

Dimethyl Sulfide Stripping Behavior During Wort Boiling Using Response Surface Methodology

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ABSTRACT

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The action of two wort variables (power input and boiling time) on the residual dimethyl sulfide (DMS) of two boiled wort substitutes (water/DMS and water/sugar/DMS) was modeled and analyzed using response surface methodology. The analysis showed that both power input and boiling time had significant impact on residual DMS during wort boiling, with power input contributions of 12.4 and 11.9% for water/DMS and water/sugar/DMS, respectively, and boiling time contributions of 45.6 and 48.8% for water/DMS and water/sugar/DMS, respectively. The interaction also had a significant impact on residual DMS for the water/DMS wort substitute, with a contribution of 2.8%. The volatilization coefficient (k_2) obtained at each power input were not statistically significantly different for the two wort substitutes but exhibited exponential growth evolution: from 0.0202 to 0.0436 min⁻¹ and from 0.0143 to 0.0360 min⁻¹ for water/DMS and water/sugar/DMS wort substitutes, respectively. To achieve an energy target of 50 ppb by minimizing the energy consumed at the end of boiling, the following conditions were adopted: for water/DMS, boiling at 500 W for 123 min (3.66 MJ); for water/sugar/DMS, boiling at 500 W for 174 min (5.19 MJ).

Keywords: Boiling time, Dimethyl sulfide, Power input, Response surface methodology, Wort boiling

DMS is a sulfur compound that is recognized as the source of off-flavor. It is volatile and results from the conversion of a precursor (*S*-methyl methionine, SMM) in malt during boiling and, to a lesser extent, during fermentation of beer. It could contribute in several ways positively or negatively to the flavors of many food products and fermented beverages (1,4,10,18,23). It is known as a significant component of beer flavor, and several studies have been done in order to identify, quantify, and understand its formation and removal from wort and beer (8,11,16,26). Many detection techniques have been developed for that purpose (4,7,9,10,14,18). For a better understanding of DMS, some kinetic models have been developed in order to predict its formation via SMM and its removal during wort boiling and fermentation (12,29). The modeling approach in the literature was predominantly empirical and focused on boiling time. The aim of this study was to investigate the behavior shown in the stripping of DMS using a response surface methodology (RSM) approach. Power input and boiling time were used as covariables. Two wort substitutes (water/DMS and water/sugar/DMS) were considered to study the impact of the main wort component (sugar) on DMS stripping.

EXPERIMENTAL

Chemicals

The chemicals used in this study were DMS solution (99% purity) and sucrose ($\geq 99.5\%$ purity) from Sigma Aldrich and dichloromethane (DCM) solution ($\geq 99.8\%$ for HPLC) from Chromasolv.

Sample Preparation

Two wort substitutes were considered: distilled water and distilled water and sugar (12°B), both doped with DMS to an initial concentration of 650 ppb (w/v). A HANNA HI 96801 refractometer, 0 to 85% Brix (from HANNA Instruments Inc., Woonsocket, RI) was used to measure sugar concentration.

The wort-boiling unit consisted of a voltage regulator (phases, 1; input, 220 V, 50 to 60 Hz; output, 0 to 250 V; capacity, 2,000 VA; max., 8 amp; model TDGC2-2kVA from AC-DC Dynamics, Johannesburg, South Africa), which was connected to a Lutron DW-6060 watt meter. The watt meter was connected to the boiling kettle. A thermometer from Thermo 3 Thermometer (manufactured in the United Kingdom by ETI Ltd.) was used to determine the wort temperature during the boiling process.

To execute the boiling experiments, a high-power input (2,000 W) was used to shorten the preheating time and bring the wort substitutes (10 L) to boiling temperature (95°C). After reaching the boiling point, the power input was reduced to the desired power using the voltage regulator, and the power input value was obtained via the watt meter according to the Doehlert experimental design (Table I). Timekeeping was then implemented immediately according to the experimental design (all the boiling experiments were done in triplicate). When boiling was complete, 100 mL of each manipulation was collected with a 250-mL Schott Duran glass (with screw top) and cooled in cold water. After cooling, 20 mL of DCM was added, and the residual DMS extraction was done at 450 rpm using a centrifuge (HT Infors AG Rittergasse CH-4103, Bottmingen, Switzerland) for 1 h. At the end of the extraction process, the organic phase was introduced into vials and crimped for GC analysis. The standard curve was prepared using a DMS concentration from 0 to 700 ppb.

Gas Chromatography Analysis of DMS

Analysis of DMS by gas chromatography (GC) was performed using a Shimadzu GC-2010 Plus capillary gas chromatograph autosampler equipped with a flame ionization detector (FID). The column used was a Restek RTX-5 (30 m \times 0.32 mm \times 0.25 μ m). The chromatograph was set for a split ratio of 5. The injection volume was 1 μ L. A volumetric flow rate of 3 mL/min with helium as the carrier gas was used with a constant column head pressure of 83 kPa. The oven temperature program started with an initial setting of 35°C for 3.5 min, followed by an immediate ramp of 40°C/min to 280°C followed by a hold of 3 min. This led to a total program time of 12.63 min. The FID burner temperature

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was 300°C with a hydrogen flow rate of 30 mL/min and an air-flow rate of 300 mL/min.

Experimental Design, Modeling, and Validation of the Model

RSM with the Doehlert design (25) was used for the experiments in order to model and optimize the DMS removal during boiling of wort substitutes. The independent factors were the power input (x_1) and the boiling time (x_2). The intervals of these factors were X_1 , 500 to 1,500 W, and X_2 , 0 to 60 min, while the response was the residual DMS in the experimental wort after boiling. The two-factor Doehlert design gave a total of eight experiments, as shown in Table I.

From the coded factors, mathematical equations were used to convert them into real values for experiments. Those equations were as follows:

$$X_i = X_{0i} + x_i \times \Delta X_i \quad (1)$$

$$N = k^2 + k + k_0 \quad (2)$$

where X_i is a real variable; X_{0i} is the center of the variable; x_i is a coded variable given by the Doehlert table; ΔX_i is the increment; k is number of variables; k_0 is the number of center points, and N is the number of experiments.

Mathematical models describing the relationships among the process-dependent responses and the independent factors in a second-order equation were developed (17). Design-based experimental data were matched according to the following second-order polynomial equation.

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum \sum_{i < j} \beta_{ij} x_i x_j \quad (3)$$

where Y is the response, x_i and x_j are the factors, β_0 is the constant, β_i is the coefficient of the linear terms, β_{ii} is the coefficient of the quadratic terms, and β_{ij} is the coefficient of the interaction terms.

The coefficients of the models were obtained using Minitab version 16 software (Minitab, Ltd., Coventry, U.K.). This software was also used to execute a statistical analysis (ANOVA) on the models, and the curves were plotted using Sigmaplot version 12.5 (Systat Software, Inc., San Jose, CA).

The validation of the models was obtained by calculating the absolute average deviation (AAD), the bias factor (B_f), and the accuracy factor (A_f) (2,34), which were obtained using equations 4, 5, and 6 below.

$$AAD = \frac{\left[\sum_{i=1}^N \left(\frac{|Y_{i,\text{exp}} - Y_{i,\text{cal}}|}{Y_{i,\text{exp}}} \right) \right]}{N} \quad (4)$$

$$B_f = 10^{\frac{1}{N} \sum_{i=1}^N \log \left(\frac{Y_{i,\text{cal}}}{Y_{i,\text{exp}}} \right)} \quad (5)$$

$$A_{f1} = 10^{\frac{1}{N} \sum_{i=1}^N \left| \log \left(\frac{Y_{i,\text{cal}}}{Y_{i,\text{exp}}} \right) \right|} \quad (6)$$

where $Y_{i,\text{exp}}$ and $Y_{i,\text{cal}}$ are experimental and calculated responses, respectively, and N is the number of experiments used in the calculation.

Estimation of DMS Volatilization Rate Coefficient k_2 and Statistical Comparison

A simulation was done using the models at fixed values of power input and the DMS concentration equation, which was as follows (29):

$$[D]_L = \frac{k_1}{k_2 - k_1} [S]_0 \{ \exp(-k_1 t) - \exp(-k_2 t) \} + [D]_{L0} \exp(-k_2 t) \quad (7)$$

where k_1 is the reaction rate coefficient from SMM to DMS; k_2 is the volatilization rate coefficient of DMS; t is boiling time; $[D]_L$ is concentration of DMS in the liquid phase; $[S]$ is concentration of SMM in the liquid phase, and the subscript "0" indicates the initial time.

Since $[S]_0 = 0$ because of the absence of SMM in the substitute worts, the DMS vaporization equation could be written as:

$$[D]_L = [D]_{L0} \exp(-k_2 t) \quad (8)$$

In order to compare the influence of wort boiling on the two wort substitutes, the data of the two models were compared statistically using the t -test (comparison of means), the F -test (comparison of standard deviations), the W -test (comparison of medians), and the Kolmogorov–Smirnov test (comparison of the distributions of the two samples). This was done using the software Statgraphics Centurion XVI (build 16.1.11 StatPoint Technologies, Inc., Warrenton, VA, U.S.A.).

TABLE I
Matrixes of Doehlert and Validation Coefficients (R^2 , AAD, B_f , A_f)^a

Coded values		Real values		Water/DMS	Water/sugar/DMS
x_1	x_2	X_1 (W)	X_2 (min)	DMS (ppb)	DMS (ppb)
0	0	1,000	30	258.00 ± 3.11	289.66 ± 2.57
0	0	1,000	30	256.14 ± 2.95	287.47 ± 3.76
1	0	1,500	30	172.66 ± 5.31	193.32 ± 7.77
0.5	0.866	1,250	60	74.85 ± 5.07	92.52 ± 4.29
-0.5	0.866	750	60	185.61 ± 6.72	224.28 ± 4.31
-1	0	500	30	303.20 ± 11.15	352.20 ± 10.15
-0.5	-0.866	750	0	615.00 ± 13.81	589.00 ± 12.43
0.5	-0.866	1,250	0	588.00 ± 7.33	618.00 ± 8.61
			R^2	0.999	0.997
			AAD	0.006	0.032
			B_f	1.001	0.994
			A_f	1.006	1.033

^a DMS = dimethyl sulfide; x_1 = power input; x_2 = boiling time; AAD = absolute average deviation, B = bias factor, A = accuracy factor.

Optimization of the Models

The optimization, which consisted of the minimization of energy consumption, was done by evaluating the minimum energy consumed by the boiling process. The target of 50 ppb (22) was set.

Energy Estimation

The calculation of the energy depends on the power of the device and its usage time. Thus the energy consumed during the boiling of the wort is estimated by the formula:

$$E = P_w \times t \quad (9)$$

where E is the energy consumed (J); P_w is the power input, and t is the boiling time.

RESULTS AND DISCUSSION

Mathematical Statistical Model for Residual DMS of Wort Substitutes

Modeling to estimate the residual DMS during boiling of wort substitutes (water/DMS and water/sugar/DMS) was done using the RSM with data reported in Table I. The mathematical statistical models obtained using ANOVA (Table II and Table III) for that purpose were as follows:

$$y_{\text{water/DMS}}(x_1, x_2) = 257.07 - 66.47x_1 - 272.10x_2 - 48.36x_1x_2 - 19.14x_1^2 + 151.45x_2^2 \quad (10)$$

$$y_{\text{water/sugar/DMS}}(x_1, x_2) = 288.57 - 70.09x_1 - 256.99x_2 - 92.82x_1x_2 - 15.81x_1^2 + 128.47x_2^2 \quad (11)$$

where $y_{\text{water/DMS}}(x_1, x_2)$ is the mathematical model for residual DMS in wort substitute water/DMS; $y_{\text{water/sugar/DMS}}(x_1, x_2)$ is the mathematical model for residual DMS in wort substitute water/sugar/DMS; x_1 is the power input (W); and x_2 is boiling time (min).

The models were found to be multivariable polynomial with correlation coefficients (R^2) of 0.999 and 0.997, respectively, for $y_{\text{water/DMS}}(x_1, x_2)$ and $y_{\text{water/sugar/DMS}}(x_1, x_2)$.

According to the literature for evaluation of real performance of predictive models in complex systems (2,34), the AAD, B_f , and A_{f1} were also calculated. These parameters were measures of the relative average deviation of predicted and observed responses. A bias factor and accuracy factor of 1 and AAD of 0 indicated perfect agreements between observed and predicted responses.

The correlation coefficient associated with AAD, B_f , and A_{f1} permitted validation of the models, as shown in Table I and according to the literature (2,34).

The factors of the models were linear or first degree (x_1 and x_2), quadratic (x_1^2 and x_2^2), and of the interaction form (x_1x_2). They were statistically considered significant or not if the probability (P) was ≤ 0.05 or ≥ 0.05 , respectively (Table II). After validation of the model, a simulation was done to view the impact of a single factor when the other one was fixed.

The models showed a negative coefficient for the power input (x_1). Increasing power input contributed significantly (Table II) to linearly reducing the residual DMS in water/DMS (wort 1, $P = 0.000$) and water/sugar/DMS (wort 2, $P = 0.017$). A simulation of power input impact is shown in Figure 1A and B for water/DMS and water/sugar/DMS, respectively. The boiling time was fixed at 0 min and 60 min. At $t = 0$ min, the ranges of residual DMS were 611 to 562 and 582 to 602 ppb for water/DMS and water/sugar/DMS wort substitutes, respectively. These differences (8 and 3.2%, respectively, for water/DMS and water/sugar/DMS) could be due to the residual values obtained after the preheating stage since there was no boiling stage. After "wort" boiling ($t = 60$ min), the greatest DMS removal was obtained for 1,500 W since the removed amounts were 555 and 600 ppb for water/DMS and water/sugar/DMS, respectively. For a power input of 500 W, after 1 h of boiling, ~387 and ~284 ppb were removed for water/DMS and water/sugar/DMS, respectively. In fact, a high evaporation rate (due to high power input) resulted in greater DMS removal and lower residual DMS in the two wort substitutes. This was similar to the literature observation (31). In the quadratic form (x_1^2), which was considered an excess of power input, the reduction of DMS was significant for water/DMS (wort 1) at $P = 0.013$ (Table II).

Concerning the boiling time (x_2), the models showed a negative coefficient, which confirmed that the boiling time had a signifi-

TABLE II
Analysis of Variance for the Model Resulting from Boiling Water/DMS (Wort 1) and Water/Sugar/DMS (Wort 2)^a

Source	Sum of Squares		Df	Mean Square		F ratio		P value		Contribution (%)	
	Wort 1	Wort 2		Wort 1	Wort 2	Wort 1	Wort 2	Wort 1	Wort 2	Wort 1	Wort 2
A: x_1	13,256.1	14,736.4	1	13,256.1	14,736.4	2,544.88	55.89	0.0004	0.0174	12.4	11.9
B: x_2	222,095.0	198,114.0	1	222,095.0	198,114.0	42,637.41	751.42	0.0000	0.0013	45.6	48.8
AA	366.34	249.798	1	366.34	249.798	70.33	0.95	0.0139	0.4330	2.8	3.4
AB	1,753.93	6,460.94	1	1,753.93	6,460.94	336.72	24.51	0.0030	0.0385	16.5	8.7
BB	22,934.1	16,499.0	1	22,934.1	16,499.0	4,402.83	62.58	0.0002	0.0156	22.8	27.2
Total error	10,4179	527.307	2	5,20893	263.654						
Total (corr.)	265,503	240,204	7								

^a DMS = dimethyl sulfide.

TABLE III
Evolution of Volatilization Rate Coefficient k_2 at Different Power Inputs for Substitute Wort Water/DMS (Wort 1) and Water/Sugar/DMS (Wort 2)^a

Model terms	Power (W)									
	500		750		1,000		1,250		1,500	
	Wort 1	Wort 2	Wort 1	Wort 2	Wort 1	Wort 2	Wort 1	Wort 2	Wort 1	Wort 2
R^2	0.979	0.942	0.991	0.982	0.997	0.997	0.996	0.996	0.981	0.981
$[D]_{L0}$	593	582	605	598	610	607	609	608	602	600
k_2 (min ⁻¹)	0.0202	0.0143	0.0236	0.0182	0.0281	0.0233	0.0345	0.0314	0.0436	0.0360

^a DMS = dimethyl sulfide, $[D]_L$ = concentration of DMS in the liquid phase, and the subscript "0" indicates the initial time.

cant impact ($P = 0.000$ for water/DMS and $P = 0.001$ for water/sugar/DMS, Table II) on the reduction of residual DMS in wort substitutes. The simulation in Figure 2A and B showed that at fixed power inputs 500, 750, 1,000, and 1,250 W, the residual DMS decreased with boiling time for both wort substitutes. This trend was similar to findings in the literature (3,6,13,33,35,40,41) and was justified by the fact that, during wort boiling, undesirable volatile compounds (i.e., DMS) were driven off with the steam produced during boiling (5,8,15,19,21,24,27,28,36,39). In the quadratic form (x_2^2), the impact of boiling time was significant for both substitute worts ($P = 0.000$, and 0.015 for worts 1 and 2, respectively) (Table II).

The interaction power input/boiling time (x_1x_2) had a significant ($P = 0.003$ for water/DMS and $P = 0.038$ for water/sugar/DMS, Table II) synergistic impact on the DMS removal.

DMS Volatilization Rate Coefficient k_2 and Statistical Comparison

The polynomial models for each substitute wort were used at fixed power input and correlated with the exponential equation of DMS volatilization in order to estimate k_2 . As shown in Table III, the higher the power input, the higher the value of k_2 ; the values were similar to values in the literature (29). This suggested that RSM could be used to evaluate k_2 since, following the Taylor and

MacLaurin series, an exponential equation could be transformed into a polynomial equation (20,32,37,38). Figure 3 shows the exponential growth of k_2 with the heat supply rate (values shown in Table IV). This exponential growth observed was similar to that

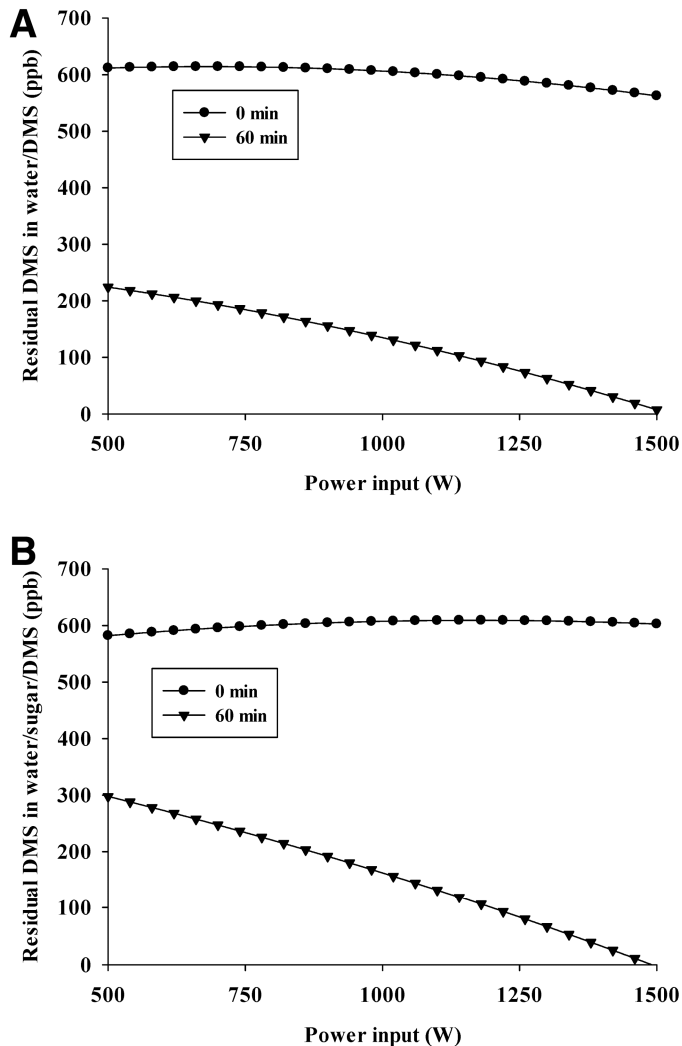


Fig. 1. Evolution of residual dimethyl sulfide (DMS) at fixed boiling times as a function of power input in A, water/DMS; and B, water/sugar/DMS (12°B).

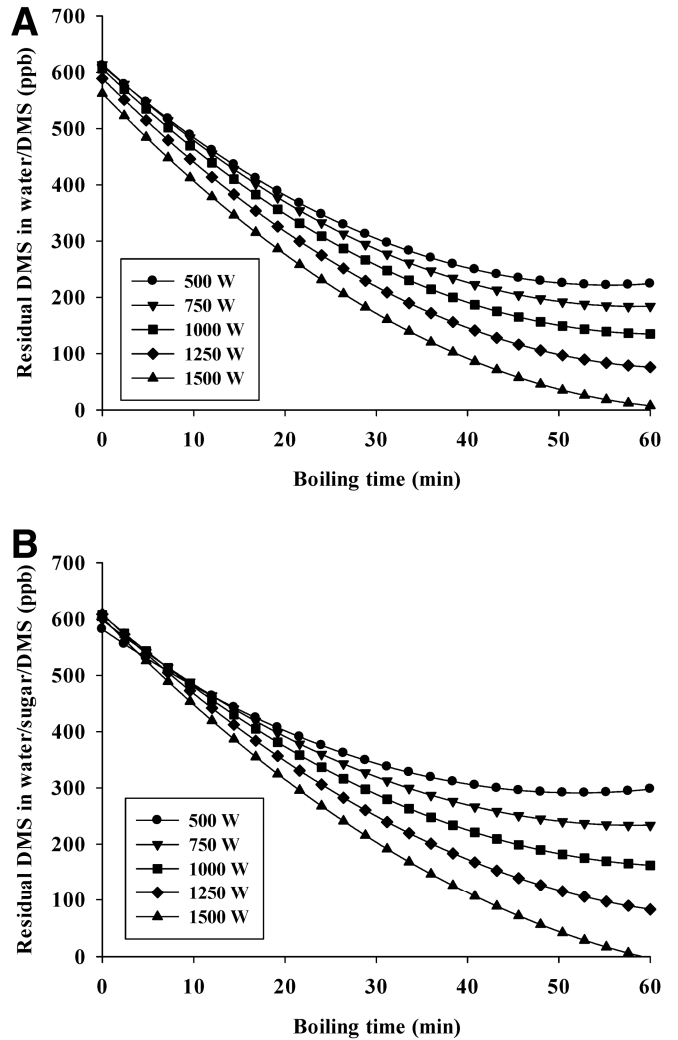


Fig. 2. Evolution of residual DMS at fixed power input as a function of boiling time in A, water/DMS; and B, water/sugar/DMS (12°B).

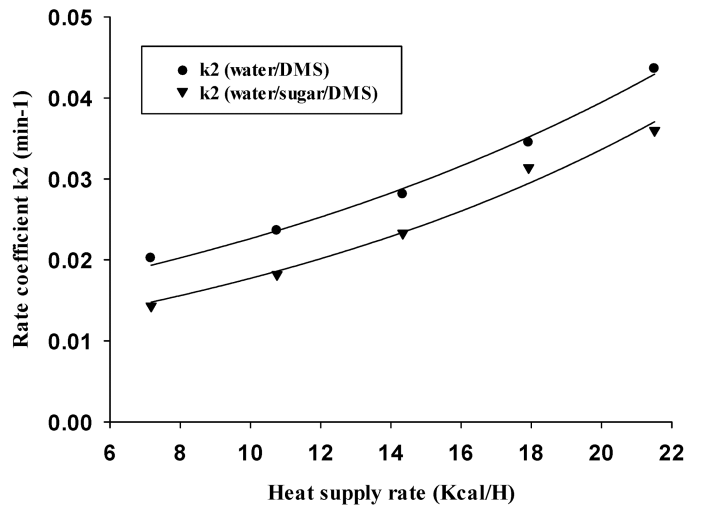


Fig. 3. Evolution of DMS volatilization coefficient k_2 .

obtained in a literature patent (30). In fact, the k_2 values obtained by Mitani et al (30) in 1998, when using a 6-m³ kettle wort boiling, was higher than the one found in the current study. This could be explained by the fact that the heat rate supply (H) was more than thousand times higher (120 to 280 Mcal/hr compared to 7 to 22 kcal/hr).

A statistical analysis using the t test, F test, W test, and Kolmogorov–Smirnov test, was done and demonstrated no significant difference between the residual values of DMS in the two wort substitutes (Table V). In addition, there was no significant difference between the values of rate coefficient k_2 of the two wort substitutes (Table VI) in spite of the fact that visually they seemed to be different.

Optimization

Since the RSM method was efficient only inside the studied domain, the exponential decay equations for residual DMS obtained for substitute wort boiling were used. The aim was to determine conditions to minimize boiling energy in order to obtain a target value of 50 ppb since the recommended value was between 40 and 60 ppb (22). A simulation was done using the initial DMS concentration of 600 ppb when the boiling point is reached.

To obtain the target of 50 ppb to minimize energy consumption during wort boiling, the power input and each boiling time were determined. For that purpose, the wort should be boiled for about 57 to 122 min for water/DMS (wort 1) and 69 to 173 min for water/sugar/DMS (wort 2), as shown in Table VI. The estimated energy was from 3.66 to 5.40 MJ and from 5.19 to 6.42 MJ for water/DMS and water/sugar/DMS, respectively (Table VI). The smallest amount of energy consumed was obtained at 500 W for both wort substitutes.

TABLE IV
Equations of k_2 Evolution Versus Heat Rate Supply of the Two Wort Substitutes^a

Terms	Water/DMS	Water/Sugar/DMS
Equation	$0.013 \times e^{0.0556 \times H}$	$0.0093 \times e^{0.0641 \times H}$
R^2	0.993	0.983

^a DMS = dimethyl sulfide, H = heat rate supply (kcal/hr).

TABLE V
Statistical Comparison Between the Residual DMS of Water/DMS and Water/Sugar/DMS^a

t test		F test		W test		Kolmogorov–Smirnov Test	
t	P	F	P	W	P	DN	P
-0.25385	0.803	1.10532	0.898	38	0.563	0.25	0.963

^a DMS = dimethyl sulfide, W = Shapiro–Wilk statistics, DN = Kolmogorov–Smirnov statistics.

TABLE VI
Energy (E) Spent During Boiling of Water/DMS (Wort 1) and Water/Sugar/DMS (Wort 2)^a

Target (ppb)	k_2			t (min)			E (MJ)	
	Wort 1	Wort 2	$[D]_L$	Wort 1	Wort 2	P (W)	Wort 1	Wort 2
50	0.0202	0.0143	593	122	173	500	3.66	5.19
50	0.0236	0.0182	605	106	137	750	4.77	6.17
50	0.0281	0.0233	610	89	107	1,000	5.34	6.42
50	0.0345	0.0314	609	72	80	1,250	5.40	6.00
50	0.0436	0.036	602	57	69	1,500	5.13	6.21

^a DMS = dimethyl sulfide, k_2 = rate coefficient, t = time, $[D]_L$ = concentration of DMS in the liquid phase, P = power.

CONCLUSION

The effects of power input and boiling time on the removal of DMS during wort boiling were studied for two wort substitutes (water/DMS and water/sugar/DMS). The two variables had significant effects on DMS, with the boiling time considered to have higher impact than the power input. The study showed that the DMS volatilization coefficient rate (k_2) progressed exponentially (showed exponential growth) with the increase of the heat rate supply and that there was no significant statistical difference between the residual DMS when the two worts substitutes were boiled. Minimization of the energy consumed when boiling was achieved at the lowest power input.

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