vitamins, minerals, antioxidants, dietary fibres, and proteins [11]. Gluten found in wheat, barley, and rye causes celiac disease (CD). The symptoms of celiac disease include damage to the intestinal epithelial cells (mucosa) in genetically susceptible individuals [12–14]. Brewing, using gluten-free ingredients such as quinoa, could produce a gluten-free beer suitable for gluten-sensitive individuals.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that is useful for the approximation and optimisation of stochastic models [15]. Experiments for fitting a predictive model involving several continuous variables are known as response surface experiments [16]. The main applications of an experimental design are screening and optimisation [17–22]. The design of experiments is intended to reduce the number of experiments with a wide range of combinations of independent variables [23]. Recently, RSM has been employed for optimisation of processes in food science and technology, material engineering, chemistry, and chemical engineering [24]. RSM has been used in the optimisation of different food processes such as extraction, drying, blanching, enzymatic hydrolysis and clarification, production of microbial metabolites, and formulation [25–27]. RSM was used to evaluate the capability of *Phormidium valderianum* on biodegradation and decolorisation of distillery spent wash [28]. Response surface methodology has been applied in malting studies as reported by several researchers [29–31]. RSM has also been used to study the influence of three malting parameters on the quality of proso millet malt [32]. Experimental data on the application of RSM in the malting of quinoa are scarce. This study seeks to explore the optimal malting conditions for quinoa malting using RSM, as an alternative to barley in beer brewing.

2. Methodology

A study to investigate the relative contributions of two predictor factors (steeping time and germination time) to the quality of barley and quinoa malt was conducted using RSM. Design Expert 7 (Stat-Ease Corporation, Minneapolis, USA) was used to construct a central composite design (CCD). Thirteen (13) runs of barley malting and 13 runs of quinoa malting were conducted as outlined in the CCD for the variables shown in Table 1. The range of values for the independent variables was defined by the operational values used in the commercial production of barley malt. The response variables for the malting process included extract (Brix value), FAN, and diastatic power.

2.1. Raw Material Collection. The barley was collected from a commercial maltster in Zimbabwe. The cultivated quinoa was collected from Midlands State University Farm in Kwekwe. The sampling, cleaning, transportation, and analysis were done under controlled conditions to minimise contamination.

2.2. Micromalting. The steeping temperature for both quinoa and barley was 15°C. Both barley and quinoa were steeped under the conditions prescribed in the CCD with variations in wet and dry conditions as shown in Table 2. The samples were allowed to germinate at 15°C [33]. After germination, the samples were kilned at 65°C for 24 hrs and the malt was analysed following the standard methods described in European Brewery Convention (EBC) Analytica [34]. All the samples were subjected to the same kilning conditions reducing the moisture content to 4.5–7% moisture within 24 hrs.

2.3. Chemicals and Reagents

2.3.1. Diastatic Power. The following chemicals and reagents were used: starch, G.R. Merck 1252; sulphuric acid (H_2SO_4), G.R. Merck Titrisol 9981 (IM); acetic acid (HCOOH), G.R. 96%, Merck 90062; sodium acetate trihydrate ($NaC_2H_3O_2$–$3H_2O$), G.R. Merck 6267; sodium hydroxide (NaOH), G.R. Merck Titrisol 9956 (M); iodine, G.R. Merck Titrisol 9910 (0.05 M); sodium thiosulphate ($Na_2S_2O_3$ $5H_2O$), G.R. Merck Titrisol s9950 (0.1 M); thymolphthalein, G.R. Merck 8175; ethyl alcohol (C_2H_4 OH), G.R. Merck 983; and iodine (I_2), G.R. Merck 4761.

2.3.2. Free Amino Nitrogen. The following chemicals and reagents were used: glycine, Merck GR 4201; di-sodium hydrogen orthophosphate ($Na_2HPO_4.12H_2O$), Merck GR 6579; potassium dihydrogen orthophosphate (KH_2PO_4), Merck GR 4873; ninhydrin (indane-trione hydrate,

Table 1: Design summary of independent variables (factors) and their actual values.

Factor	Name	Units	Type	Coded low	Coded high	Mean	Std. Dev.
A	Steeping time	hrs	Numeric	12.00	48.00	30.00	14.70
B	Germination time	hrs	Numeric	24.00	96.00	60.00	29.39

Key: Std. Dev. = standard deviation, hrs = hours.

Table 2: Steeping time with variations in wet and dry conditions.

Steeping time (hrs)	Underwater (hrs)	Dry (hrs)	Underwater (hrs)	Dry (hrs)	Underwater (hrs)	Dry (hrs)
4.54	2.54	2.00				
12.00	8.00	6.00				
30.00	6.00	16.00	6.00	2.00		
48.00	4.00	18.00	4.00	12.00	4.00	6.00
55.46	10.46	18.00	12.00	10.00	3.00	2.00

$C_9H_6O_4$), Merck AP 006762.100; D(-)fructose (laevulose), Merck 5323; potassium iodate, Merck GR 5051; ethanol, 96% Merck 971; pentachlorophenol, Merck 277392R; Kieselguhr (standard brewery grade); nitric acid, RG concentrated; sodium hydroxide 2.0 M (AR) reagent; and hydrochloric acid 1.0 M (AR) reagent.

3. Malt Characteristics

3.1. Moisture Content. Moisture content was determined after driving out moisture by heat from a ground sample for 2 hrs. The malt was ground using a Bühler Miag disc mill. The ground samples were placed in sampling bottles. The mass of the weighing dish with lid was determined, and approximately 5 g of the samples were weighed. The mass of the dish, lid, and sample was recorded. The samples were dried at 105°C for 3 hours until a constant mass was recorded. The sample and dish were cooled in desiccators. The moisture content was determined as a percentage using the following equation:

$$\%\text{Moisture content} = \text{Loss for mass on drying}^{*}100\% = \left[\frac{(W_2 - W_3)}{(W_2 - W_1)}\right]^{*}100\%, \quad (1)$$

where W_1 = mass of the empty dish and lid; W_2 = mass of the sample, dish, and lid before drying at 105°C; and W_3 = mass of the sample, dish, and lid after drying at 105°C.

3.2. Micromashing. Twenty-six samples (barley malt and quinoa malt) were analysed using a programmable mashing bath. The mashing process was carried out in the mash bath with stirrers set to run at 80–100 rpm, at 45°C for 30 minutes. The temperature of the mash bath was raised approximately 1°C per minute; hence, the mash temperature of 70°C was achieved exactly 25 minutes after the commencement of the heating. Distilled water preheated to 70°C was added to the malt in the mash bath. The mash was held at 70°C for exactly 60 minutes, and at the end of the mashing period, the mash was cooled to 20°C for 10–15 minutes. The mass of the contents was adjusted to 450 g ± 0.01 g, by the addition of distilled water. The mash was thoroughly stirred and filtered into 500 cm^3 conical flasks, returning the first 100 cm^3 to the funnel. The filtrates were used to determine extract (Brix), diastatic power, and free amino nitrogen.

3.3. Mash Analysis. The Alcolyzer Beer Analysing System (DMA-4500M; Anton Paar, Austria) was used to measure the density, original extract, real extract, calories, turbidity, colour, and pH value of the wort produced from the mashing stage. The vials for the prepared samples were thoroughly rinsed and then filled up to about 8–10 ml. A printed sheet with the results done by the microprocessor was produced for traceability. Free amino nitrogen was determined according to the European Brewery Convention (EBC) method by colour absorbance at 570 nm and reported as mg/L with glycine as standard. Diastatic power indicates the total enzymatic power of malt, both α amylase and β amylase. It was determined by measuring the breakdown of starch, and this breakdown was measured by reaction with potassium ferricyanide and expressed in degrees Lintner (°L). This reagent reacts with the reducing sugars produced by the action of the enzyme. This was determined by measuring the amount of a buffered starch solution, which was degraded by a 5 cm^3 aliquot of an extract of the malt.

4. Results

Table 3 shows the overall results of the malt parameters that were analysed for barley grains, which were used as controls. The grained grains were steeped and germinated at different intervals. A maximum Brix value of 8.10°Bx was recorded in this design. There are notably low values recorded in Run 4 (4.54 hrs steeping time; 60 hrs germination time) for Brix,

Table 3: A central composite design (CCD) for barley malting using response surface methodology.

Std	Run	Block	Steeping time (hrs)	Germination time (hrs)	Brix (°Bx)	FAN (mg/L)	Diastatic power (°L)
1	11	Block 1	12.00	24.00	6.64	123.20	152.00
2	13	Block 1	48.00	24.00	8.09	160.50	264.00
3	12	Block 1	12.00	96.00	6.80	127.90	156.90
4	8	Block 1	48.00	96.00	8.10	161.50	268.00
5	4	Block 1	4.54	60.00	4.58	98.10	132.30
6	2	Block 1	55.46	60.00	7.94	162.00	270.00
7	7	Block 1	30.00	9.09	7.17	118.60	160.40
8	3	Block 1	30.00	110.91	8.05	150.90	258.40
9	10	Block 1	30.00	60.00	8.02	145.10	220.40
10	9	Block 1	30.00	60.00	7.98	142.90	215.90
11	6	Block 1	30.00	60.00	8.01	144.00	219.20
12	5	Block 1	30.00	60.00	8.00	142.30	211.10
13	1	Block 1	30.00	60.00	8.04	143.90	209.70

FAN, and diastatic power with 4.58°Bx, 98.10 mg/L, and 132.30°L, respectively. A strong positive correlation exists between the FAN and diastatic power.

The results obtained from the analysis of variance (ANOVA) based on experimental data are presented in Table 4. The model F value of 14.44 implies the model is significant. There is only a 0.14% chance that an F value this large could occur due to noise. Statistical noise is unexplained variability within a data sample that is rendered meaningless by the existence of too many variables. P values less than 0.05 indicate model terms are significant. In this case, A and A^2 are significant model terms. Adequate Precision measures the signal-to-noise ratio. A ratio greater than 4 is desirable. A ratio of 11.46 obtained in this analysis indicates an adequate signal. The model can be used to navigate the design space.

Table 5 shows the summary of the steeping and germination time that were used during the malting process of quinoa grains. Run 8 (4.54 hrs steeping time; 60 hrs germination time) had the lowest values for all the responses recorded in this study. The maximum values for Brix, FAN, and diastatic power were 8.11°Bx, 165.60 mg/L, and 268.70°L, respectively.

The model for Brix from the two variables used in malting had a high F value (11.98) and low p value ($p = 0.0025$) (Table 6), which indicated that the model was highly significant. In this case, A and A^2 are significant model terms. The good correlation between the experimental and predicted values was confirmed by the proximity of the determination (R^2) and adjusted determination (R^2_{adj}) values 0.8954 and 0.8207, respectively. An R^2 value close to unity and R^2_{adj} close to R^2 ensure satisfactory fitting of the model to the real system [35]. An adequate precision ratio of 10.52 indicates an adequate signal. The established model is satisfactory and confirms response surface methodology is a promising tool in the selection of malting variables.

Table 7 shows that, for quinoa malt, there was a notable weak positive correlation between germination time and Brix ($r = +0.119$). However, there was a strong positive correlation between steeping time and diastatic power ($r = +0.893$). A similar trend was noted for barley with a weak positive correlation between germination time and Brix ($r = +0.142$). A strong positive correlation was also recorded between steeping time and diastatic power ($r = +0.897$) during the malting of barley. There was a relatively stronger correlation between steeping time and FAN ($r = +0.895$) than germination time and FAN ($r = + 0.275$) in quinoa malt.

The contour and surface plots of the response functions are useful in understanding both the individual and the combined effects of the factors. Figure 1(a) shows the relationship between steeping time and germination time with the amount of sugar concentration (Brix) produced in the barley malt. The higher the steeping time and germination time, the higher the concentration of sugar produced. This is shown as 8.10°Bx was obtained after steeping and germinating for longer hours, 48 hrs and 96 hrs, respectively. The least concentration of Brix was obtained when barley was steeped for a shorter time (12 hrs) having 6.64°Bx. The relationship between steeping time and germination time with the amount of sugar concentration (Brix) produced in the quinoa malt is shown in Figure 1(b). The contours indicate higher response levels as the steeping time and germination time increases. A high concentration of the sugar in quinoa malt (8.09°Bx) was recorded at a steeping time of 48 hrs and germination time of 96 hrs. The trend noted in barley is also similar to that in the malting of quinoa with lower Brix values recorded at lower malting variables.

Figure 2(a) shows the relationship between the steeping time and germination time with the free amino nitrogen obtained in barley malt. The FAN increases as the steeping and germination processes increase with a high FAN value (161.50 mg/L) recorded after a steeping time of 48 hrs and germination time of 96 hrs for barley malt. The relationship between steeping time and germination time with the FAN obtained in quinoa malt is shown in Figure 2(b). Coincidentally, the highest FAN value recorded (163.00 mg/L) in the malting of quinoa was obtained from the same steeping and germination time as in barley malting (48 hrs steeping and 96 hrs germination time).

Figure 3(a) shows the diastatic power of barley malt after steeping and germinating the grains at different intervals. For barley malt, as steeping time and germination increase so does the diastatic power in the malt with 268.00°L being recorded at 48 hrs/96 hrs compared with 152.00°L at 12 hrs/24 hrs. Figure 3(b) shows that low diastatic power (152.40°L)

Table 4: ANOVA results for quadratic modelling of Brix content during barley malting.

Source	SS	df	MS	F value	p value	
Model	11.2800	5	2.2600	14.4400	0.0014	Significant
A-steeping time	7.0300	1	7.0300	45.0200	0.0003	
B-germination time	0.2501	1	0.2501	1.6000	0.2463	
AB	0.0056	1	0.0056	0.0360	0.8549	
A^2	3.9900	1	3.9900	25.5100	0.0015	
B^2	0.0466	1	0.0466	0.2985	0.6018	
Residual	1.0900	7	0.1562			
Lack of fit	1.0900	3	0.3639	727.8100	<0.0001	
Pure error	0.0020	4	0.0005			
Cor total	12.37	12				

SS: sum of squares; MS: mean square.

Table 5: A central composite design (CCD) for quinoa malting using response surface methodology.

Std	Run	Block	Steeping time (hrs)	Germination time (hrs)	Brix (°Bx)	FAN (mg/L)	Diastatic power (°L)
1	12	Block 1	12.00	24.00	6.23	124.40	152.40
2	9	Block 1	48.00	24.00	8.06	162.40	261.50
3	10	Block 1	12.00	96.00	6.50	129.60	158.00
4	13	Block 1	48.00	96.00	8.09	163.00	265.30
5	8	Block 1	4.54	60.00	3.17	99.50	134.90
6	7	Block 1	55.46	60.00	8.11	165.60	268.70
7	11	Block 1	30.00	9.09	7.10	122.10	162.10
8	2	Block 1	30.00	110.91	8.05	153.80	260.00
9	1	Block 1	30.00	60.00	8.03	144.20	211.90
10	5	Block 1	30.00	60.00	8.00	143.40	218.90
11	6	Block 1	30.00	60.00	8.03	145.30	216.60
12	4	Block 1	30.00	60.00	7.95	144.50	215.30
13	3	Block 1	30.00	60.00	7.97	143.20	213.60

Table 6: ANOVA results for quadratic modelling of Brix content during quinoa malting.

Source	Sum of squares	Df	Mean square	F value	p value	
Model	21.2400	5	4.2500	11.9800	0.0025	Significant
A-steeping time	13.5400	1	13.5400	38.1900	0.0005	
B-germination time	0.3376	1	0.3376	0.9525	0.3616	
AB	0.0144	1	0.0144	0.0406	0.8460	
A^2	7.3100	1	7.3100	20.6100	0.0027	
B^2	0.0229	1	0.0229	0.0646	0.8067	
Residual	2.4800	7	0.3545			
Lack of fit	2.4800	3	0.8254	644.8300	<0.0001	
Pure error	0.0051	4	0.0013			
Cor total	23.72	12				

Table 7: Correlation coefficient (r) between independent and response variables during malting.

Response variable	Barley malt Germination time	Steeping time	Quinoa malt Germination time	Steeping time
Brix (°Bx)	+0.142	+0.754	+0.119	+0.755
FAN (mg/L)	+0.280	+0.880	+0.275	+0.895
Diastatic power (°L)	+0.317	+0.897	+0.326	+0.893

was obtained at a shorter steeping time (12 hrs) and germination time. The diastatic power increased as the time of steeping increased ($r = +0.893$) with 265.30°L being recorded at 48 hrs as shown in Figure 4.

Figure 5 compares actual values of Brix in 5(a) barley malt and 5(b) quinoa malt with the predicted values obtained from the statistical process model. The figure demonstrates good agreement between the experimental and predicted values as most of the points are located in the range of 7.06–8.36°Bx.

The plot of the residuals versus normal probability is shown in Figure 6. The residuals must be normally distributed for the results of an ANOVA to be valid, and thus the normal probability plot should resemble a straight line to indicate the underlying error distribution is normal [36]. It can be observed from Figure 6 that the normality

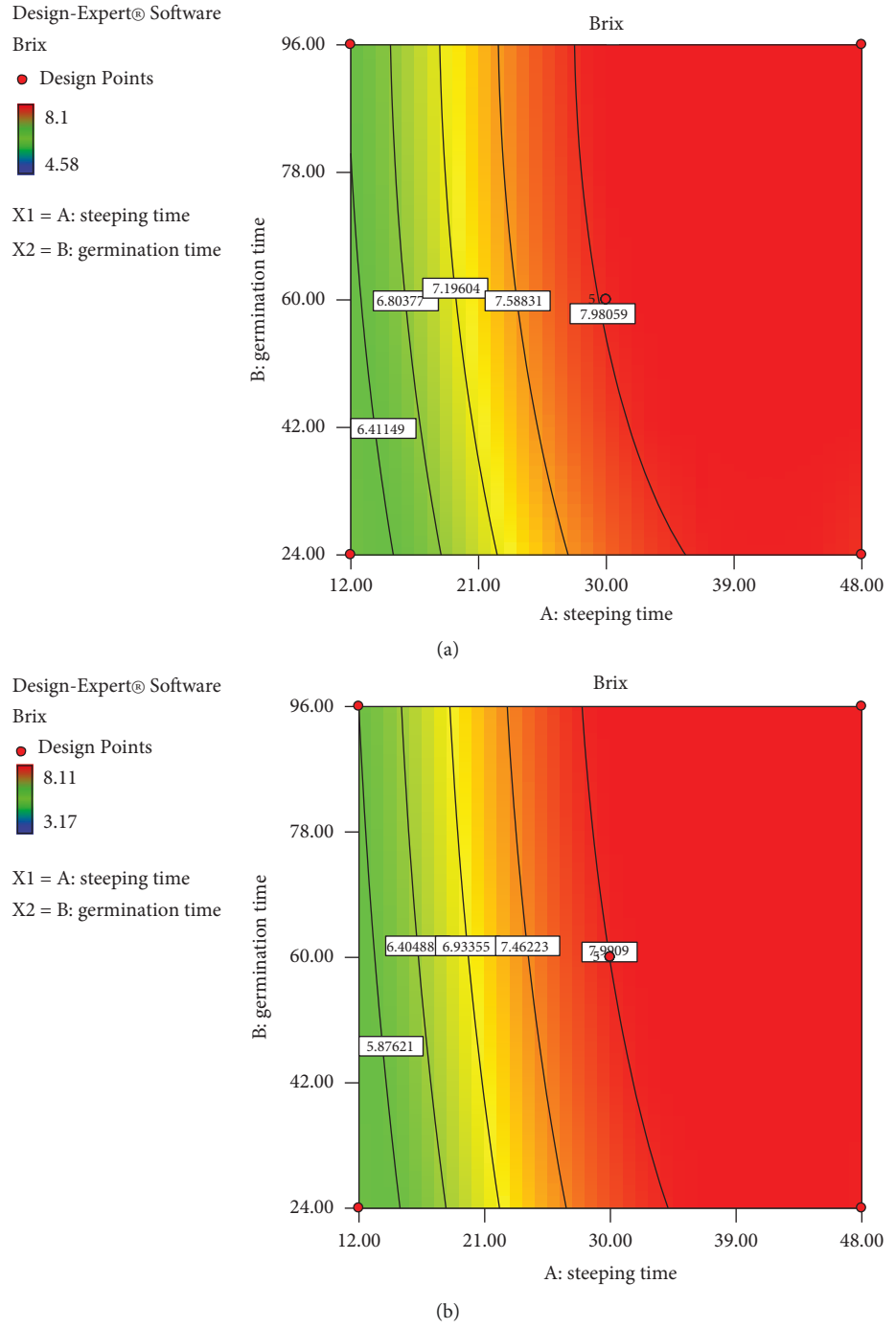

Figure 1: Contour plot for steeping time, germination time, and Brix value of (a) barley malt and (b) quinoa malt.

assumption is relatively satisfied as the points in the plot form a fairly straight line. So it can be concluded that the empirical model is adequate to describe the malting process as described in this study.

The residuals versus the experimental run order checks for lurking variables that may have influenced the response during the experiment. It is important to note that the runs are within the control limit as shown in both Figures 7(a) and 7(b).

Process optimisation involves the determination of the values of the design parameters at which the response reaches its optimum, which could be either a maximum or a minimum of the developed function [36]. The numerical optimisation was performed as facilitated in Design-Expert 7 software. RSM was used to determine the optimum process parameters that yield high malting characteristics. For numerical optimisation, the goals (none, maximum, minimum, target, or range) should be set for both the independent and response variables where all goals are combined into one desirable function [37]. Maximum values were set for the responses (i.e., Brix, FAN, and diastatic power). For barley,

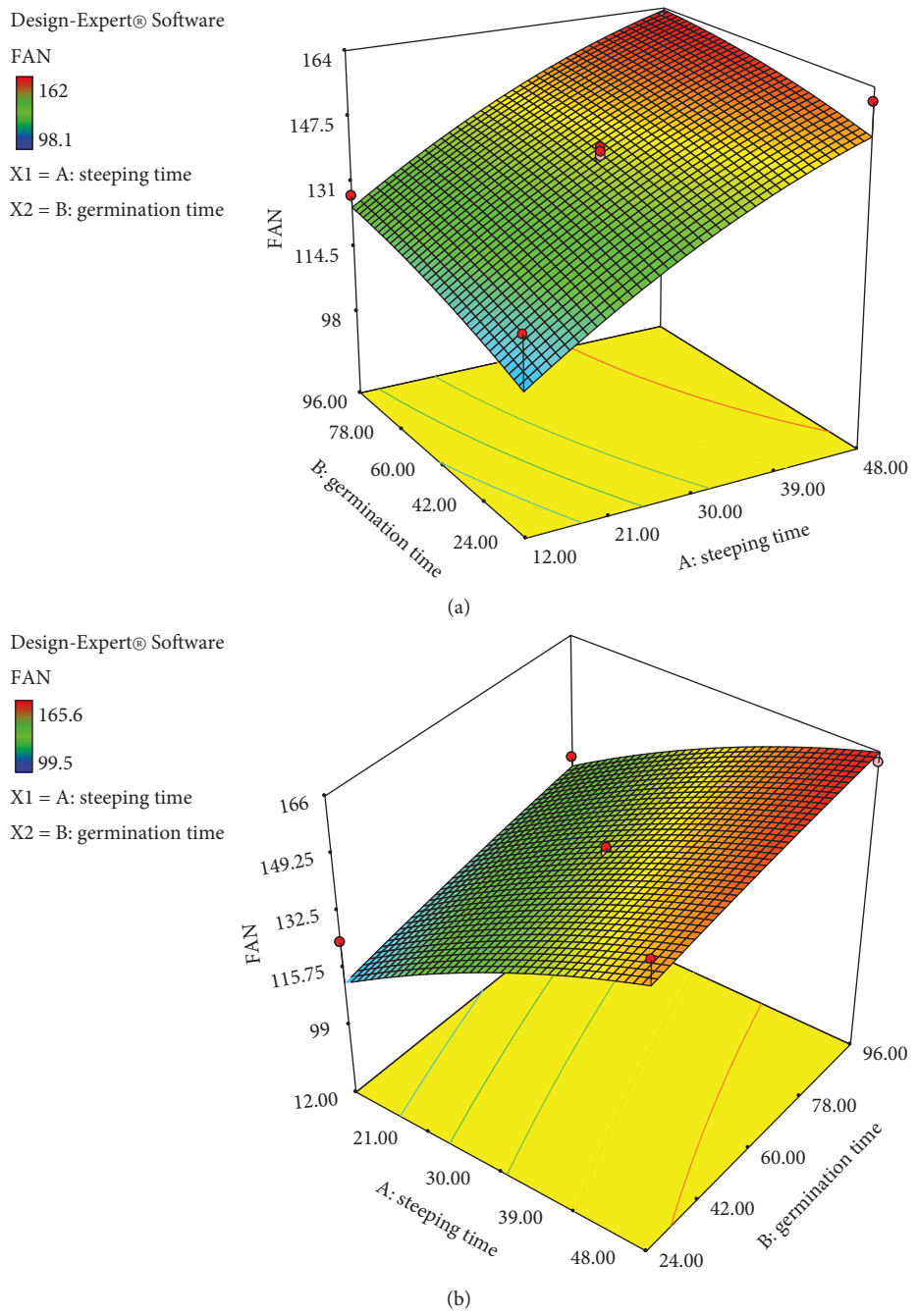

Figure 2: Response surface plots of steeping time and germination time on free amino nitrogen of (a) barley malt and (b) quinoa malt.

the numerical optimisation established that the desirability function was maximised at a Brix in the range of 4.58–8.1°Bx, FAN in the range of 98.1–162 mg/L, and diastatic power in the range of 132.3–270°L. The optimum values (Table 8) for the malting of barley were 47.68 hrs steeping time and 82.55 hrs germination time with a desirability value of 1.00. To produce quinoa malt with Brix, FAN, and diastatic power of 8.37°Bx, 165.60 mg/L, and 275.86°L, respectively, malting conditions of 47.69 hrs steeping time and 95.81 hrs germination time are required. For quinoa, the numerical optimisation established that the desirability function was maximised at a Brix in the range 3.17–8.11°Bx, FAN in the range of 99.5–165.6 mg/L, and diastatic power in the range of 134.9–268.7°L. However, the diastatic power is higher in quinoa than in barley at similar optimum steeping conditions.

5. Discussion

5.1. Effect of Steeping Time and Germination Time on Brix Content in Barley and Quinoa Malt. Good modification requires the grains to remain in the compartment for 4–5 days under controlled temperature, and this is the degree to which enzymes break down the endosperm. This can be

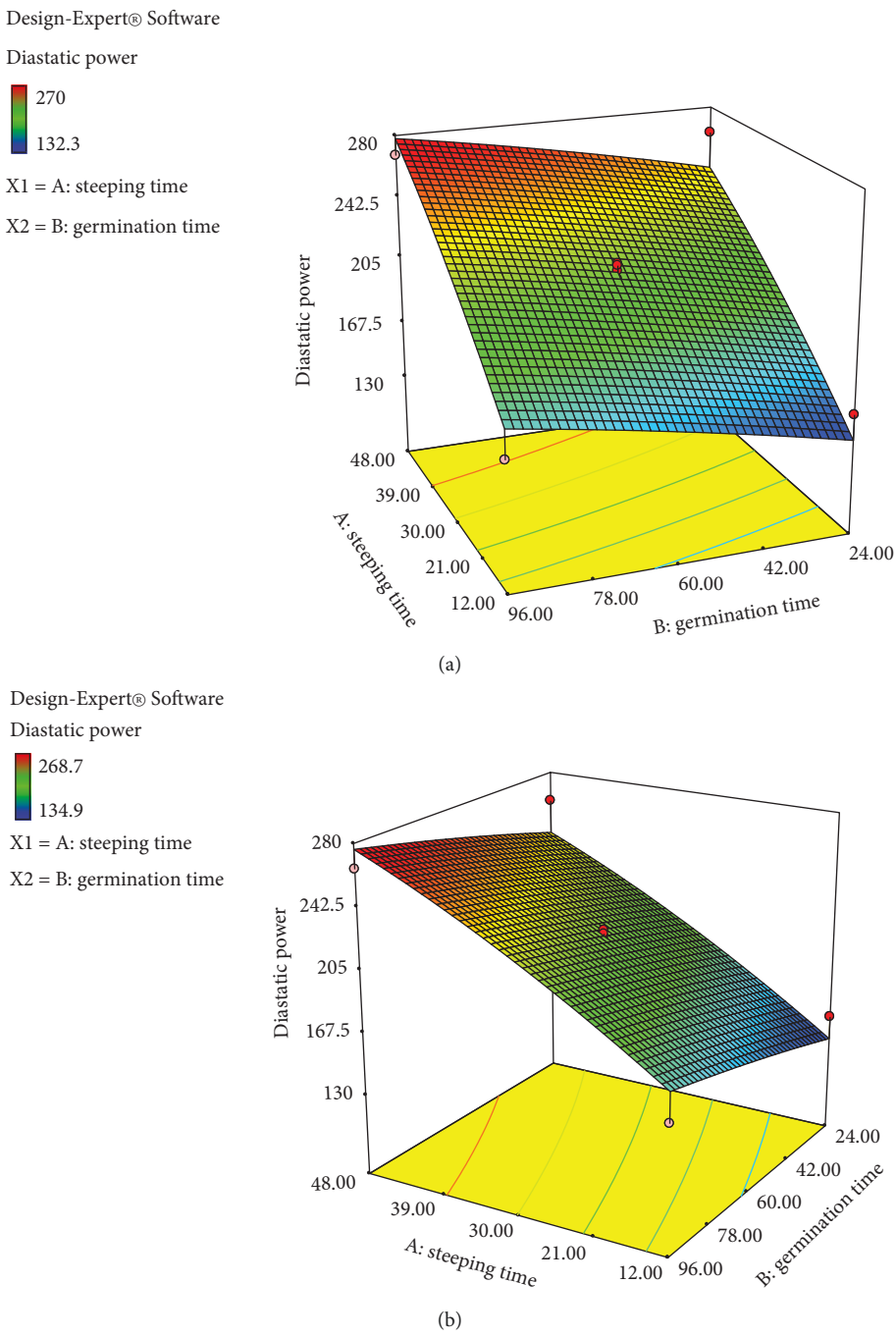

Figure 3: Contour plots for steeping time and germination time on diastatic power of (a) barley malt and (b) quinoa malt.

shown by a lower Brix value, where quinoa was 3.17°Bx and barley was 4.58°Bx as they were subjected to short steeping time and germination time (4.54 hrs steeping and 60 hrs germination). The texture of the endosperm affects water uptake and ultimately enzyme synthesis within the endosperm [4]. This means there was no modification as less water was absorbed to activate the enzymes within the grains. As the steeping time and germination time increase so does the Brix value within the grains [38]. During the steeping process, the absorbed water actives the naturally existing enzymes within the grains to break down starch granules into simpler fermentable sugar in the endosperm. The higher Brix value was obtained when the grains were steeped for 48 hrs and 96 hrs of germination with 8.09°Bx quinoa and 8.1°Bx barley. Quinoa had slightly lower Brix values than barley. This may be attributed to the high protein content in quinoa grains (13.8% to 16.5%, with an average of 15%) than in barley grains (between 9% and 15% dry matter) [10, 39, 40]. The surfaces and internal structures of malt may influence the rate of enzyme hydrolysis with undegraded proteins limiting the movement of enzymes in the starchy endosperm. The uneven pattern of modification results in poor-quality wort with low extract, higher viscosity, and slow wort separation (filtration) [41, 42].

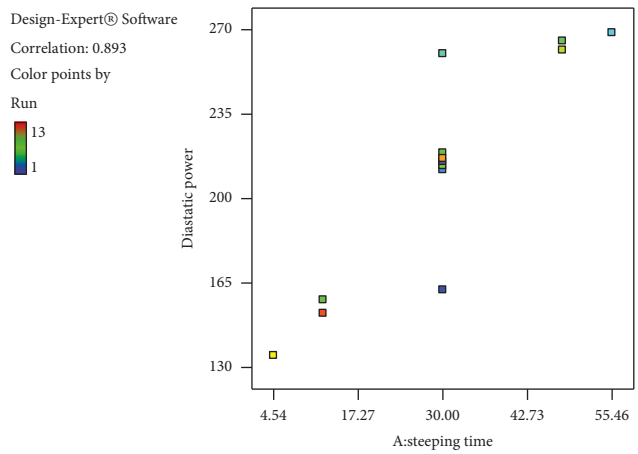

Figure 4: Correlation between steeping time and diastatic power during quinoa malting.

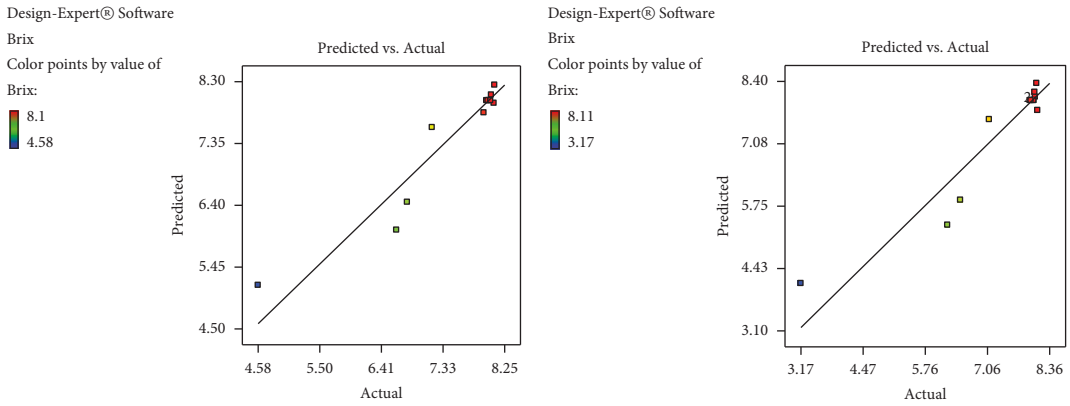

Figure 5: Actual vs predicted values of Brix in the malting process.

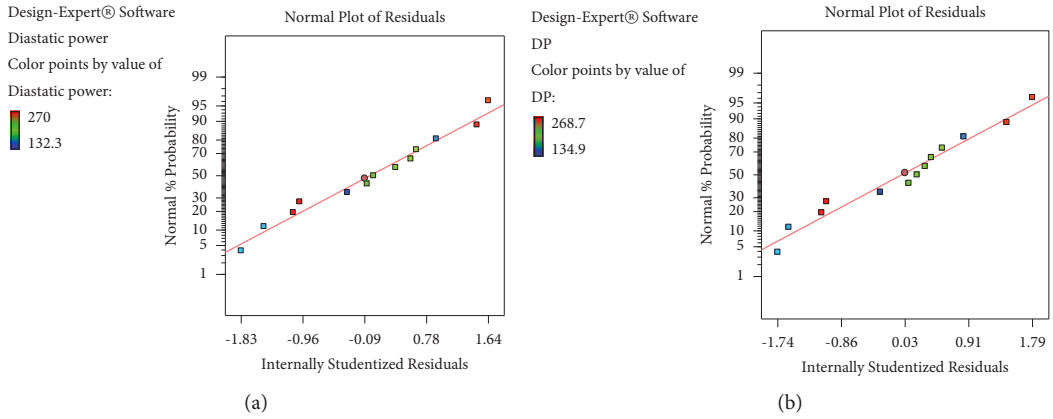

Figure 6: Normal probability plot of residuals for (a) barley diastatic power and (b) quinoa diastatic power.

5.2. Effect of Steeping Time and Germination Time on Free Amino Nitrogen in Barley and Quinoa. During malting and mashing, the proteinases are critical because several aspects of the brewing process are affected by the soluble proteins, peptides, and/or amino acids that they release. As the diastatic enzymes are proteins, their levels are directly related to protein concentration in the grain. The four distinct classes of barley proteins are globulin, glutelin, prolamin, and albumin [8]. As steeping time and germination times prolong, more water is absorbed and used to activate enzymes within the grains. This increases protein modification during the germination process. Proteolytic modification promotes the development of enzymes required to modify starch in the endosperm [8]. The FAN is an indicator suitable for the

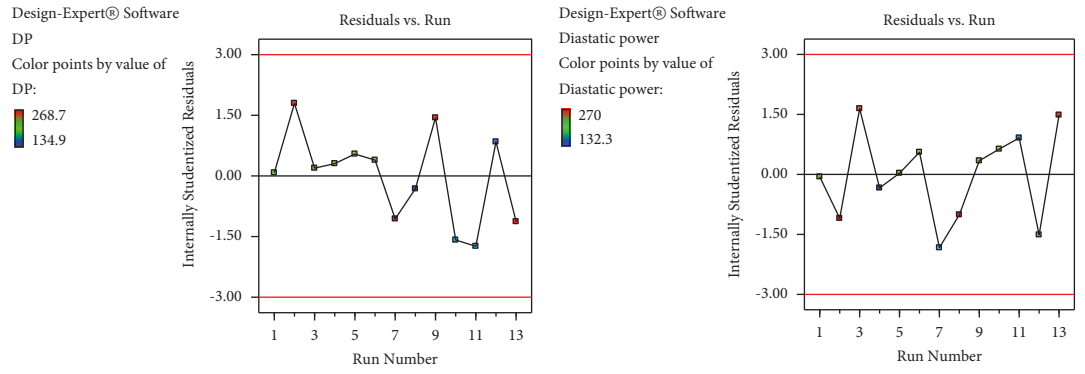

Figure 7: Residuals vs run plot for diastatic power in the malting process for (a) quinoa and (b) barley.

Table 8: Optimisation of the malting conditions of barley and quinoa grains.

Samples	Steeping time (hrs)	Germination time (hrs)	Brix (°Bx)	FAN (mg/L)	Diastatic power (°L)	Desirability	
Barley	47.68	82.55	8.25	162.28	271.69	1.00	Selected
Quinoa	47.69	95.81	8.37	165.60	275.86	1.00	Selected

Table 9: Summary of FAN values from malting studies using RSM.

Grain	Model, design	FAN	References
Buckwheat malt	RSM, central composite design	144.26 mg/L	[50]
Sorghum malt	RSM, face-centred cube design	117.80 mg/100 g	[51]
Rice wort	RSM, central composite design	357.00 mg/L	[52]
Quinoa malt	RSM, central composite design	165.60 mg/L	This study
Proso millet wort	RSM, face-centred design	365.00 mg/100 ml	[32]

prediction of the viability of yeast and the efficiency of fermentation [42]. A low FAN content delays the ageing process, whilst a very high FAN content affects the sensory properties of the beer and its microbiological quality.

Quinoa had a slightly higher amount of FAN (163.00 mg/L) than barley (161.50 mg/L) after steeping for 48 hrs and germinated for 96 hrs. In wort, FAN content should range from 120 to 200 mg/L to form approximately 21–22% of the soluble nitrogen [43–45]. Therefore, the values recorded in this study were within the expected range. The higher FAN content of quinoa (283 mg/L) was reported in a study [12], with FAN in the range of 170–200 mg/L reported elsewhere [46–48]. In a related study, the FAN content of triticale malt (a cross-breed of wheat and rye) was lower (170 mg/l) in comparison with barley malt (210 mg/L) [49]. The filterability of the beer depends on the concentration of high-molecular-weight protein and directly influences the foam stability, taste of beer, and storage quality. Comparative values of FAN in malt and wort are shown in Table 9.

5.3. Effect of Steeping Time, Germination Time, and Diastatic Power on Barley and Quinoa. Gluten-free malt has a comparatively similar diastatic power (265.30°L compared with 268.00°L for barley) as indicated in Figure 3. For malting, the recommended diastatic power should be above 100°L. The activity of one enzyme group, the β-amylases, is regarded as being the major contributor to diastatic power generation [53]. High levels of diastatic power recorded in this study indicate there is more concentration of diastase enzymes that are capable of converting starch into simpler sugars that will be consumed by yeast cells during the fermentation process and alcohol will be produced [53]. Gluten-free grains often require prolonged germination times compared with barley [13]. From Figure 4, the strong positive correlation indicates steeping time should be longer as more enzymes necessary for the breakdown of starch will be activated, thereby converting more starch into simpler sugars.

6. Conclusion

The results indicated that optimum values can be obtained in the malting of quinoa that can satisfy the malt quality required for brewing. To produce quinoa malt with Brix, FAN, and diastatic power of 8.37°Bx, 165.60 mg/L, and 275.86°L, respectively, malting conditions of 47.69 hrs steeping time and 95.81 hrs germination time are required. Moreover, the diastatic power is higher in quinoa than barley at similar optimum steeping conditions. Therefore, quinoa has a potential application in the malting process for the production of gluten-free beer.

Data Availability

Data are available on request.

Conflicts of Interest

The authors do not have any conflicts of interest to declare.

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