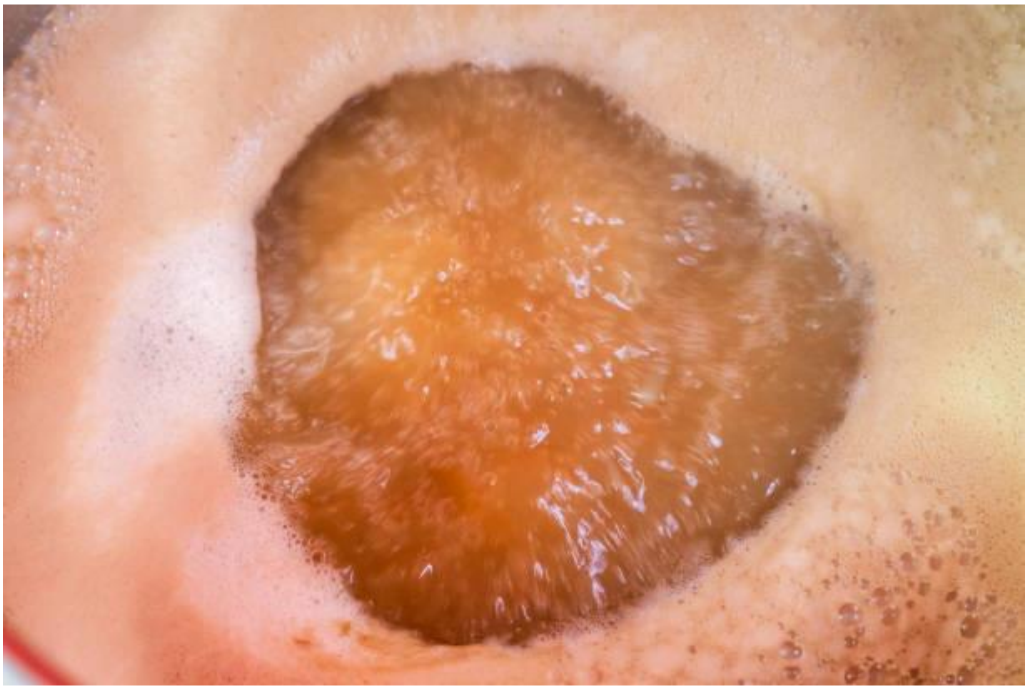
Literature review

Formation of dimethyl sulfide in wort



Scandinavian School of Brewing

Report

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Literature review

Formation of dimethyl sulfide in wort

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VIRTUAL WATER TECHNOLOGY

1 Introduction

This report describes the kinetics and equilibriums of importance for dimethyl sulfide (DMS) formation and removal in beer wort based on available data in the literature. The purpose is to use available studies to establish a mathematical understanding of the processes, that can be used in a numerical model describing the processes.

In the process of brewing beer, DMS is formed from a thermally induced decomposition of S-methyl methionine (SMM). This process only takes place at elevated temperatures and will thus happen during the kilning, wort boiling and wort separation in the whirlpool. During kilning, some DMS is oxidized to dimethyl sulphoxide (DMSO), which in turn may be oxidized further to dimethyl sulphone ($DMSO_2$). In the fermentation process DMSO can be converted back to DMS by enzymatic pathways in the yeast. These reactions are illustrated in Figure 1.1.

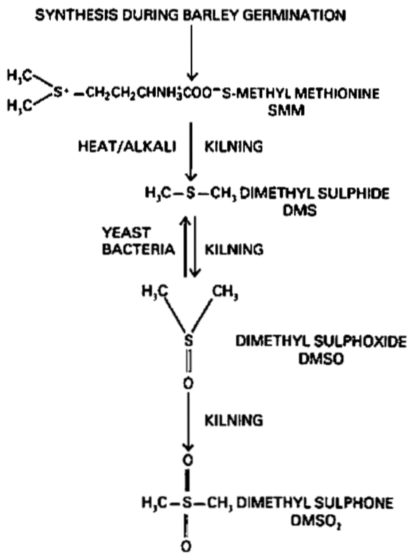

Figure 1.1 Pathways of DMS formation and conversion /1/.

An example of the formation and degradation of SMM, DMS and DMSO during a kilning process can be found in Figure 1.2, where the gradual increase in DMS and DMSO concentrations are observed while the SMM concentration decreases. Beer types using barley with long kilning times will typically experience less problems with elevated DMS levels as a substantial amount of SMM is removed prior to the wort boiling and wort separation.

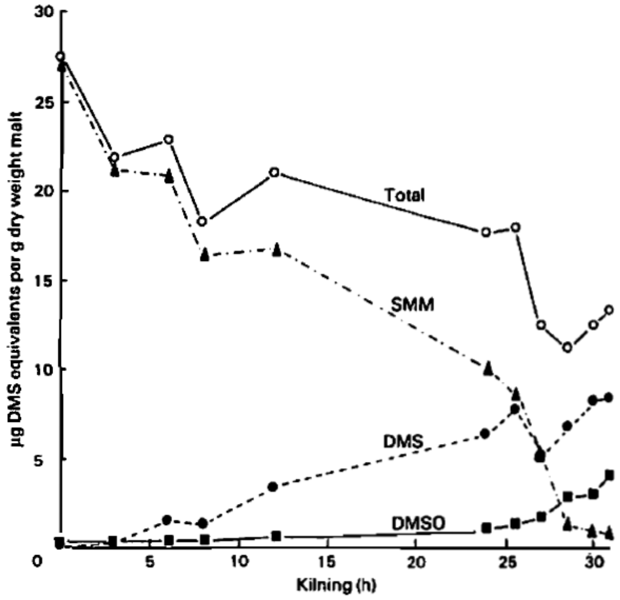

Figure 1.2 The effect of kilning on the levels of SMM, DMS and DMSO in malt. Kilning schedule: 24 h at 65°C; 3 h at 85°C; 3 h at 95°C; 1 h at 105°C. ▲ SMM; ● DMS; ○ SMM+DMSO; ■ DMSO /1/.

During the wort boiling process, the formed DMS is efficiently removed through volatilization with the water vapor formed by the boiling wort. However, once the boiling process is over and the evaporation become less important, the rate of formation exceeds the rate of removal and the DMS concentration increases. Once the wort is cooled, the formation stops. In the fermentation process DMS can both be formed and removed by yeast induced reduction of DMSO and stripping by formed CO_2 gas, respectively. It is the balance of all of the above processes that determines the final concentration of DMS in the beer. In the following chapter relevant kinetic and equilibrium data from the available literature is reported.

2 Literature review

2.1 Formation of dimethyl sulfide

As illustrated in Figure 1.1, DMS can be formed by two pathways: thermal degradation of SMM and yeast induced reduction of DMSO.

2.1.1 Thermal degradation of S-methylmethionine

The content of SMM in malt varies and is dependent on barley variety, malting conditions, storage time before malting /1/. Typical content of SMM in malt is 10-30 µg DMS equivalents per g dry weight malt /1/. SMM has a high solubility in water and is not volatile /1/, thus it does not evaporate during wort boiling.

The thermal degradation of SMM to DMS is a 1st order process /1/ and can be described as

$$\frac{d[SMM]}{dt} = -k_1 t$$

where k_1 is the 1st order rate constant.

The temperature dependency of the rate constant can be describe using the Arrhenius equation:

$$k = Aexp\left(-\frac{E_A}{RT}\right)$$

where A is the Arrhenius factor, E_A the activation energy, R the gas constant and T the temperature.

Several studies have reported values for the rate constant and its temperature dependency. Table 2.1 summarizes the reported values.

Table 2.1 Kinetic constants for the degradation of SMM to DMS

Reference	Rate constant k_1 [min^{-1}]	Activation Energy E_A [kJ/mol]	Arrhenius Factor A [min^{-1}]	Reference temperature [C]	pH [-]
/1/	0.0198	-	-	-	5.4
/3/	0.0099	-	-	97	5.4
/4/	0.0054	-	-	95	5.4
/6/	0.0180	-	-	100	4.9
/6/	0.01824	138	-	100	5.2
/6/	0.0213	-	-	100	5.5
/8/	0.018	-	-	100	-
/8/	0.022	-	-	100	-
/7/[1]	0.0258	121.779	$2.88 \cdot 10^{15}$	100	-
/7/[2]	0.0245	115.015	$3.09 \cdot 10^{14}$	100	-
/7/[3]	0.0367	182	$4 \cdot 10^{24}$	100	-
/7/[4]	0.0231	-	-	-	-
/7/[5]	0.0165	-	-	-	-
/7/[6]	0.115	-	-	-	-
/7/[7]	0.0116	81.3	$2.79 \cdot 10^{9}$	100	-

The reported values vary substantially, and in particular the rate constant of 0.115 min^{-1} reported in /7/ is much higher than the rest. Disregarding this value, the average value of the rate constant is 0.0193 min^{-1} with a standard deviation of 0.0076 min^{-1}. Less data is available on the temperature dependence of the rate constant. The average value of the reported activation

[1] Values are referred by /7/ from ZÜRCHER et al., 1979, Technologische Maßnahmen zur Reduzierung des Dimethylsufidgehaltes im Bier, EBC-Proceeding, Berlin, 175–188.

[2] Values are referred by /7/ from RÜBSAM, H.T. and KROTTENTHALER, M., 2010, Optimierung der Sudhaustechnologie mit Dimethylsulfid als Leitkomponente, Brauwelt 150, 534–539.

[3] Values are referred by /7/ from SCHEUREN, H.P., 2010, Modellierung gekoppelter Austreibungsund Nachbildungsprozesse aromatischer Komponenten in der Lebensmittelindustrie am Beispiel der der Würzebereitung, Dissertation, München, Germany.

[4] Values are referred by /7/ from HERTEL et al., 2006, Engineering investigations of the recreation kinetics of flavour-components during the boiling of wort, Monatsschrift Brauwiss, 59(Jan./Feb.), 45–55.

[5] Values are referred by /7/ from SCHWILL-MIEDANER, A., 2002, Würzekochung heute – gibt es Alternativen? Brauwelt 142, 603–615.

[6] Values are referred by /7/ from FELGENTRÄGER,W., 1993, Numerische Modellierung des Abbzw. Aufbaues der wichtigsten Leitsubstanzen des Bieres während der Produktion, Dissertation, München, Germany.

[7] Data are obtained using the Coats–Redfern method.

energies is 128 kJ/mol ± 37 kJ/mol. It should be noted that the data from /6/ demonstrates a pH dependence of the rate constant as it increases with pH. Thus, decreasing the pH by CO_2 sparging will reduce the formation rate of DMS.

Figure 2.1 shows an example of the degradation of SMM during wort boiling. It is observed that the increase in DMS does not match the decrease in SMM as the formed DMS is evaporated during the boil.

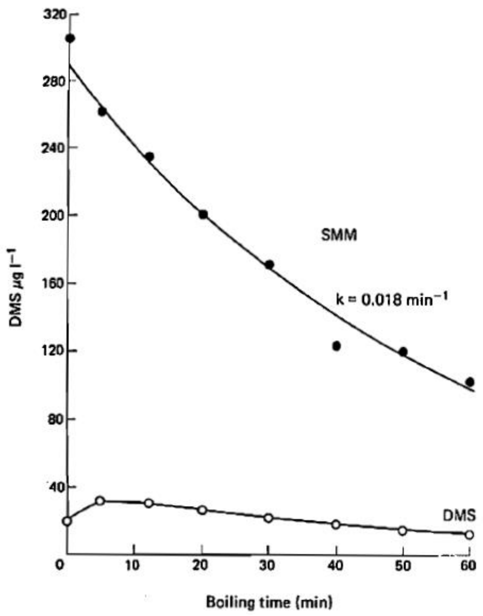

Figure 2.1 The effect of boil time on the levels of DMS and SMM in an imitation sweet wort to which SMM has been added /8/.

DMS has a low boiling point of 38°C and solubility of 300 mM /1/. In addition, the Henry constant is $5.6 \cdot 10^{-3}$ mol/($m^3 \cdot$Pa) (enthalpy of solubilization of -29.1 kJ/mol) makes it highly volatile. Thus, DMS formed during the wort boil will be volatilized. Rate constants (k_2) for the removal of DMS due to volatilization are reported in the literature and they depend on the geometry of the wort boiler, the power input and the composition of the wort:

- k_2 = 0.02049 - 0.07882 min^{-1} /3/. Measured with varying power input and CO_2 stripping gas flow.
- k_2 = 0.0151 - 0.407 min^{-1} /4/.
- k_2 = 0.0202 - 0.0436 min^{-1} /5/. Measured on a DMS/water mixture with variable power input.
- k_2 = 0.0143 - 0.036 min^{-1} /5/. Measured on a DMS/sugar/water mixture with variable power input.

Provided knowledge of k_1, k_2 and the initial SMM concentration, the Mitani model /3/ below can be used to predict the evolution of DMS during the wort boil and subsequent treatment(s) at known temperature(s).

$$[DMS] = \frac{k_1[SMM]_0}{k_2 - k_1}\left[\exp(-k_1 t) - \exp(-k_2 t)\right] + [DMS]_0 \exp(-k_2 t)$$

2.1.2 Yeast reduction of DMSO

During the fermentation process, enzymatic processes involving methionine sulfoxide reductase initiated by the yeast result in a reduction of DMSO and the formation of DMS. Some studies have shown that 80% of DMS present in beer originated from DMSO /2/. DMSO is formed by oxidation of DMS during kilning, and concentrations increases at higher kilning temperatures. During wort boiling, no significant changes in DMSO is observed and a typical boiled wort contains 200-400 µg DMSO/L /1/.

DMSO has a high solubility in water /1/ and the Henry constant is $9.8 \cdot 10^2$ mol/($m^3 \cdot$Pa) (enthalpy of solubilization of -10.8 kJ/mol) /9/ make it non-volatile. The boiling point of DMSO is 189°C /1/. These physico-chemical properties of DMSO explain why is not removed during the boiling process.

Approximately 5% of the DMSO present in the wort is converted into DMS during fermentation /1/ . Some dependency on yeast strain, fermentation temperature, pH, composition of the medium and the nature of the fermentation vessel has been demonstrated /1/. A typical formation rate of DMS during fermentation is 20-60 ng DMS/min per g wet yeast grown on wort.

2.1.3 DMS stripping by CO2 during fermentation

Initially DMS concentration will drop during the fermentation process due to stripping with CO_2 from fermentation. At later stages an increase due to the formation from DMSO is typically observed /1/.

3 Conclusion

Kinetic and equilibrium data relating to the DMS formation and removal from beer wort has been extracted from scientific studies.

The data shows some variation in the values but provides a catalogue for choosing reasonable and relevant values for parameters to be used in numeric models of the DMS concentration.

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