Impact of Gaseous Carbon Dioxide and Boiling Power on Dimethyl Sulfide Stripping Behavior During Wort Boiling

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ABSTRACT

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The impact of carbon dioxide (CO_2) supply flow rate on dimethyl sulfide (DMS) removal during wort boiling was studied when applying a 1 h hold between the end of preheating and the beginning of boiling. This was done during wort boiling by varying the boiling power (from 500 to 1,500 W), aiming to reduce energy consumption to reach the target of an end-of-boil DMS concentration of 100 ppb (w/v). When using the Mitani equation, which describes *S*-methyl methionine (SMM) conversion into DMS and DMS stripping, the preboiling step allowed a reaction rate coefficient of SMM conversion (k_1) value of 0.0099 min^{-1} to be obtained. The values of volatilization rate coefficient of DMS (k_2) during the provision of CO_2 at a flow rate between 5 and 11 L/min and boiling power between 500 and 1,500 W were between 0.02049 and 0.07882 min^{-1}. It was found that the coefficient k_2 increased with the increase of CO_2 supply flow rate and the increase of boiling power. At a fixed boiling power of 1,500 W, the use of CO_2 supply flow rate permitted the target of 100 ppb to be attained in an interval of 39.21 min for 11 L/min to 62.31 min for 5 L/min. The energy saved in the boiling process when applying CO_2 supply flow rate between 5 and 11 L/min was 2.49–4.57 MJ.

Keywords: Boiling power, Boiling time, Dimethyl sulfide, Wort boiling, CO_2 supply flow rate

Reducing energy production costs is a major concern for food industries in general and breweries in particular. One major target is the reduction of process time in energy-intensive steps (37–39,43, 47,54). This reduction in process time must not impact negatively on the quality of the product, allowing good qualitative and physicochemical characteristics of the product to develop. In the brewing process, wort boiling is one of the most energy-intensive steps (25,26,51), and it is one of the last processing steps in which wort physicochemical characteristics are fixed before fermentation. During the boiling step, wort profile characteristics are developed, including the development of numerous undesirable flavors (off-flavors). Among the multitude of off-flavor components, dimethyl sulfide (DMS) is a major concern (1,3,4,7,18,27,35,49). DMS develops from *S*-methyl methionine (SMM) and increases during the malting process (4,53). The thermal conversion of SMM to DMS, the oxidation of DMS to dimethyl sulfoxide (DMSO) (1,2), and the fact that DMS is volatile allow the wort boiling step to potentially be a method of eliminating this off-flavor. Many efficient chromatographic protocols reported in the literature enable the evaluation of residual concentrations of DMS after malting, wort boiling, and fermentation (7,14,17,18,23,27). The wort boiling procedures in the brewhouse (and research on it) consist of executing a continuous boil and applying theoretical model to estimate some parameters linked to DMS stripping (8–10,17,31, 32,43,44,50,52) or, more recently, a polynomial model using the response surface methodology (19); also, a derived equation and application of a simultaneous volatile formation and stripping kinetics for wort boiling was developed (20). Some studies reported using CO_2 supply flow rate (16,43) to accelerate DMS stripping, but none of them studied the simultaneous impact of CO_2 supply flow rate and boiling power variation, as energy reduction factors, on DMS-stripping behavior.

EXPERIMENTAL

Chemicals

The chemicals used for this study were DMS solution (Sigma-Aldrich, 99% purity), dichloromethane (DCM) solution (Chromasolv, 99.8% for HPLC), and CO_2 in a pressure bottle (35 kg), chemically pure (99.0%) (material number 514202-SE-C, Afrox, South Africa).

Brewing

The brewing was done using a Braumeister all-in-one electric all-grain brewing unit (Speidel, Germany). In the unit were first placed the malt pipe, the first filter plate, and the first fine sieve. It was then filled with water (50 L) to reach a notch on the center post. The temperature was initially set to 65°C, and when the water reached the correct temperature, 10 kg of the milled malt (milled using a two-roller mill with the gap of the drill drive grain mill adjusted to 0.7 mm) was added, and the mixture was stirred and allowed to swell for a few minutes. Then, the second fine sieve was positioned onto the malt, followed by the second filter plate, and finished with the hold-down notch, which was installed and fixed well by utilizing a wing nut. The pump was then switched on, and the mashing was conducted at that temperature (65°C) for 1 h. During that period, the liquid wort was circulated through the mash and then cascaded down between the malt pipe and the outer wall of the Braumeister unit. The pH and the degrees Brix of the wort obtained after the mashing process were 5.4 and 10.5°B, respectively. The wort was then stored in a deep-freezer at –20°C in 25 L closed plastic buckets.

Wort Boiling Unit

The wort boiling unit consisted of a 25 L insulated vessel equipped with an electrical heating element. It was connected to a voltage regulator (phases, 1; input, 220 V and 50–60 Hz; output, 0–250 V; capacity, 2,000 VA max.; 8 amp; TDGC2-2kVA, AC-DC Dynamics, South Africa), which itself was connected to a Lutron DW-6060 watt meter. A Therma 3 thermometer (ETI, U.K.) was used to determine the wort temperature during the boiling process.

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The CO_2 distribution system consisted of a compressed gas cylinder fitted with a flow regulation valve and volumetric flow meter (Afrox Saffire ArC 20L) capable of metering gas flow rate up to 20 L/min. The sparger was a sintered metal porous cylindrical metal device that permitted sparging the gas in all the directions in the vessel.

Boiling and Preparation of Samples

The boiling trials were done utilizing a single boiling power (2,000 W) for preheating 10 L wort batches to reach 97°C, which is the boiling point of the wort at the atmospheric pressure of the site (altitude above sea level for Johannesburg, South Africa, 1,753 m). After reaching the boiling point, the heating element was de-energized, wort boiling was arrested, and the insulated vessel was closed for 60 min, during which time the temperature dropped from 97 to 94°C. During this 60 min period, conversion of SMM to DMS was undertaken. Loss of DMS from the boiler was considered negligible owing to the closure of the vessel. This 60 min period was considered as part of a laboratory method only to allow the rate constant of DMS formation to be empirically determined, in the absence of stripping. Any impact of this period on other wort quality parameters or kettle cycle time was not considered. Samples (50 mL, collected into a 250 mL Schott Duran glass with a screw top and cooled in cold water to about 1–2°C) were collected through this 60 min period after 0, 15, 30, 45, and 60 min. After this 60 min period had elapsed, the vessel was opened, the CO_2 distribution system was switched on at an adequate flow rate (0, 5, 6, 8, 10, and 11 L/min), and the wort was then boiled at a specific boiling power (500, 1,000, and 1,500 W) for 90 min (Fig. 1). The samples, for each boiling power and CO_2 supply flow rate, were collected after 0, 15, 30, 45, 60, 75, and 90 min during the boiling stage (50 mL, collected using a 250 mL Schott Duran glass with a screw top and cooled in an ice-water mixture to about 1–2°C). Once the wort was cooled, 50 mL of dichloromethane (DCM) was added, and the mixture was shaken at 450 rpm using a lab shaker (HT Infors, Switzerland) for 2 h, to enhance DMS extraction by the solvent phase (DCM). That solvent phase (1.5 mL) was transferred into 2 mL vials and crimped for GC-MS analysis. The standard curve (0–1,000 ppb) was prepared using DMS solution (Sigma-Aldrich, 99% purity).

Conditions for Wort Analysis

The Pegasus 4D GC×GC time-of-flight mass spectrometer (TOFMS) (Leco, U.S.A.) was used to determine the concentration of DMS in each step of the study with reference to the standard curve using DMS solution (Sigma-Aldrich, 99% purity). Identification of peak, signal deconvolution, and computation for distinctive analytes inside the sample were achieved with automated data processing. Wiley and National Institute of Standards and Technology libraries w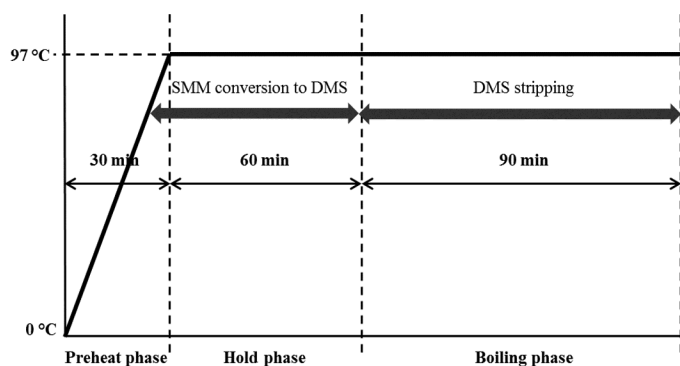ere utilized for peak identification with signal-to-noise ratio > 200, eliminating low similarity compounds (less than 650).

For the analysis, conducted in triplicate, 2 mL crimped vials containing the DMS extracted from wort were analyzed, and after defining the parameters shown in Table I, 1 μL of the solution from the vials was automatically redirected into the inlet of the Leco Pegasus 4D GC×GC-TOFMS. Data were obtained with Leco's ChromaTOF software.

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

Taking into consideration the fact that the SMM conversion to DMS reaction was considered to be represented as a first-order reaction kinetic equation (43) and also that it could be simultaneous with the DMS stripping, the estimation of k_1 was determined during the 60 min holding period prior to the boil. This was done at that stage because the DMS removal was assumed to be weak because boiling was not present. Once the wort had reached boiling temperature achieved by turning the heating element off and closing the vessel, the insulated vessel permitted the temperature (during 1 h) to be maintained in the system to within 3°C of the boiling point. Considering the mass balance principle between the SMM converted and the DMS formed, the experimental DMS values were correlated to an exponential equation expressed as follows:

$$[DMS] = [DMS]_0 \exp(k_1 t) \tag{1}$$

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

The DMS value at the end of the 1 h holding period was used to calculate the initial SMM concentration ($[SMM]_0$) as DMS equivalent and k_1.

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

To obtain the value of k_2, the data considered were obtained on analysis of the samples taken during wort boiling, and the Mitani theoretical equation (which express DMS stripping during wort

Fig. 1. Wort boiling diagram.

TABLE I
Conditions of LECO Pegasus Equipment for DMS Detection

Equipment	Specifications
Detector	Pegasus 4D GC×GC-TOFMS (Leco)
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

boiling) was computed using Matlab R2014a software (8.3.0.532, The Mathworks, U.S.A.) to correlate it with the experimental data and determine all the constant terms of that equation. This was done by introducing the obtained values of $[SMM]_0$ and k_1 because the SMM conversion to DMS was considered temperature dependent and the boiling process was done at atmospheric pressure with the temperature remaining at 97°C. The Mitani model was expressed as follows:

$$[DMS] = \frac{k_1[SMM]_0}{k_2 - k_1}\Big[\exp(-k_1 t) - \exp(-k_2 t)\Big] + [DMS]_0 \exp(-k_2 t) \quad (2)$$

where $[DMS]$ is the residual DMS in wort at time t during boiling, $[SMM]_0$ is the initial concentration of SMM, k_1 is the reaction rate coefficient of SMM conversion to DMS, k_2 is the volatilization rate coefficient of DMS, and $[DMS]_0$ is the initial concentration of DMS.

Statistical Analysis

The multiple sample comparison tool of Statgraphics Centurion XVI software (build 16.1.11, Statpoint Technologies, U.S.A.) was utilized for data analysis including analysis of variance (ANOVA) and the multiple range tests, which used Fisher's least significant difference (LSD) procedure. Fisher's LSD method was utilized as a part of ANOVA to generate confidence intervals for all pairwise variation between variable levels means while controlling the individual error rate to a significance level that was indicated. Fisher's LSD technique then utilized the individual error rate and number of correlations to estimate the simultaneous confidence level for all confidence intervals. This concurrent confidence level was the probability that all confidence intervals contained the true difference.

For each batch of analysis, the data were arranged into four columns. These columns were sample labels, sample sizes, sample means, and sample standard deviations. The labels were assigned for the different boiling conditions by assigning codes to the samples, and each measurement of DMS was done in triplicate. The column reflecting the means contained the mean value of each sample (each measurement was done in triplicate), as did the standard deviations column, which reflected the standard deviation obtained for each sample.
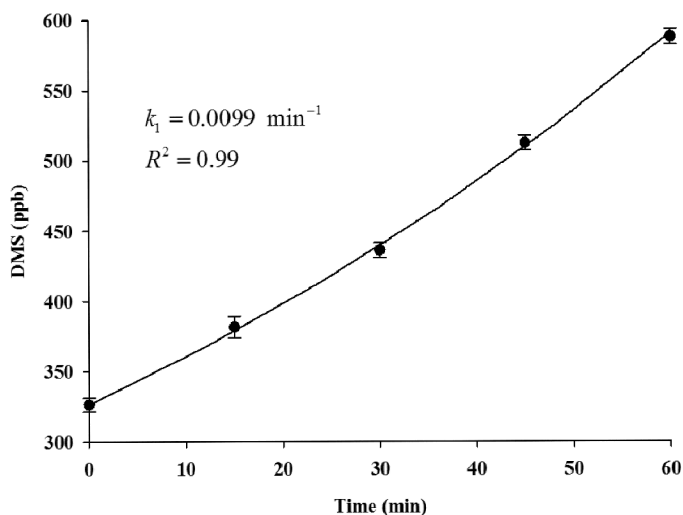

Fig. 2. Evolution of DMS during the holding phase.

Optimization

Optimization was realized by fixing a target of residual DMS concentration in the wort (100 ppb) and a maximum acceptable time to reach the target (90 min). A boiling time of 90 min allowed a value of residual DMS ≤ 100 ppb to be obtained, and the time to reach 100 ppb was then calculated using Scientific WorkPlace 5.5 software, build 2890 (MacKichan Software, U.S.A.) to solve the Mitani equation.

Energy Calculation

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

$$E = P_i t \quad (3)$$

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

RESULTS AND DISCUSSION

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

The first-order equation (equation 1) was fitted to experimental data (Fig. 2) during the arrested boiling step (at 0, 15, 30, 45, and 60 min), and a value of $k_1 = 0.0099$ min^{-1} was elicited. After determining the amount of DMS produced, the initial concentration of SMM was estimated at 807 ppb as DMS equivalent. There was a possibility during wort boiling that a part of DMSO was reduced to DMS by sulfhydryl compounds at the same time that DMS produced was oxidized to DMSO (2). According to the literature, these reactions are balanced or insignificant (1). By considering the conversion of SMM to DMS, with no loss of either from the system owing to the absence of boiling and hence stripping, the quantity of DMS produced could be equated to SMM consumed at any time t and expressed as a rate equation as follows:

$$[SMM] = 807 \times \exp(-0.0099t) \quad (4)$$

where $[SMM]$ is the concentration of SMM in the wort and t is the time.

The elicited k_1 value was about 34% lower than the value obtained by Mitani et al. (43), and it was about 41% lower than the value obtained when exploiting data from Dickenson (21). This could be interpreted by the reaction rate coefficient, which could change, being dependent upon on the running settings (1,19,21, 43,55). The reason why k_1 was lower than the one obtained by Mitani et al. (43) and Dickenson (21) could be explained also by the fact that it is a known function of temperature, and the SMM was converted to DMS at significantly lower temperatures than Mitani et al. and Dickenson used, owing to the holding phase and the low energy involved. Mitani et al. (43) reported the energy use for their operating system was 160 MJ·m^{-3}·h^{-1} for a type 1 vessel (0.4 m^3) and 150 MJ·m^{-3}·h^{-1} for a type 2 vessel (6 m^3). These conditions were undoubtedly more severe than our study conditions (0.075–0.225 MJ·m^{-3}·h^{-1}).

Impact of Boiling Conditions on Wort Residual DMS

For the boiling conditions with no CO$_2$ supply flow rate applied (Fig. 3A), it was observed that, from the initial DMS concentration around 587 ppb, the DMS concentration decreased to 378.3 ± 7.34, 253 ± 4.36, and 109.6 ± 2.87 ppb, respectively, for 500, 1,000, and 1,500 W. The decrease of DMS in wort during the boiling stage was also observed by many authors (5,13,19,22,46, 48,57,58). The values obtained at the end of the boiling process

were statistically different (Table II). The increasing rate of DMS removal with boiling power was owing to the increase in the liberated flow rate of steam because of the increased boiling power (12,15,24,29,33,36,40–42,45,50,56). It was also mentioned in the literature that DMS could be oxidized to DMSO during wort boiling (2).

For boiling conditions using 500 W with a CO_2 supply flow rate of 5, 6, 8, 10, and 11 L/min (Fig. 3B), a DMS concentration
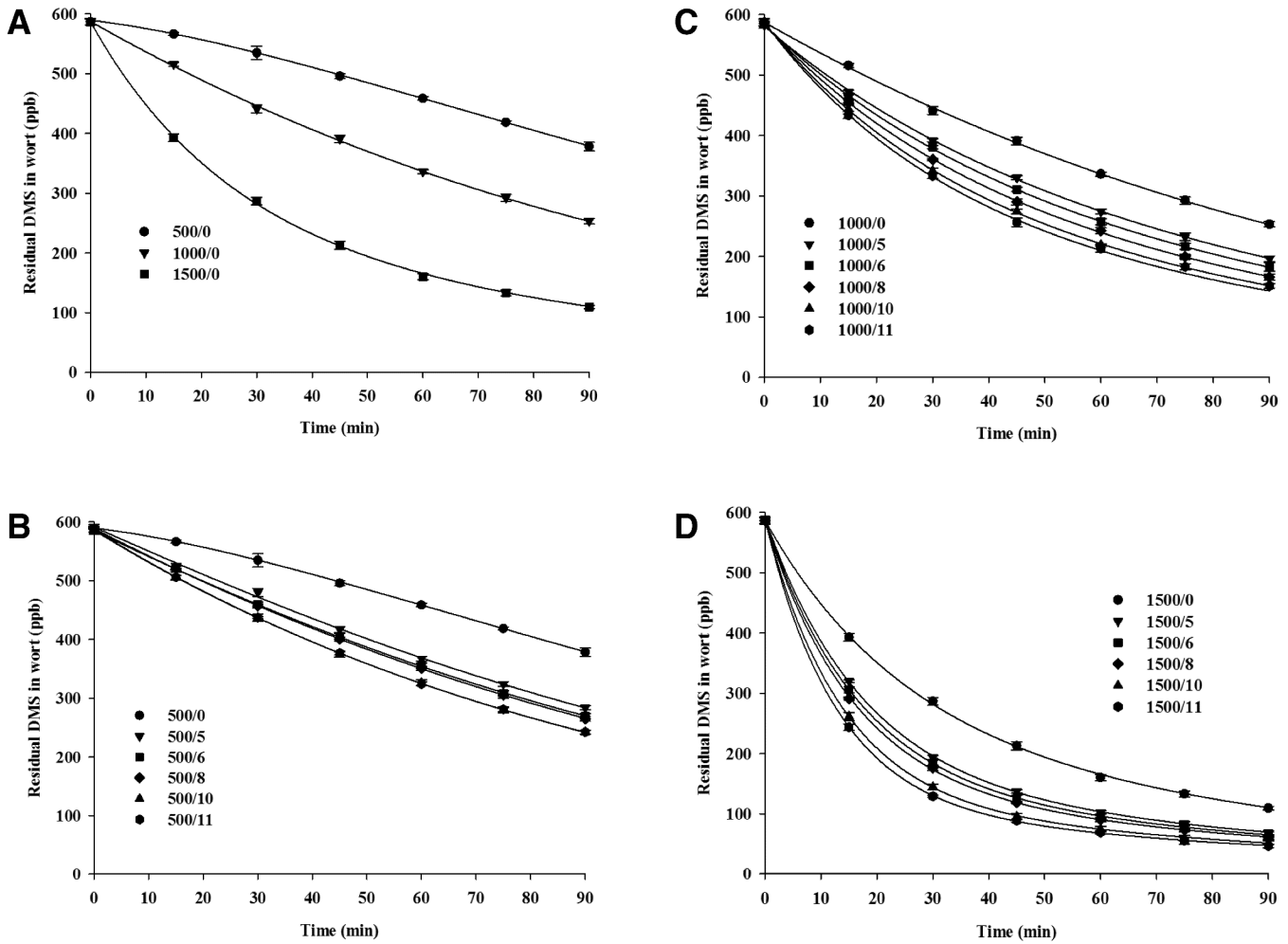
Fig. 3. Evolution of DMS during boiling: **A,** at each boiling power and with no CO_2 supply flow rate; **B,** 500 W, when applying different CO_2 supply flow rates (0, 5, 6, 8, 10 and 11 L/min); **C,** 1,000 W, when applying different CO_2 supply flow rates; and **D,** 1,500 W, when applying different CO_2 supply flow rates. Sample designations list power level followed by flow rate.

TABLE II
Statistical Comparison Between Power Input Impact on Residual DMS After 90 min Boiling Time and No CO_2 Supply Flow Rate[a]

ANOVA					
Source	Sum of squares	df	Mean square	F ratio	P value
Between groups	108,438.7	2	54,219.1	2,003.75	0.0000
Within groups	162.353	6	27.0589		
Total (corr.)	108,601.0	8			

Method: 95.0% LSD			
Power (W)/flow rate (L/min)	Count	Mean	Homogeneous groups
1,500/0	3	109.6	X
1,000/0	3	253.033	X
500/0	3	378.267	X

Contrast	Significance	Difference	+/– Limits
500/0 vs. 1,000/0	*	125.233	10.3927
500/0 vs. 1,500/0	*	268.667	10.3927
1,000/0 vs. 1,500/0	*	143.433	10.3927

[a] Asterisk (*) denotes a statistically significant difference. Placement of "X" indicates homogeneous groups.

decrease was noticed for all the CO_2 supply flow rates, from a start-of-boil value around 570 ppb to an end-of-boil value around 242.5 ± 3.35 ppb obtained (at 11 L/min) after 90 min of boiling. At the end of that boiling process, when comparing the residual DMS in the wort, it was statistically demonstrated that there was no significant difference when applying 6 and 8 L/min and when applying 10 and 11 L/min sparging rate, whereas for the other combinations there were significant differences when using the 95% Fisher's LSD method (Table III). The decrease of DMS concentration for all the CO_2 supply flow rates could be owing to the contribution of CO_2 on DMS stripping. The increased removal rate of DMS with an increase of CO_2 supply flow rate was also observed by Mitani et al. The boiling conditions utilizing 1,000 W with a CO_2 supply flow rate of 5, 6, 8, 10, and 11 L/min (Fig. 3C) showed that the DMS concentration also decreased to a minimum (end-of-boil) value of 151.4 ± 3.80 ppb at a CO_2 supply flow rate of 11 L/min. For this case, statistical analysis exhibited for the residual DMS concentration that there was no significant difference when implementing CO_2 supply flow rates of 8 and 10 L/min, whereas all the other pairwise comparisons were significantly different when using the 95% Fisher's LSD method (Table IV). As with the previous case (500 W), an increase of CO_2 supply flow rate generated an increased rate of DMS stripping (43).

When boiling at 1,500 W with a CO_2 supply flow rate of 5, 6, 8, 10, and 11 L/min (Fig. 3D), the decrease of DMS in wort after 90 min reached a minimum (end-of-boil) value of 47.3 ± 2.50 ppb when using a CO_2 supply flow rate of 11 L/min. Statistical analysis revealed that there was no significant difference when comparing 5 and 6 L/min, 6 and 8 L/min, and 10 and 11 L/min (Table V). For other pairwise comparisons, there was significant difference observed (Table V), and greater DMS stripping was exhibited when raising the CO_2 supply flow rate.

Volatilization Rate Coefficient (k_2) and Initial DMS Concentration ($[DMS]_0$)

The reaction rate coefficient k_1 and $[SMM]_0$ were elicited using the arrested boiling period data and were introduced into the Mitani equation (equation 2). After fitting that equation to boiling-stage data, volatilization rate coefficient (k_2) and initial DMS concentration ($[DMS]_0$) were obtained as presented in Table VI. The values of $[DMS]_0$ were between 580.9 and 591.2 ppb, and the values of k_2 varied from 0.01544 to 0.07882 min^{-1} (Table VI). These values of k_2 obtained for this study were not of the same order of magnitude as that sourced from Mitani et al. in 1999 (43), owing in part to the energy involved. In this case, the heat supply was between 0.075 and 0.225 MJ/m^3·h. In addition, the scale (400 L pilot and 6,000 L commercial scale) and the type of kettles (technology) were different compared with the 25 L kettle used in this study.

Impact of CO_2 Supply Flow Rate on Volatilization Rate Coefficient k_2

An analysis of Figure 4 shows that the volatilization rate coefficient k_2 increased with CO_2 flow rate, increasing at higher boiling powers. The CO_2 sparging disturbed the equilibrium condition (liquid/vapor interface equilibrium) (6) of DMS in the wort matrix. Thus, the gas absorbed and carried the contaminant (DMS) with it as it progressed to the surface and was vented away from the process stream and vessel. In fact, sparging produced a condition in which a large surface area of the wort to be treated was exposed to CO_2, which promoted transfer of the contaminant (DMS) from the liquid phase to the gaseous phase (30,43). This occurred because under normal conditions the concentration of contaminant in ambient air was much lower than the concentration in aqueous solution (wort) (30). The result of that phenomenon

TABLE III
Statistical Comparison Between CO_2 Supply Flow Rate Impact on Residual DMS After 90 min Boiling Time and 500 W[a]

ANOVA

Source	Sum of squares	df	Mean square	F ratio	P value
Between groups	38,584.6	5	7,716.92	374.00	0.0000
Within groups	247.6	12	20.6333		
Total (corr.)	38,832.2	17			

Method: 95.0% LSD

Power (W)/flow rate (L/min)	Count	Mean	Homogeneous groups
500/11	3	242.467	X
500/10	3	242.033	X
500/8	3	264.8	X
500/6	3	269.6	X
500/5	3	284.0	X
500/0	3	378.267	X

Contrast	Significance	Difference	+/– Limits
500/0 vs. 500/5	*	94.2667	8.0809
500/0 vs. 500/6	*	108.667	8.0809
500/0 vs. 500/8	*	113.467	8.0809
500/0 vs. 500/10	*	136.233	8.0809
500/0 vs. 500/11	*	135.8	8.0809
500/5 vs. 500/6	*	14.4	8.0809
500/5 vs. 500/8	*	19.2	8.0809
500/5 vs. 500/10	*	41.9667	8.0809
500/5 vs. 500/11	*	41.5333	8.0809
500/6 vs. 500/8		**4.8**	8.0809
500/6 vs. 500/10	*	27.5667	8.0809
500/6 vs. 500/11	*	27.1333	8.0809
500/8 vs. 500/10	*	22.7667	8.0809
500/8 vs. 500/11	*	22.3333	8.0809
500/10 vs. 500/11		**–0.43333**	8.0809

[a] Asterisk (*) denotes a statistically significant difference. Boldface differences were not statistically significant. Placement of "X" indicates homogeneous groups.

TABLE IV
Statistical Comparison Between CO_2 Supply Flow Rate Impact on Residual DMS After 90 min Boiling Time and 1,000 W[a]

ANOVA					
Source	Sum of squares	df	Mean square	F ratio	P value
Between groups	19,820.6	5	3,964.12	153.48	0.0000
Within groups	309.933	12	25.8278		
Total (corr.)	20,130.6	17			

Method: 95.0% LSD			
Power (W)/flow rate (L/min)	Count	Mean	Homogeneous groups
1,000/11	3	151.4	X
1,000/10	3	165.933	X
1,000/8	3	165.967	X
1,000/6	3	182.367	X
1,000/5	3	195.967	X
1,000/0	3	253.033	X

Contrast	Significance	Difference	+/– Limits
1,000/0 vs. 1,000/5	*	57.0667	9.04105
1,000/0 vs. 1,000/6	*	70.6667	9.04105
1,000/0 vs. 1,000/8	*	87.0667	9.04105
1,000/0 vs. 1,000/10	*	87.1	9.04105
1,000/0 vs. 1,000/11	*	101.633	9.04105
1,000/5 vs. 1,000/6	*	13.6	9.04105
1,000/5 vs. 1,000/8	*	30.0	9.04105
1,000/5 vs. 1,000/10	*	30.0333	9.04105
1,000/5 vs. 1,000/11	*	44.5667	9.04105
1,000/6 vs. 1,000/8	*	16.4	9.04105
1,000/6 vs. 1,000/10	*	16.4333	9.04105
1,000/6 vs. 1,000/11	*	30.9667	9.04105
1,000/8 vs. 1,000/10		**0.03333**	9.04105
1,000/8 vs. 1,000/11	*	14.5667	9.04105
1,000/10 vs. 1,000/11	*	14.5333	9.04105

[a] Asterisk (*) denotes a statistically significant difference. Boldface differences were not statistically significant. Placement of "X" indicates homogeneous groups.

TABLE V
Statistical Comparison Between CO_2 Supply Flow Rate Impact on Residual DMS After 90 min Boiling Time and 1,500 W[a]

ANOVA					
Source	Sum of squares	df	Mean square	F ratio	P value
Between groups	7,327.05	5	1,465.41	162.71	0.0000
Within groups	108.073	12	9.00611		
Total (corr.)	7,435.12	17			

Method: 95.0% LSD			
Power (W)/flow rate (L/min)	Count	Mean	Homogeneous groups
1,500/11	3	47.333	X
1,500/10	3	52.6	X
1,500/8	3	61.3	X
1,500/6	3	66.5667	XX
1,500/5	3	69.0	X
1,500/0	3	109.6	X

Contrast	Significance	Difference	+/– Limits
1,500/0 vs. 1,500/5	*	40.6	5.3388
1,500/0 vs. 1,500/6	*	43.0333	5.3388
1,500/0 vs. 1,500/8	*	48.3	5.3388
1,500/0 vs. 1,500/10	*	57.0	5.3388
1,500/0 vs. 1,500/11	*	62.2667	5.3388
1,500/5 vs. 1,500/6		**2.4333**	5.3388
1,500/5 vs. 1,500/8	*	7.7	5.3388
1,500/5 vs. 1,500/10	*	16.4	5.3388
1,500/5 vs. 1,500/11	*	21.6667	5.3388
1,500/6 vs. 1,500/8		**5.26667**	5.3388
1,500/6 vs. 1,500/10	*	13.9667	5.3388
1,500/6 vs. 1,500/11	*	19.2333	5.3388
1,500/8 vs. 1,500/10	*	8.7	5.3388
1,500/8 vs. 1,500/11	*	13.9667	5.3388
1,500/10 vs. 1,500/11		**5.26667**	5.3388

[a] Asterisk (*) denotes a statistically significant difference. Boldface differences were not statistically significant. Placement of "X" indicates homogeneous groups.

combined with the power of boiling was an increase of the volatilization rate coefficient (k_2).

Optimization

In this section, the parameters of CO_2 flow rate and boiling power were manipulated to optimize end-of-boil DMS against energy utilized during boiling. Any energy associated with the production or provision of the differing quantities of carbon dioxide was not considered in this optimization process. The optimization method used consisted of minimizing the boiling time (which must be less than the baseline of 90 min), thus reducing energy consumed, to attain 100 ppb, which was the established target for residual DMS (1,11,12,28,34). The results presented in Table VII for that purpose showed that it was impossible to attain the target of 100 ppb in less than 90 min boiling time when using 500 and 1,000 W of boiling power, whatever the CO_2 supply flow rate utilized. Therefore, there was no energy reduction to consider in this case. This could be explained by the fact that the enhancement of the volatilization rate coefficients owing to the presence of gaseous CO_2 was not sufficient to achieve an end-of-boil DMS
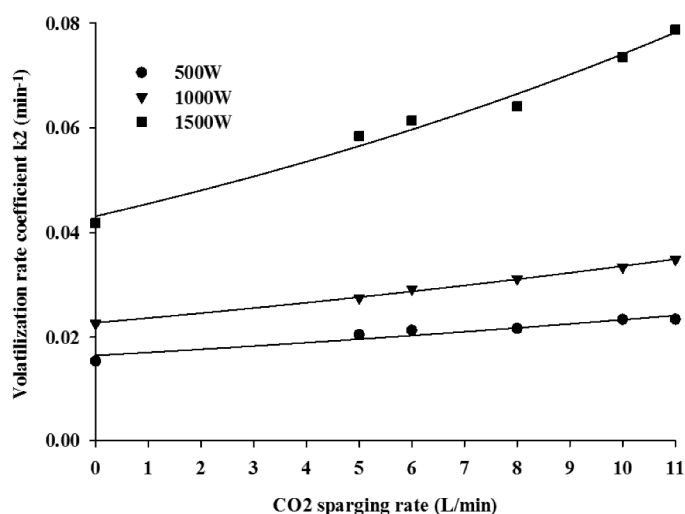

Fig. 4. Effect of CO_2 supply flow rate on volatilization rate coefficient k_2.

TABLE VI
Estimation of Mitani Equation Parameters at 500, 1,000, and 1,500 W Power Input and 5–11 L/min CO_2 Supply Flow Rate, and No CO_2 Supply[a]

Power input	CO_2 (L/min)	R^2	k_2 (min^{-1})	$[DMS]_0$ (ppb)	Mitani equations
500 W					
	0	0.99	0.01544	589.6	$[0.0099/(0.01544 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.01544t)] + 589.6 \times \exp(-0.01544t)$
	5	0.99	0.02049	591.2	$[0.0099/(0.02049 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.02049t)] + 591.2 \times \exp(-0.02049t)$
	6	0.99	0.02133	585.2	$[0.0099/(0.02133 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.02133t)] + 585.2 \times \exp(-0.02133t)$
	8	0.99	0.02165	588.4	$[0.0099/(0.02165 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.02165t)] + 588.4 \times \exp(-0.02165t)$
	10	0.99	0.02341	585.9	$[0.0099/(0.02341 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.02341t)] + 585.9 \times \exp(-0.02341t)$
	11	0.99	0.02343	586.8	$[0.0099/(0.02343 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.02343t)] + 586.8 \times \exp(-0.02343t)$
1,000 W					
	0	0.99	0.02260	587.5	$[0.0099/(0.02260 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.02260t)] + 587.5 \times \exp(-0.02260t)$
	5	0.99	0.02751	580.9	$[0.0099/(0.02751 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.02751t)] + 580.9 \times \exp(-0.02751t)$
	6	0.99	0.02920	583.6	$[0.0099/(0.02920 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.02920t)] + 583.6 \times \exp(-0.02920t)$
	8	0.99	0.03118	584.9	$[0.0099/(0.03118 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.03118t)] + 584.9 \times \exp(-0.03118t)$
	10	0.99	0.03342	586.8	$[0.0099/(0.03342 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.03342t)] + 586.8 \times \exp(-0.03342t)$
	11	0.99	0.03487	587.5	$[0.0099/(0.03487 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.03487t)] + 587.5 \times \exp(-0.03487t)$
1,500 W					
	0	0.99	0.04180	586.3	$[0.0099/(0.04180 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.04180t)] + 586.3 \times \exp(-0.04180t)$
	5	0.99	0.05842	589.4	$[0.0099/(0.05842 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.05842t)] + 589.4 \times \exp(-0.05842t)$
	6	0.99	0.06141	587.8	$[0.0099/(0.06141 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.06141t)] + 587.8 \times \exp(-0.06141t)$
	8	0.99	0.06415	585.8	$[0.0099/(0.06415 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.06415t)] + 585.8 \times \exp(-0.06415t)$
	10	0.99	0.07358	586.7	$[0.0099/(0.07358 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.07358t)] + 586.7 \times \exp(-0.07358t)$
	11	0.99	0.07882	586.0	$[0.0099/(0.07882 - 0.0099)] \times 807 \times [\exp(-0.0099t) - \exp(-0.07882t)] + 586.0 \times \exp(-0.07882t)$

[a] The Mitani equation calculates $[DMS]$, the residual DMS in wort at time t during boiling (equation 2). k_2 = volatilization rate coefficient of DMS; and $[DMS]_0$ = the initial concentration of DMS at the beginning of the arrested boiling period.

TABLE VII
Impact of CO_2 Supply Flow Rate on the Residual DMS Concentration and Energy Saved (Targeted DMS Concentration is 100 ppb)

Power input (W)	Parameter	CO_2 supply flow rate (L/min)					
		0	5	6	8	10	11
500	$[DMS]$ reached in 90 min (ppb)	378.3 ± 7.34	284.0 ± 3.46	269.6 ± 4.27	264.8 ± 4.06	242.0 ± 3.45	242.5 ± 3.35
	Time to reach target (min)[a]	/	/	/	/	/	/
	Energy spent (MJ)	2.7	2.7	2.7	2.7	2.7	2.7
	Energy saved (MJ)	/	/	/	/	/	/
1,000	$[DMS]$ reached in 90 min (ppb)	253.0 ± 4.36	196 ± 4.81	182.4 ± 7.20	166.0 ± 4.74	165.9 ± 4.89	151.4 ± 3.80
	Time to reach target (min)[a]	/	/	/	/	/	/
	Energy spent (MJ)	5.4	5.4	5.4	5.4	5.4	5.4
	Energy saved (MJ)	/	/	/	/	/	/
1,500	$[DMS]$ reached in 90 min (ppb)	109.6 ± 2.87	69 ± 2.88	66.6 ± 3.22	61.3 ± 3.48	52.6 ± 2.98	47.3 ± 2.50
	Time to reach target (min)[a]	90	62.31	57.77	54.00	43.66	39.21
	Energy spent (MJ)	**8.1**	**5.61**	**5.20**	**4.86**	**3.93**	**3.53**
	Time saved (min)	**0**	**27.69**	**32.23**	**36.00**	**46.34**	**50.79**
	Energy saved (MJ)	**0**	**2.49**	**2.90**	**3.24**	**4.17**	**4.57**

[a] Only times < 90 min are considered. Slash (/) indicates not applicable. Boldface listings highlight the savings achieved at 1,500 W.

target of 100 ppb to be reached in 90 min. However, the energy spent when using 500 and 1,000 W during 90 min of boiling was 2.7 and 5.4 MJ, respectively (Table VII). Furthermore, it was also observed in Table VII for 1,500 W of boiling power that the use of CO_2 supply flow rate permitted reaching 100 ppb at maximum and minimum boiling times of 62.31 and 39.21 min, respectively. This trend was observed in the literature, in which the use of gas sparging (nitrogen) reduced a conventional boil from 50 to 25 min duration for an equivalent end-of-boil DMS concentration (43). These reduced boiling times equated to utilized energy values ranging from 3.53 to 5.61 MJ. This represented a reduction of 31–56% in utilized energy, because the energy required to boil for 90 min at 1,500 W was calculated at 8.1 MJ (Table VII). That boiling time reduction could therefore provoke incomplete progress or completion of other important reactions and processes occurring during wort boiling.

CONCLUSIONS

The boiling power and the CO_2 supply flow rate effects on DMS removal from wort were studied when applied to a constant arrested boiling time of 1 h. The boiling power combined with the CO_2 supply flow rate permitted an increase of the volatilization coefficient rate of DMS. The CO_2 supply flow rate allowed also significant boiling time reduction and associated energy reductions (the energy required to produce the CO_2 was not considered), with the minimum utilized boiling energy arising from maximizing boiling power and CO_2 flow rate. As indicated in the discussion of the results, the impact of the scale of the wort kettle on the stripping behavior and any associated energy benefit would need to be considered if extrapolating up to and including industrial-scale wort kettles. Practical implementation of such a gas stripping technique into a production brewery would require consideration of the impact of the energy and financial cost of CO_2 together with the safety aspects of using CO_2 in the brewhouse.

ACKNOWLEDGMENTS

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