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Decomposition kinetics of dimethyl sulphide

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Dimethyl sulphide is a well characterized off-flavour in the brewing industry. The thermal re-creation of dimethyl sulphide by the decomposition of dimethyl sulphide precursor in standardized wort is measured using pressure-controlled boiling processes at different temperatures. The results are used for the calculation of decomposition speed constants and Arrhenius activation energies. Using these data the re-creation of dimethyl sulphide during the wort production processes can be calculated and thereby optimized. Copyright © 2014 The Institute of Brewing & Distilling

Keywords: dimethyl sulphide; dimethyl sulphide precursor; wort; wort quality

Introduction

Dimethyl sulphide (DMS) is an important flavour for the validation of wort quality *(1)* and the vaporization of dimethyl sulphide is of great interest for validation of the boiling process *(2,3)*. The known precursors of DMS are *S*-methylmethionine (SMM) and dimethyl sulfoxide (DMSO), both of which originate from malt *(4)*. SMM is cleaved to DMS by heating, whereas DMSO is reduced to DMS by yeast metabolism during fermentation *(5,6)*.

Two other possible sources of DMS may be noted. DMS has been found in infected wort *(7)*. However, its impact is negligible as this cannot be responsible for the relative consistency of DMS levels in products from different breweries. In addition, DMS has been found in hops, but not at a level sufficient to contribute to the flavour of the final product, particularly since much of the DMS in hops would be expected to be lost by boiling *(8)*.

The determinant of the beer DMS level has to be found in SMM *(9)*. The kinetics of decomposition is dependent to the process parameters of temperature, time, pH value and extract. However, some data are known about the contribution of temperature to decomposition kinetics of DMS. The present study was to investigate the re-creation of DMS over a broader temperature range by a new method of thermal decomposition of SMM.

Recently, different methods and techniques have been used to determine the kinetics needed for the decomposition of SMM *(6,10–13)*. These studies suggest the heating of a defined volume of a liquid sample. Homogenous heating of the whole liquid is challenging because the required heat flow has to be transported along a temperature gradient. Thus, the heated liquid samples have on the average over the total volume the defined process temperature, but there is always a distribution from overheated to sub-cooled areas. In order to minimize the width of the distribution, the relation of the heated surface to the volume of the liquid samples can be optimized. Increasing the volume of the heated surfaces reduces the homogeneity of the liquid phase owing to raised interactions between surface and liquid.

In this work, pressure-controlled boiling processes at different temperatures were used to reduce the width of the heat distribution. Compared with the classical heat transfer procedures, pressure-controlled boiling processes take advantage of the steam bubbles rising through the liquid and the limitation of heat spots caused by the boiling temperature used *(9)*. As a consequence the heat distribution in the boiling wort is optimized.

Basics

The threshold of DMS in beer is in the range from 30 to 60 μg/L *(14–16)*; furthermore the odour threshold value of DMS in water is 0.3 μg/L *(17)*. It is recommended that the sum of DMS and SMM at the beginning of fermentation should be below 100–120 μg/L *(18)*.

By cleaving the precursor SMM during heating, DMS is recreated during the wort production. This process can be modelled as a first-order reaction as follows *(6,13)*:

$$c(t) = c_0 \cdot e^{-k.t} \tag{1}$$

where the parameter *c*(*t*) is the time *t*-dependent concentration of SMM and c_0 is the initial concentration of SMM. The parameter *k* describes the temperature *T*-dependent reaction speed. Its temperature dependence can be calculated using the following equation:

$$k(T) = k_0 \cdot e^{-\frac{E_A}{R \cdot T}} \tag{2}$$

where the parameter E_A is the activation energy and the parameter *R* is the universal gas constant. The activation energy E_A has to be parameterized by measuring the temperature-dependent decomposition of SMM.

The method is based on the pressure dependent boiling of wort, which is produced industrially from barley. Accordingly,

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the thermodynamic behaviour of a boiling wort is considered to be comparable to the thermodynamic behaviour of water. The pressure range varies from an atmospheric pressure of about 1 bar (the resulting measured boiling temperature is 98.5 °C) to a low pressure of 0.844 bar (the resulting measured boiling temperature is 80.0 °C). In this setup, SMM is degraded in a temperature-dependent manner. After finishing the single experiments, the overall evaporation was measured gravimetrically. The initial and the final concentrations of SMM were measured. In addition, the process time was monitored and thereby the temperature-dependent reaction speed was calculated.

Experimental

The kinetics for the decomposition of SMM are dependent on the process parameters temperature, time, pH value and extract. The present study focused on the function of temperature and time. The parameters for pH value and extract were used according to brewing standards. The experiments of the decomposition of SMM were performed at temperatures of 80, 85, 90, 95, 97 and 98.5 °C.

The experimental setup consisted of a rotation evaporator. The evaporator had a rotating glass flask in a water bath for heating and vaporization of the boiling wort. In addition, there was a water-cooled glass flask for collection of the condensation of the resulting vapour. For maintaining and controlling the different pressures, a self-adjusting vacuum pump was installed. The accuracy of the pressure maintenance was 1 mbar.

Preparation

First, a volume of industrial standard wort was boiled in the evaporator at 0.044 bar and freed of any volatile DMS. In the next step, the wort was fixed to an extract of 12% and a pH value of 5.2. The wort (500 mL) was placed into an experimental glass flask and the heating process to the boiling temperature was initiated. Close to the boiling temperature, a blank sample was taken and the mass was gravimetrically measured, reflecting the starting point of the experiment. After the pressure-dependent boiling time the experiment was stopped (the boiling times varied from 0.6 to 2 h). The overall evaporation was measured by a second weighing, followed by a re-dilution of the wort. The wort was cooled and a second sample was taken. The samples were prepared for SMM and analysed by gas chromatograph *(19)*.

For the calculation of the temperature- and time-dependent decomposition constants k the following equation, based on eqn (1), was used:

$$k(T) = -\frac{\ln c(t_2) - \ln(t_1)}{t_2 - t_1} \tag{3}$$

For calculating the activation energy E_A the following equation was used:

$$\frac{E_A}{R} = \frac{\ln k(T_2) - \ln k(T_1)}{\frac{1}{T_2} - \frac{1}{T_1}} \tag{4}$$

Using the Arrhenius equation the pre-exponential parameter could be calculated for different temperatures:

$$k_0 = e^{\ln k(T_1) + \frac{E_A}{R \cdot T_1}} \tag{5}$$

In order to measure different temperature-dependent changes in DMS, it was possible to formulate and parameterize the complete equation that describes and predicts the decomposition of SMM.

Results and discussion

The measured time-dependent speed constants and their confidence intervals (95%) are summarized in Table 1.

These results and cited literature data are shown in Fig. 1 *(10–13)*. A comparison between the different values and their associated confidences (95%) shows that the measured values are lower. The differences can be caused by the more accurate determination method using a defined and constant boiling pressure at different temperatures.

The activation energy E_A can be determined by using equation (4) or by a logarithmic drawing of the single decomposition constants against the temperature. The slope of the line displays the activation energy E_A.

$$E_A = (186 \pm 12) \cdot \frac{\text{kJ}}{\text{mol}} \tag{6}$$

Furthermore, the pre-exponential parameter k_0 can be calculated using eqn (5):

$$k_0 = (4 \pm 0.3) \cdot 10^{24} \cdot \frac{1}{\text{min}} \tag{7}$$

Using the activation energy and the pre-exponential parameter, the Arrhenius equations can be parameterized and used for interpolation of speed constants. Applying eqn (1), the creation of DMS during wort production can be calculated. In particular, the wort boiling process or the whirlpool can be calculated in regard to the required time for an extensive SMM decomposition. In accordance with previous reports, the half-life of SMM at 98.5 °C is 30.5 min *(6)*.

Summary and perspectives

The decomposition speed of SMM to DMS is strongly dependent on temperature. A new determination method was formulated using a defined pressure for wort boiling below atmospheric conditions. The advantage of this method, compared with classical heat transfer procedures, is based on an optimized heat distribution in the boiling wort.

The impact of different temperatures on the decomposition dynamics/kinetics of SMM is reported in this paper. It will be of interest to investigate the impact of pH value and extract in future studies. Notably, the pH value is considered to strongly influence the mechanism of decomposition *(10,18)*. On the one

Table 1. Overview of the measured decomposition constants

Overview of decomposition of *S*-methylmethionine

Temperature (°C)	Decomposition constants (1/min)	Confidence (95%) (1/min)
80.0	0.0009	0.0003
85.0	0.0015	0.0003
90.0	0.0039	0.0009
95.0	0.0100	0.0010
97.0	0.0146	0.0017
98.5	0.0227	0.0024

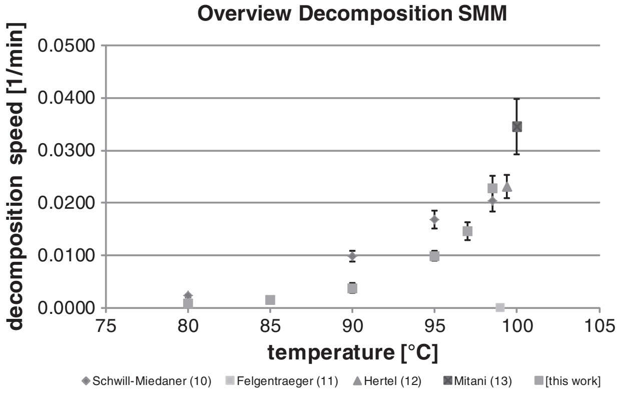

Figure 1. Overview of measured values and literature data *(10–13)*.

hand, a high pH value affects the intramolecular substitution of the SMM-carboxyl unit, while on the other hand a low pH value promotes the nucleophile substitution of the sulphur unit by water *(20)*.

In summary, the kinetics of the SMM decomposition, together with the volatility of DMS, can be used to calculate and predict the DMS content in a wort, which constitutes a useful tool for the optimization of the wort production.

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