

Modeling of Dimethyl Sulfide Stripping Behavior When Applying Delayed Onset of Boiling During Wort Boiling

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ABSTRACT

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The response surface methodology, using the central composite design as a tool for modeling, was used to study the impact of two parameters (power supply and boiling time) and their effect on dimethyl sulfide (DMS) removal during wort boiling, when applying delayed onset of boiling. It was observed that the two parameters were significantly impacting the DMS removal with a 21% contribution for power supply and a 58% contribution for the boiling time ($P = 0.000$ for both). The interaction of the two factors was also significant ($P = 0.008$) with a contribution of 7%. With the *S*-methyl methionine conversion to DMS following the pseudo first-order kinetics reaction, k_1 was computed as 0.0054 min^{-1} , and the values of k_2 were between 0.0151 and 0.407 min^{-1} . After several statistical analyses, we learned that the results coming from the theoretical equations for DMS removal at each studied power supply were not significantly different from the experimental value obtained in the laboratory, validated by the use of these equations. The time spent to reach the residual DMS target of 30, 50, and 100 ppb was 141–377, 94–295, and 60–197 min, respectively, and the energy used to reach the same target was 11.31–12.69, 8.46–8.85, and 5.40–5.91 MJ, respectively.

Keywords: Power supply, Boiling time, Dimethyl sulfide, Wort boiling, Central composite design (CCD), Response surface methodology (RSM)

Beer making, which is a complex process, generates some flavor during several treatments such as malting, mashing, boiling, and fermentation. During the malting process, a chemical named *S*-methyl methionine (SMM), whose level increases during germination, is responsible for dimethyl sulfide (DMS) formation (3,34). A portion of SMM is transformed into DMS during mashing and boiling and, because the DMS itself is very volatile, it is removed during the boiling stage, and sulfur components occurring from that process are mainly sources of off-flavors, which are globally linked to DMS (1–3,6,11,18,22,33). The high volatility of DMS and the lower concentration obtained after boiling permit the use of multiple techniques such as chromatography to estimate its residual concentration (6,9–11,14,18). Previous work demonstrated the importance of wort boiling on DMS removal, and kinetics models were presented (12,28). But in all these papers, the boiling process was continuous (12,32), apart from the Shoko process system, which used a heated holding time (26). In fact, during normal wort boiling, a batch of wort is heated continuously to reach the boiling point, and the boiling process is realized at a target evaporation rate for the duration of the boil. The target evaporation rate is intended to produce all of the classical wort boiling functions such as volatile formation, volatile stripping, sterilization, hop isomerization, hot break formation, and so on. Typical evaporation rates have gradually been reduced over the years from 10–15% per hour (volumetric % per hour) in the 1980s to currently 4–7% per hour. The primary driver behind this reduction has been the imperative to save energy and conse-

quently reduce production costs and the environmental footprint of the brewing process. In this study, using the same energy-saving purpose, the delayed onset of boiling (DOOBOIL) was implemented and the impact of power supply and boiling time using response surface methodology was studied on the DMS removal and kinetic reaction coefficients.

EXPERIMENTAL

Chemicals

The chemicals utilized here were DMS solution (99% purity, Sigma-Aldrich) and dichloromethane (DCM) solution (99.8% for HPLC, Chromasolv).

Boiling Procedure and Preparation of Samples

The wort at pH 5.4 and 10°P was obtained using an all-in-one, electric all-grain brewing unit system (Braumeister, Speidel, Germany), in which 10 kg of malt (obtained from SABMiller) and 50 L of water were mashed during 1 h at 65°C. The quantity of wort obtained was 45 L per brew. Many brews were done and mixed together to obtain 200 L of wort. The wort was then divided into 10 L batches for boiling trials and placed in buckets. Each bucket containing wort was placed in a deep freezer at –25°C for future use. The wort-boiling unit comprised a voltage regulator (phases, 1; input, 220 V, 50–60 Hz; output, 0–250 V; capacity, 2,000 W; max., 8 amp; model TDGC2-2kVA, AC-DC Dynamics, Johannesburg, South Africa), which was linked to a Lutron DW-6060 watt meter. The watt meter was attached to the boiling kettle. A thermometer from Thermo 3 Thermometer (manufactured in the United Kingdom by ETI Ltd.) was utilized to measure the wort temperature during the boiling process (12). To realize the boiling trials, a singular power supply (1,500 W) was utilized to reduce the preheating time of 10 L of wort and permitted it to reach the boiling point (95°C). After that, the power supply using the voltage regulator was stopped, and the wort was allowed to rest (DOOBOIL) in an insulated and closed bucket (to maintain the temperature of 95°C) for a period between 0 and 60 min according to the experimental design. This resting period was to create the conditions for SMM conversion into DMS. After the targeted resting period, the cover of the bucket was removed and the wort was then boiled according to a specific power supply (using the voltage regulator) and time. The samples (50 mL, collected using a 250 mL Schott Duran glass with screw top and cooled in cold water) were taken at specific points in the process (before preheating, at the end of preheating, at the end of the resting period, and at the end of boiling). After chilling the wort, 50 mL of dichloromethane (DCM) was added, and the DMS removal from the wort was executed at 450 rpm utilizing a centrifuge (HT Infors, Bottmingen, Switzerland) for 1 h. The DCM phase containing DMS was brought into 2 mL vials and crimped for GC-MS analysis. The standard curve was done using pure DMS from Sigma-Aldrich from 0 to 1,000 ppb.

Conditions for Wort Analysis

For the analysis executed in triplicate, 2 mL crimped vials composed of the DMS drawn out from wort were analyzed and, after designating the parameters presented in Table I, 1 μL of the solu-

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tion from the vials was automatically reflected in the inlet of a LECO Pegasus 4D GC×GC-TOFMS. Data were acquired using LECO's ChromaTOF software.

The Pegasus 4D GC×GC-TOFMS (LECO Corporation, U.S.A.) was utilized to estimate the concentration of DMS in every step of the study in respect of the standard curve utilizing DMS solution (Sigma-Aldrich, 99% purity). Peak identification, signal deconvolution, and computation for distinctive analytes inside the sample were attained with automated data processing. Wiley and NIST libraries were used for peak identification with signal to noise (S/N) > 200, eliminating low similarity compounds (less than 650).

Modeling

The response surface methodology (RSM) with central composite design (CCD) was adapted to the study to model and optimize

the DMS removal from wort during boiling. The RSM theory provided the conditions for which the best accuracy was achieved with minimal testing and therefore the minimum cost (17). In statistics, a CCD is an experimental design, appropriate in RSM, for constructing a quadratic model for the response variable without demanding a full three-level factorial experiment. After the designed experiment is achieved, linear regression is applied, sometimes iteratively, to have results. Coded variables are usually utilized when building this design. The independent variables were the power supply (x_1) and boiling time (x_2). The intervals of variables were, respectively, 500–1,500 W and 0–60 min (Table II). The gaps were taken according to the literature (12).

From the CCD matrix, the transformation into real variables for laboratory purposes was done and the equations used were as follows:

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

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

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

With a total of 13 experiments (five replicates at the central point), the value of α was estimated for the sake of the respect orthogonality criterion (24) using the following formula:

$$\alpha = \left(\frac{2^k \left(\sqrt{2^k + 2k + k_0} + \sqrt{2^k} \right)^2}{4} \right)^{\frac{1}{4}} \quad (3)$$

where k is the number of variables and k_0 is the number of center points.

The statistical model illustrating the relation among the response and independent variables were established as a second-order polynomial equation as stated in the literature (16) as follows:

TABLE I
Conditions of LECO Pegasus Equipment for Dimethyl Sulfide Detection

Equipment	Specifications
Detector	LECO Pegasus
Rate of acquisition	200 spectra/s
Delay of acquisition	3 min
Range of mass stored	29–500 u
Temperature of transfer line	250°C
Temperature of the source	250°C
Voltage of the detector	–1,800 V
Mass defect settling	0 mu/100 u
Column 1 type	Rtx-WAX, 30 m length × 0.25 mm internal diameter, 0.25 μm film thickness
Column 2 type	DB-1, 1.0 m length × 0.1 mm internal diameter, 0.10 μm film thickness
Oven of column 1	1 min at 35°C, 4°C/min from 35 to 250°C, 10 min hold at 250°C
Oven of column 2	1 min at 45°C, 4°C/min from 45 to 360°C, 10 min hold at 360°C
Period of modulation	10 s
Offset temperature of the modulator	30°C
Inlet	Splitless at 230°C
Injection volume	1 μL
Gas	He, 1.0 mL/min constant flow

TABLE II
Central Composite Design Matrixes and Model Validation Tools (R^2 , AAD, B_f , A_{fl})^a

Number	Variables				Response		
	Coded variables		Real variables		Residual DMS (ppb)		
	Power supply, x_1	Boiling time, x_2	Power supply, X_1	Boiling time, X_2	Experimental	Theoretical	Residue
1	1	1	1,354	51	124.55 ± 2.90	123.15	1.40
2	0	0	1,000	30	360.31 ± 4.29	360.45	–0.14
3	1	–1	1,354	9	520.66 ± 2.72	519.13	1.53
4	1.414	0	1,500	30	245.7 ± 3.91	250.51	–4.81
5	0	0	1,000	30	355.24 ± 5.18	360.45	–5.21
6	0	0	1,000	30	354.44 ± 4.04	360.45	–6.01
7	0	–1.414	1,000	0	685.21 ± 3.50	678.71	6.50
8	–1	–1	646	9	590.67 ± 5.37	605.13	–14.46
9	–1	1	646	51	282.49 ± 2.60	297.07	–14.58
10	0	1.414	1,000	60	187.54 ± 2.15	180.95	6.59
11	–1.414	0	500	30	452.12 ± 2.81	434.28	17.84
12	0	0	1,000	30	371.08 ± 3.47	360.45	10.63
13	0	0	1,000	30	361.18 ± 1.50	360.45	0.73
			R^2	0.996			
			AAD	0.020			
			B_f	1.000			
			A_{fl}	1.018			

^a AAD = absolute average deviation; B_f = bias factor; A_{fl} = accuracy factor; and DMS = dimethyl sulfide.

$$y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i < j} \beta_{ij} x_i x_j + \varepsilon \quad (4)$$

where y is response, x_i and x_j are variables, β_0 is the constant, β_i is the linear term coefficient, β_{ii} is the quadratic term coefficient, and β_{ij} is the interaction term coefficient.

The model and statistics were accessed utilizing Minitab 16 software (Minitab, Coventry, U.K.), and graphs were plotted by applying Sigmaplot version 13, build 13.0.0.83 (Dundas Software, Wpcubed GmbH, Germany).

The validation of the model was done by estimating the absolute average deviation (AAD), the bias factor (B_f), and accuracy factor (A_f) (4,31), which were asserted as follows:

$$AAD = \frac{\left[\sum_{i=1}^N \left(\frac{|y_{i,\text{exp}} - y_{i,\text{cal}}|}{y_{i,\text{exp}}} \right) \right]}{N} \quad (5)$$

$$B_f = 10 \frac{1}{N} \sum_{i=1}^N \log \left(\frac{y_{i,\text{cal}}}{y_{i,\text{exp}}} \right) \quad (6)$$

$$A_f = 10 \frac{1}{N} \sum_{i=1}^N \left| \log \left(\frac{y_{i,\text{cal}}}{y_{i,\text{exp}}} \right) \right| \quad (7)$$

where $y_{i,\text{exp}}$ and $y_{i,\text{cal}}$ are experimental and theoretical responses, respectively, and N is the number of trials.

The contributions of the linear, quadratic, and interaction terms for each variable were estimated as follows:

$$\text{linear (\%)} = \frac{|\beta_i|}{\sum_{i=1}^k |\beta_i| + \sum_{i=1}^k |\beta_{ii}| + \sum_{i < j} |\beta_{ij}|} \quad (8)$$

$$\text{quadratic (\%)} = \frac{|\beta_{ii}|}{\sum_{i=1}^k |\beta_i| + \sum_{i=1}^k |\beta_{ii}| + \sum_{i < j} |\beta_{ij}|} \quad (9)$$

$$\text{interaction (\%)} = \frac{|\beta_{ij}|}{\sum_{i=1}^k |\beta_i| + \sum_{i=1}^k |\beta_{ii}| + \sum_{i < j} |\beta_{ij}|} \quad (10)$$

Evaluation of Reaction Rate Coefficient of SMM Conversion to DMS (k_1)

Taking into consideration that the reaction was assumed to be of first-order reaction kinetics, and also that it could be simultaneous, the estimation k_1 was executed during the resting period. This was done at that stage as the DMS stripping was weak because of no boiling and a closed bucket. The insulated bucket allowed maintenance of the temperature in the system at the boiling point (95°C), and thus the conversion of SMM was the main reaction. At the end of each resting period (0, 9, 30, 51, and 60 min), samples were taken for DMS analysis. Because the reaction kinetic rate of DMS generated was considered equal to the SMM elimination, the values of DMS obtained were used and, considering the reaction as stoichiometric, the value of $[A]_0$ was calculated.

The values of DMS obtained were plotted in a graph, and a regression using the first-order kinetics reaction equation was im-

plemented to determine the value of k_1 . That first-order kinetic reaction equation was expressed as follows:

$$[A] = [A]_0 \exp(-k_1 t) \quad (11)$$

where $[A]$ is SMM concentration at any time t , $[A]_0$ is the initial concentration of SMM, and k_1 is the reaction rate coefficient of SMM conversion to DMS.

Evaluation of Volatility Rate Coefficient of DMS (k_2) and Other Constant Terms

The validated polynomial multivariable model was used at each fixed value power supply, and the DMS model, which was remaining as a function of time, was correlated to the theoretical established model to determine k_2 and other constant coefficients. That model was as follows:

$$[DMS]_T = \frac{k_1 [A]_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) + [B]_0 e^{-k_2 t} \quad (12)$$

where $[DMS]_T$ is residual DMS in the wort after boiling, k_2 is the volatility rate coefficient of DMS, and $[B]_0$ is the initial concentration of DMS.

To obtain the value of k_2 , the theoretical equation was introduced in Sigmaplot 13.0 (regression wizard) in order to plot and determine all the constant terms of that equation. This was done by introducing the obtained value of $[A]_0$ and k_1 because the SMM conversion to DMS was considered temperature dependent and the boiling process was done at atmospheric pressure with that temperature remaining at 95°C.

Statistical analysis was performed to compare the value obtained from the theoretical established equation and the experimental results. This was done to validate the theoretical equations obtained.

Optimization

Lastly, optimization was realized by fixing three targets of residual DMS concentration in the wort (30, 50, and 100 ppb). The time was calculated using Scientific WorkPlace 5.5 software, build 2890 (MacKichan Software) to solve the equations. The graphs were executed with Sigmaplot 13.0, build 13.0.0.83 (Dundas Software).

Energy Calculation

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 following formula:

$$E = P_i t \quad (13)$$

where E is the energy consumed (J), P_i is the power supply, and t is the boiling time.

RESULTS AND DISCUSSION

RSM for Residual Wort DMS Modeling

RSM was used to assess the model for DMS removal during wort boiling unit operation after DOOBOIL, and ANOVA was utilized for statistical analysis on the model (Table II). DMS was detected using the LECO GC-MS (Fig. 1), and the model acquired was as follows:

$$y(x_1, x_2) = 360.45 - 64.98x_1 - 176.01x_2 - 21.98x_1x_2 - 9.03x_1^2 + 34.7x_2^2 \quad (14)$$

where $y(x_1, x_2)$ is the model for residual DMS, x_1 is the power supply, and x_2 is the boiling time.

The obtained model was polynomial multivariable, with a correlation coefficient (R^2) of 0.996. The model was validated by determining AAD, B_f , and A_{fit} . The values of 0.020, 1.000, and 1.018 were obtained, respectively (Table II). Also, a nonsignificant value of the lack-of-fit (0.052) confirmed that the model was adequate.

In Table II, values of $P < 0.050$ designated that model terms were significant. In this case, x_1 , x_2 , x_1x_2 , and x_2^2 were significant model terms. Values higher than 0.050 indicated the model terms were not significant (x_1^2). With the certification of the model validation accomplished, the simulation of the impact of each singular and interaction factor was then assessed.

Impact of power supply. The influence of power supply (x_1) on DMS removal was significant ($P = 0.000$, Table III). Its contribution to DMS removal was estimated at 21% (Table III). Its effect is shown in Figure 2A when fixing the boiling time (x_2) at 30 min. In fact, DMS decreased from 434.28 ppb at 500 W to 250.51 ppb at 1,500 W. An increase in power supply (and in turn, energy load and evaporation rate) raised DMS removal and reduced residual DMS in wort. This could be seen because the DMS, which derived from SMM by heat during wort boiling (1), was dissipated and whisked away with the steam (36).

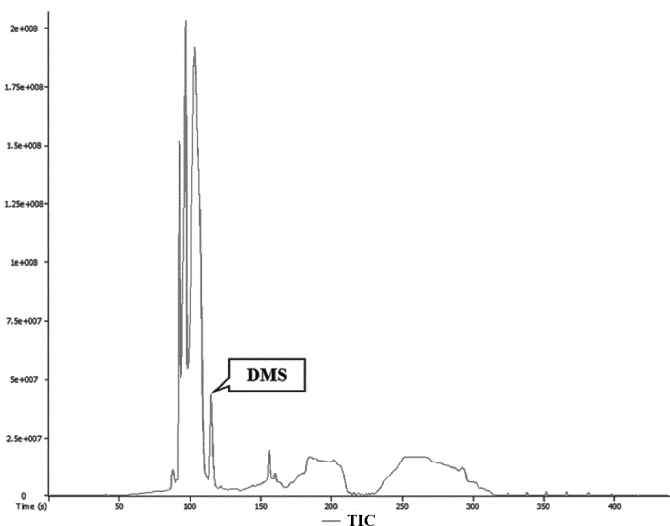


Fig. 1. Chromatogram of wort for dimethyl sulfide (DMS) detection.

TABLE III
Analysis of Variance for Dimethyl Sulfide Model

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Regression	5	293,237	293,237	58,647	398.96	0.000
Linear	2	281,627	281,627	140,814	957.92	0.000
x_1	1	33,783	33,783	33,783	229.82	0.000
x_2	1	247,844	247,844	247,844	1,686.01	0.000
Square	2	9,677	9,677	4,839	32.92	0.000
x_1^2	1	1,301	568	568	3.86	0.090
x_2^2	1	8,376	8,376	8,376	56.98	0.000
Interaction	1	1,933	1,933	1,933	13.15	0.008
$x_1 x_2$	1	1,933	1,933	1,933	13.15	0.008
Residual error	7	1,029	1,029	147		
Lack-of-fit	3	852	852	284	6.43	0.052
Pure error	4	177	177	44		
Total	12	294,266				

^a DF = degrees of freedom; Seq SS = sequential sum of squares; Adj SS = adjusted sum of squares; and Adj MS = adjusted mean squares.

Impact of boiling time. The effect of the boiling time (x_2) on DMS elimination was significant ($P = 0.000$, Table III). Its impact is shown in Figure 2B when adjusting the power supply (x_1) at 500 W. It was therefore observed that DMS declined from 708.59 ppb initially (at $t = 0$ min) to 298.72 ppb at 60 min. In fact, because the half-life of DMS was between 30 and 70 min (1,13, 29,37), the longer the boiling time, the higher the DMS that was discarded from wort (5,8,12,15,19,20,23,25,27,30). Its contribution to DMS removal was calculated at 58% (Table III).

Impact of power supply/boiling time interaction. The impact of power supply/boiling time (x_1x_2) on DMS discharge was significant ($P = 0.008$, Table III). It was observed (Fig. 3) that there was a synergistic effect between the two factors on the discharge of DMS during wort boiling. This can be seen because, when increasing the power supply, the evaporation rate increased, and with an increase of the boiling time, a significant amount of DMS was removed from wort (12). Its contribution was yielded at 7%.

Determination of Reaction Rate Coefficient of SMM Conversion to DMS (k_1)

During the trials, the DOOBOIL was between 0 and 60 min. It was used to obtain the data in Figure 4. Because the kinetic energy of discharge of SMM was considered equal to the kinetic energy of generation of DMS, the value of k_1 , which was 0.0054

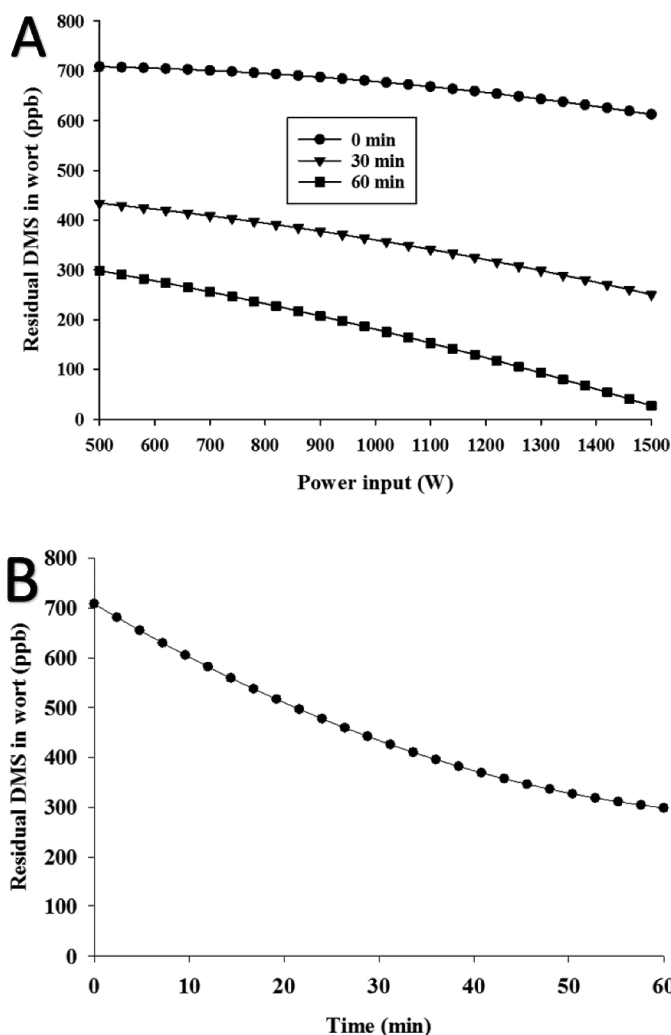


Fig. 2. Residual dimethyl sulfide (DMS) evolution: A, at fixed boiling times, and B, at a 500 W fixed value of power supply.

min^{-1} , was estimated using the DMS generation (Fig. 4). The stoichiometric relation between SMM and DMS was used and calculated the value of $[A]_0$, which was 390.54 ppb. The equation was written as follows:

$$[A] = 390.54 \times \exp(-0.0054t) \quad (15)$$

where S is residual concentration of SMM in the wort and t is time.

The estimated value of k_1 was about 1.85 times lower than the values (0.01 min^{-1} at 95°C) obtained by the literature (32). In fact, this could be explained by the fact that a reaction rate coefficient could vary depending on the operating conditions (13,35). For the Mitani case, after exploiting the data, the calculated power supply for their operating system was 11,850 W for a type 1 vessel and 4,900 W for a type 2 vessel. These conditions were obviously far more severe than the conditions used for this work. In fact, an increase in power supply for a specified time generated a global energy that contributed to increase the final temperature of the wort and thus an increase of k_1 . The consequence was a weaker

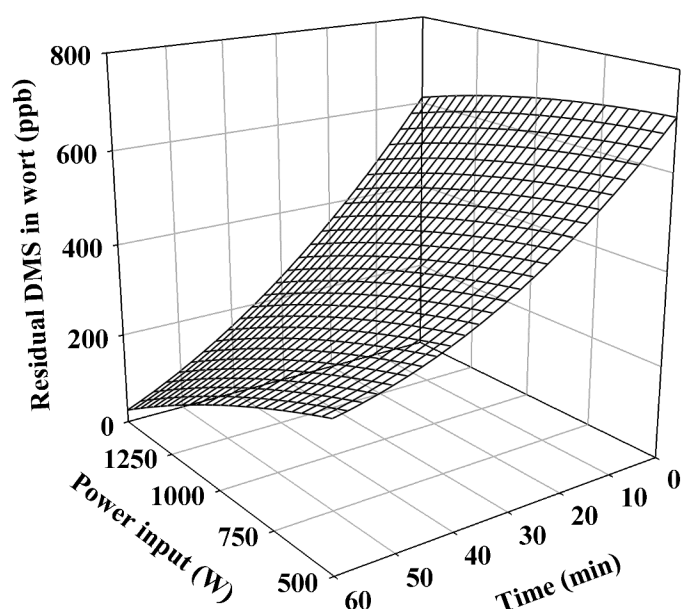


Fig. 3. Effect of power supply (power input)/boiling time interaction on the residual dimethyl sulfide (DMS) content of wort.

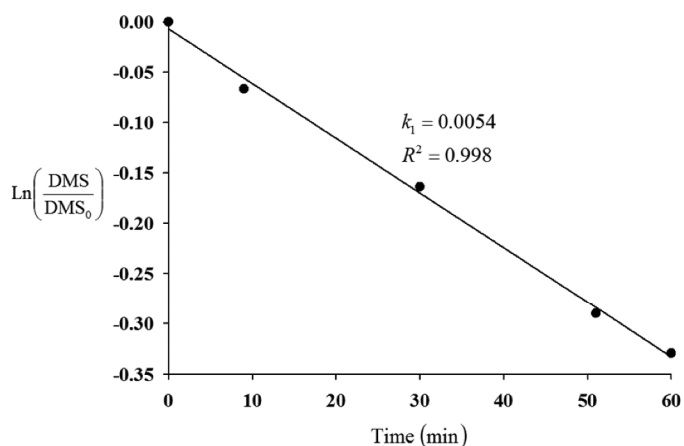


Fig. 4. Estimation of reaction rate coefficient of *S*-methyl methionine conversion to dimethyl sulfide (DMS) (k_1).

efficiency of SMM conversion to DMS, meaning a lower value of k_1 .

Determination Volatility Rate Coefficient of DMS (k_2) and Other Constants

After estimating the reaction rate k_1 and $[A]_0$ obtained after the DOOBOIL, the introduction of the theoretical model in Sigmaplot 13.0, taking into account the previous value calculated for SMM conversion kinetics, permitted us to obtain the complete equations for DMS stripping as follows for each power supply:

$$[DMS]_{T_{500}} = \frac{0.0054}{0.0151 - 0.0054} \times 390.54 [\exp(-0.0054t) - \exp(-0.0151t)] + 696.35 \exp(-0.0151t) \quad (16)$$

$$[DMS]_{T_{646}} = \frac{0.0054}{0.0168 - 0.0054} \times 390.54 [\exp(-0.0054t) - \exp(-0.0168t)] + 697.39 \exp(-0.0168t) \quad (17)$$

$$[DMS]_{T_{1000}} = \frac{0.0054}{0.0222 - 0.0054} \times 390.54 [\exp(-0.0054t) - \exp(-0.0222t)] + 693.45 \exp(-0.0222t) \quad (18)$$

$$[DMS]_{T_{1354}} = \frac{0.0054}{0.0322 - 0.0054} \times 390.54 [\exp(-0.0054t) - \exp(-0.0322t)] + 691.46 \exp(-0.0322t) \quad (19)$$

$$[DMS]_{T_{1500}} = \frac{0.0054}{0.0407 - 0.0054} \times 390.54 [\exp(-0.0054t) - \exp(-0.0407t)] + 706.56 \exp(-0.0407t) \quad (20)$$

where $[DMS]_{T_{500}}$, $[DMS]_{T_{646}}$, $[DMS]_{T_{1000}}$, $[DMS]_{T_{1354}}$, and $[DMS]_{T_{1500}}$ are the equations for DMS volatility when boiling was realized at 500, 646, 1,000, 1,354, and 1,500 W, respectively.

The value of k_1 remained constant because the heating process until boiling was executed using the same power supply (1,500 W), whereas the increase of k_2 observed with the increase of power supply could be interpreted by the fact that the modification of operating conditions changed the volatility rate coefficient value, as observed in the literature (1,12,13,28). The values obtained were similar to those of Mitani (28) and of the substitute wort water/DMS/sugar (12), which used the same boiling unit equipment.

A simulation was done to estimate the value of residual DMS in wort using the global equations (Mitani equation) to compare the values with experimental data. All the data were summarized in Table III. Three statistical analyses (ANOVA, variance check, and Kruskal–Wallis test) were executed to see whether there was a statistical difference or not between the data. The ANOVA table broke up the variance of the data into two constituents, the between-group constituent and the within-group constituent. The P values of the F test were greater than 0.05 (Table IV); there was not a statistically significant difference between the means of the two compared variables. For the variance check, the statistic dis-

played the null hypothesis that the standard deviations within both groups of data were the same. Considering that the P values were greater than 0.05 (Table IV), there was not a statistically significant difference among the standard deviations of the compared variables. The Kruskal–Wallis test tested the null hypothesis that the medians within each of the two variables were the same. The data from all the samples were first combined and ranked from smallest to largest. The average rank was then calculated for the data in each sample. Because the P values were greater than 0.05 (Table IV), there was not a statistically significant difference among the medians.

The different statistical analyses confirmed that the equations established (Mitani equation) followed the effective DMS removal during wort boiling. Therefore, the theoretical equations were used for the optimization process because the RSM could not allow investigations out of the intervals studied.

Optimization

The target values of residual DMS in wort were fixed at 30, 50, and 100 ppb because the supported values in the literature were from 30 to 100 ppb (7,8,19,21). Using Scientific Workplace 5.5 and Sigmaplot 13.0 software, the Mitani equations were solved and the different times to reach the targets were assessed. These targets were chosen to examine the efficiency of the laboratory boiling conditions when applying DOOBOIL on the removal of DMS.

The boiling times estimated for 30, 50, and 100 ppb were then 141–377, 94–295, and 60–197 min, respectively, as observed in Figure 5. These data suggested that the boiling conditions (DOOBOIL) executed were not suitable to reach a low level (30 ppb) and medium level (50 ppb) of DMS unless the boiling stage was realized for a very long period. This aspect implied high energy to spend,

meaning 11.31–12.69 and 8.46–8.85 MJ, respectively, to reach 30 and 50 ppb. It was therefore suitable to reach a residual value of 100 ppb because the boiling time was 60–197 min and the energy spent was 5.40–5.91 MJ.

The values of energy spent to reach the target of 50 ppb were higher than the one spent to reach the same target using wort substitutes, which was between 3.66 and 6.42 MJ (12). This could be explained by the presence of SMM and its low value of k_1 , which were the elements that could be responsible for the longer boiling time estimated to reach the targets. In fact, the low value of k_1 enabled a slower conversion of SMM into DMS and then a longer period of DMS removal.

CONCLUSIONS

Impacts of boiling time and power supply on DMS stripping from wort were investigated. The influence of these variables and the interaction between them were significant. When applying the DOOBOIL during wort boiling, it was found that the value of reaction rate coefficient of SMM conversion to DMS (k_1) was lower than the volatility rate coefficient of DMS (k_2). That situation generated very long boiling times and high energy spent to reach some targets (30 and 50 ppb). It then became obvious that DOOBOIL was not suitable for these targets at laboratory-scale wort boiling with nonpressure vessels. It would be therefore relevant to investigate a combination of gas sparging and DOOBOIL effects.

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TABLE IV

Statistical Analysis (Probability Values, P) Comparison Between Mitani Equation Theoretical Data and Response Surface Methodology Model at Each Power Supply

Power supply (W)	ANOVA	Variance check	Kruskal–Wallis test
500	0.404	0.519	0.317
646	0.453	0.577	0.369
1,000	0.543	0.703	0.457
1,354	0.655	0.875	0.555
1,500	0.747	0.973	0.738

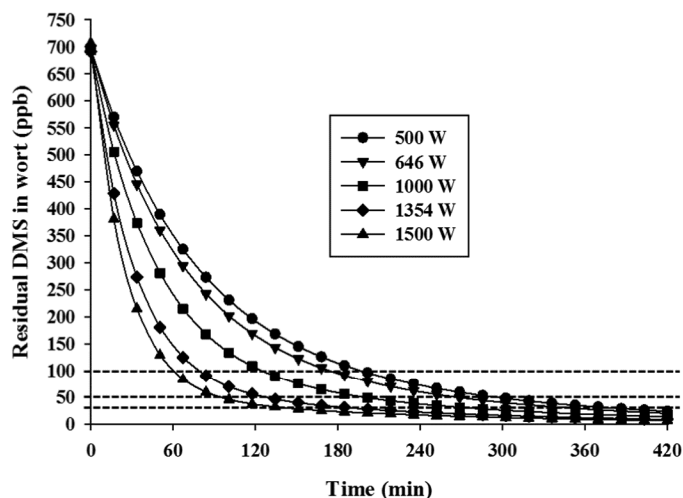


Fig. 5. Estimation of boiling time necessary to reach the targets of 30, 50, and 100 ppb of dimethyl sulfide (DMS).

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