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Thermodynamic Validation of Wort Boiling Systems

Regarding evaporation and formation of DMS wort boiling is calculable. Particularly the needed evaporation heat during the boiling step is predictable. Every form of boiling can be put down to two principles: The conventional direct heating of the wort kettle is called kettle boil while the use of a calandria (internal or external boiler) operates with a flash evaporation.

This article compares both principles in terms of separate evaporation and formation of DMS (comparison 1) as well as simultaneous evaporation and formation of DMS (comparison 2) via validated calculations. For both comparisons it will be verified whether flash evaporation is better, equal or worse concerning the decrease of DMS compared to a kettle boil.

Descriptors: boiling, energy, DMS, DMSP, wort, vaporisation

1 Introduction

An efficient evaporation of DMS is always a very important subject at any time due to the needed energy consumption. Procedural insights into different evaporation behaviour and its energy demand are known and disclosed [2, 3]. The literature concludes: Processes which perform a flash evaporation by releasing wort from a higher pressure to a lower pressure (internal or external boiler) are less efficient than the conventional, directly heated vessel (kettle boil). Important questions of detail are to be answered regarding the particular characteristics of every boiling system (temperature, process guidance, prevalent fugacity etc.) by its own.

These reflections will be extended by the following remarks. For the first time not only the evaporation of different boilers is considered but also the heat-holding and according DMSP cleavage taking place with different boilers is regarded. Depending on the process parameters this leads to additional awareness.

This article compares both principles in terms of separate evaporation and formation of DMS as well as simultaneous evaporation and formation of DMS via validated calculations. The separate evaporation and formation is called comparison 1, the simultaneous evaporation and formation is called comparison 2.

In order to compare both boiling principles in respect of the separate or simultaneous evaporation and formation during the boiling process and thus under real conditions enabling their ranking special equations have to be formulated. These equations have to regard a decrease of the DMS content via evaporation and/or formation within an infinitesimal period, particularly. That's done by differential equations which will be explained and presented.

The deducted equations can thus be used to predict the decrease of any aroma compound in wort. Only thermodynamic and kinetic compound data (data on chemical media) have to be adjusted accordingly. Furthermore the different forms of formation kinetics have to be regarded. Reactions contributing are zero-order reactions as well as more complex second-order reactions and reactions of disrupted order.

For the brewing industry dimethyl sulphide (DMS) as an aroma compound is the leading one for evaluating wort boiling. That means the indice (i) stands for the solute DMS, furthermore the indice (j) symbolizes water as the solvent. All of the following remarks and information refer to these components.

2 Basics Comparison 1

DMS content in wort is determined by evaporation and formation. Both processes are calculable and the following equations have been validated by several authors with independent experiments [1, 2, 3, 4].

The formation happens by cleavage of DMSP into DMS and is given by a decomposition reaction (first order reaction) while cleavage velocity depends on temperature. So, for a kettle boil the differential equation in order to calculate cleavage of DMSP and formation of DMS is as follows [2]:

$$c_{i,1} = c_{i,0} \cdot e^{-k \cdot t_1} \qquad \text{eq. 1}$$

On the left there is DMSP concentration ($c_{i,1}$) at a given instant in time of the (evaporation) process (state 1). The right side shows an Euler Function including parameters rate constant (k) and time (t) as exponent multiplicated with the initial DMSP content.

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For a flash evaporation the differential equation for calculating of DSMP cleavage and DMS formation is more extensive. This is due to only a certain part of the entire wort volume (L) being physically in the boiler (F) at that considered instant of time (F). As in the boiler the temperatures are higher, formation velocity in the boiler (k_A) is higher than the formation velocity in the kettle (k) itself. Thus, the period of time for this particular enhanced formation is given by the time (u). Besides the volumes‘ ratio also the streams of vapour ($\dot{D}$) and wort ($\dot{L}$) within the boiler have to be regarded by the equation.

Based on equation 1 the new equation is given as follows:

$$c_{i,g}(t) = c_{i,0} \cdot \left(\frac{L-F}{L} \cdot e^{-k \cdot u} + \frac{F}{L} \cdot \frac{\dot{L}}{\dot{L}-\dot{D}} \cdot e^{-k_A \cdot u} \right)^{\frac{t}{u}} \qquad \text{eq. 2}$$

For solving both equations the temperature dependent rate constant k has to be determined. Different data is disclosed in literature enabling to predict the formation.

Evaporation of free DMS is a thermodynamic separation process. In more descriptive words this means that more DMS molecules will evaporate compared to water molecules. Hence, the DMS content in the remaining liquid will decrease. DMS’ behaviour in water during phase change is described by fugacity (K). (K) is also known as separation factor and refers to the different concentrations of a considered component in a liquid and the corresponding vapour phase as follows:

$$K_i = \frac{y_i}{x_i} \qquad \text{eq. 3}$$

DMS fugacity in water is needed in order to calculate the evaporation and known for a wide range of different temperatures for the currently considered concentration area of infinite solution which can be found in literature [1, 2, 3].

Thus, in terms of evaporation of DMS from water kettle boiling can be calculated as follows:

$$\frac{dx_i}{dt} = \frac{-\dot{D} \cdot x_i \cdot (K_i - 1)}{L} \qquad \text{eq. 4}$$

On the left the modification in DMS content (dx_i) depending on process time (dt) is indicated. The right side contains vapour stream ($\dot{D}$), wort volume (L), concentration (x_i) and fugacity (K_i).

For calculating a calandria the parameters of flash evaporation have to be regarded additionally, as a closed boil is performed in contrast to a kettle boil. Superheated wort is relieved while the extent of flash evaporation depends on the difference between boiler temperature and the component’s boiling temperature at the given process pressure. In order to quantify the difference between kettle boil and flash evaporation the following equation invents a correction factor (ω_i) which can be calculated either via the mentioned energy difference or via balancing volume or particle stream through the boiler:

$$\frac{dx_i}{dt} = \frac{-\dot{D} \cdot x_i \cdot (\omega_i \cdot K_i - 1)}{L} \qquad \text{eq. 5}$$

Equations 4 and 5 can either be solved analytically using an integration factor or numerically.

3 Basics Comparison 2

In case of a kettle boil the simultaneous evaporation and formation of DMS are calculated based on a mass balance. The mass balance for the present situation is as follows:

$$L_0 \cdot x_{i,0} = L_1 \cdot x_{i,1} + (L_0 - L_1) \cdot y_{i,1} + (L_0 \cdot c_{i,0} - L_1 \cdot c_{i,1}) \qquad \text{eq. 6}$$

On the left side there is the product of amount of liquid L_0 and aroma compound’s concentration ($x_{i,0}$). The right side contains the amount of liquid (L_1) and the aroma compound’s concentration ($x_{i,1}$) at process moment 1. The difference in the liquid amounts is the generated steam/vapour ($L_0 - L_1 = D_1$) with the corresponding aroma compound’s concentration ($y_{i,1}$). Furthermore the formed amount of DMS ($c_{i,0}$, $c_{i',1}$) including the effect of enrichment via evaporation (L_0, L_1) is regarded.

In order to transfer the mass balance into a differential equation for simultaneous evaporation and formation the following terms have to be inserted as shown below:

$$dL = L_0 - L_1 \qquad \text{eq. 7}$$

This term describes the change in liquid’s amount during the process. If the change is considered all over the process moments Beginning (0) and End (1), the change in liquid’s amount conforms to the over-all evaporation.

$$dx = x_{i,0} - x_{i,1} \qquad \text{eq. 8}$$

This term describes the change in aroma compound’s concentration from process moment Beginning (0) to End (1).

$$\frac{dx_i}{dL} = \frac{x_i \cdot (K_i - 1)}{L} \qquad \text{eq. 9}$$

This equation covers the change in aroma compound’s concentration as a function of the performed over-all evaporation between process moment Beginning (0) and End (1) (view basics comparison 1).

$$\frac{dc_i}{dt} = k \cdot c_{i,0} \cdot e^{-k \cdot t} \qquad \text{eq. 10}$$

This equation covers the time dependent formation of aroma compound via cleavage of precursor from process moment Beginning (0) to End (1) (view basics comparison 1).

Putting the shown equations together leads to a term enabling calculation of time dependent change in aroma compound’s concentration caused by evaporation and formation:

$$L_0 \cdot dx_i = dL \cdot (K_i \cdot x_i - x_i - c_{i,0}) - L_0 \cdot dc_i \qquad \text{eq. 11}$$

Additionally the steam/vapour stream ($\dot{D}$) is considered as the change in liquid’s amount over the observed time:

$$\dot{D} = -\frac{dL}{dt} \qquad \text{eq. 12}$$

Thus the final equation for calculating and predicting an aroma compound’s simultaneous evaporation and formation during a kettle boil is given by the following:

$$\frac{dx_i}{dt} = -\frac{\dot{D}}{L_0} \cdot \left(K_i \cdot x_i - x_i - c_{i,0}\right) + \cdot k \cdot c_{i,0} \cdot e^{-k \cdot t} \qquad \text{eq. 13}$$

The simultaneous evaporation and formation of DMS in case of flash evaporation differs from a kettle boil in the fact that due to the different thermodynamic conditions depleting of DMS within the calandria (internal/external boilers) is different from the depleting in the kettle itself.

Nevertheless flash evaporation is also calculated based on a mass balance which refers to equation 6 in terms of its structure:

$$L_0 \cdot x_0 = L_1\, x_{i,1} + (L_0 - L_1)\, y_{i,\,ent,\,1} + (L_0 \cdot c_{i,\,0} - L_1 \cdot c_{i,\,g,\,1}) \qquad \text{eq. 14}$$

Differing from kettle boil this equation contains quantities ($y_{i,ent,1}$) and ($c_{i,g,1}$) covering the impacts of the thermodynamic differences between flash evaporation and kettle boil.

In order to transfer the mass balance into a differential equation for simultaneous evaporation and formation equations 7, 8 and 12 as shown above have to be used and the equations shown in basics comparison 1 have to be inserted leading to the following equation:

$$\frac{dx_i}{dL} = \frac{x_i \cdot (\omega_i \cdot K_i - 1)}{L} \qquad \text{eq. 15}$$

Furthermore the particular conditions of a flash evaporation have to be regarded which is done via the correction factor (ω_i). This factor can be derived and calculated from the described energy difference or from a balance of volume or particle flow through the boiler.

$$c_{i,g}(t) = c_{i,0} \cdot \left(\frac{L-F}{L} \cdot e^{-k \cdot u} + \frac{F}{L} \cdot \frac{\dot{L}}{\dot{L} - \dot{D}} \cdot e^{-k_A \cdot u}\right)^{\frac{t}{u}} \qquad \text{eq. 16}$$

Is equation 16 inserted accordingly the formation parameters are covered, too, so that the final differential equation 17 as shown below can be used to predict DMS' evaporation and formation during a flash evaporation:

$$\frac{dx_i}{dt} = -\frac{\dot{D}}{L_0} \cdot \left(\omega_i \cdot K_i \cdot x_i - x_i - c_{i,0}\right) + n_{i,g}(t) \qquad \text{eq. 17}$$

Term ($n_{i,g}$(t)) summarizes the differential equation contributing the formation of the regarded aroma compound.

Both equations 13 and 17 can be solved analytically via an integration factor or numerically.

The equations describing the flash evaporation differ from the ones for the kettle boil mainly by the appearance of pump around velocity of wort through the boiler (mass stream, turn rate) as parameter of influence which is not existent in terms of a kettle boil. Particularly boilers operating with a forced flow have to be pointed out as with them a variation of pump around velocity is enabled while having a constant heating performance.

In case of high volume stream of wort pumped through the calandria its temperature will be near 100 °C. If a very low volume flow of wort is pumped through the calandria it will show a higher temperature of 101 to 106 °C. Due to the low volume flow the heat provided by fresh steam is entirely transferred into a low volume of wort and thus temperature is considerably increased. In contrast, a very high volume flow of wort leads to lower wort temperatures as the heat provided by fresh steam is transferred to a high wort volume. Hence, the variation of pump around velocity and thus volume flow causes changed boiling temperatures and therefore different wort treating.

This article compares both principles in terms of separate evaporation and formation of DMS (comparison 1) as well as simultaneous evaporation and formation of DMS (comparison 2) via validated calculations. In the next chapter it will be verified for both comparisons whether flash evaporation is better, equal or worse concerning the decrease of DMS compared to a kettle boil.

4 Results and Discussion Comparison 1

It is possible to calculate evaporation of DMS from wort for both flash evaporation and kettle boil using equation 1–5. Therefore the results are shown in figure 1.

It is obvious, that evaporation of DMS is more efficient with kettle boiling compared to the flash evaporation. Already at an early state of kettle boiling DMS content can be reduced under the threshold of 100 µg/l. Flash evaporation needs more time to reach that particular threshold and thus is more energy intense.

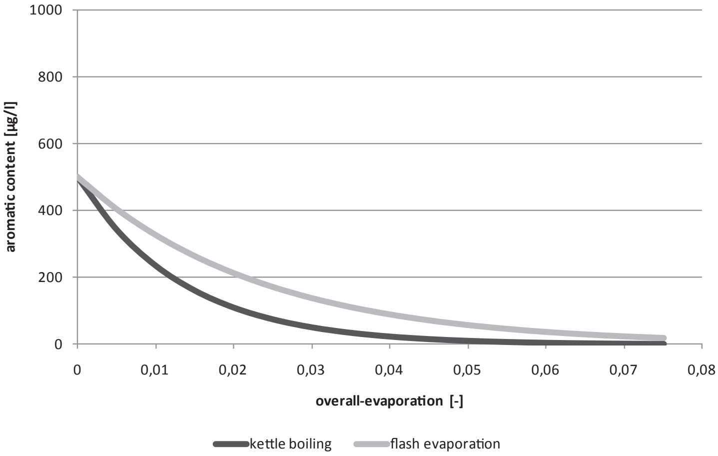

Fig. 1 **Vaporization with Kettle Boil and Flash Evaporation; Comparison 1 (process' conditions view Table 1)**

Table 1 **Process' Conditions Figure 1**

DMS [µg/l]	500
DMSP [µg/l]	0
Evaporation Velocity [GV/h]	0,05
Pump Around Velocity [turns/h]	5

For both boiling principles the formation of DMS via DMSP-decomposition is of particular interest wherefore the results are shown in figure 2.

For the flash evaporation DMSP content responsible for DMS formation decreases faster compared to kettle boil. This is due to

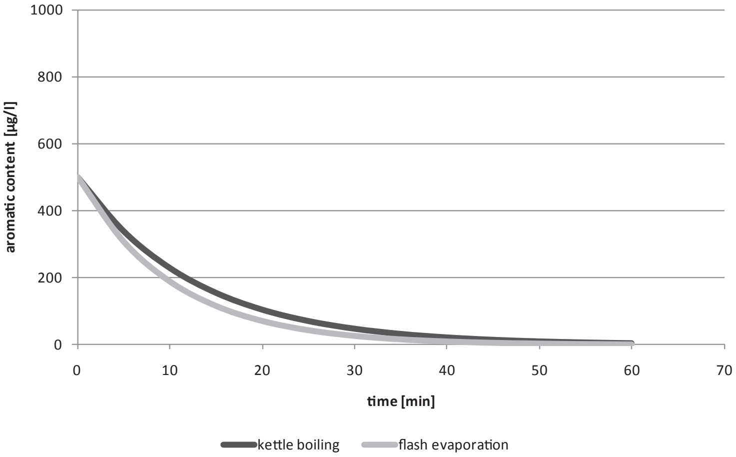

Fig. 2 Formation with Kettle Boil and Flash Evaporation; Comparison 1 (process' conditions view Table 2)

Table 2 Process' Conditions Figure 2

DMS [µg/l]	0
DMSP [µg/l]	500
Evaporation Velocity [GV/h]	0,05
Pump Around Velocity [turns/h]	5

calandria's temperature profile. Within the boiler the temperature is higher (101–106 °C) as anywhere during a kettle boil and subsequently the formation of DMS is enhanced – a positive aspect as only formed and thus free DMS can be evaporated.

For flash evaporation adjustment and regulation of the wort's temperature leaving the boiler is of particular interest. Constant heating steam temperature and supply assumed the temperature within the boiler varies depending on the mass stream of wort. Is the latter high the temperature will be rather low compared to a low wort flow.

5 Results and Discussion Comparison 2

For both flash evaporation and kettle boil simultaneous evaporation and formation can be calculated and predicted via the equation 6–17. The main influence was found to be the pump around velocity (turn rate). Within the following paragraphs the results of exemplary calculations for an unmodified kettle boil and for a flash evaporation with different pump around velocities will be compared to each other.

Figure 3 shows the comparison of flash evaporation and kettle boil for a given evaporation (over all evaporation: 5 % per hour) while the calandria is run with a rather low pump around velocity (5 times the kettle volume per hour):

It can be seen that the DMS reduction (reduction means simultaneous formation and evaporation) is worse for flash evaporation compared to kettle boil. After all, formation has to be better for the calandria due to higher temperatures but the worsen evaporation due to the flash evaporation prevails the improved formation.

Figure 4 shows the process for a very high volume flow (20 times the kettle volume per hour) pumped through the calandria while keeping the other process parameters:

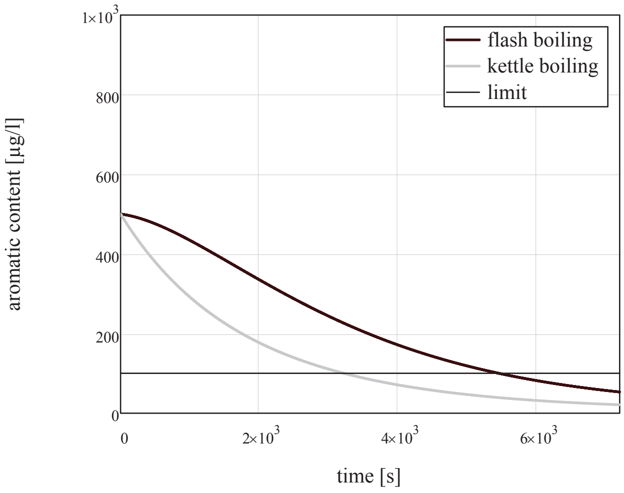

Fig. 3 Decrease with Kettle Boil and Flash Evaporation; Comparison 2 (process' conditions view Table 3)

Table 3 Process' Conditions Figure 3

DMS [µg/l]	500
DMSP [µg/l]	500
Evaporation Velocity [GV/h]	0,05
Pump Around Velocity [turns/h]	5

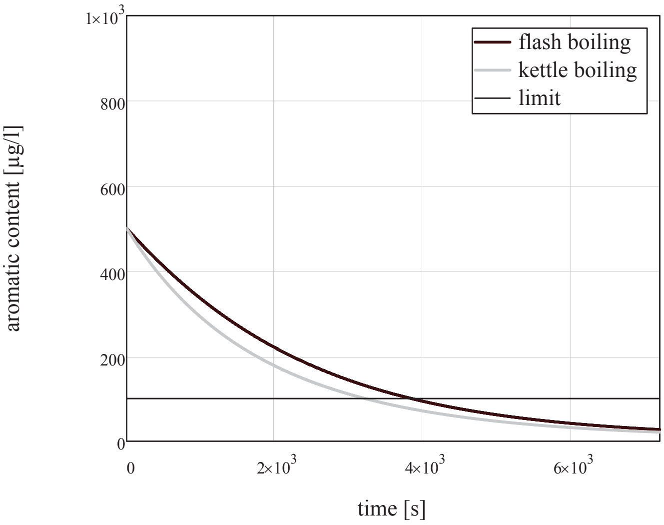

Fig. 4 Decrease with Kettle Boil and Flash Evaporation; Comparison 2 (process' conditions view Table 4)

Table 4 Process' Conditions Figure 4

DMS [µg/l]	500
DMSP [µg/l]	500
Evaporation Velocity [GV/h]	0,05
Pump Around Velocity [turns/h]	20

It can be seen that the two curves for the different boiling principles converge strongly. Temperature within the calandria is now lower compared to the previous example but the evaporation via flash evaporation is improved.

Comparing the two results concerning the initial question whether flash evaporation is better, equal or worse in terms of DMS reduction compared to the kettle boil leads to the following statement: A high turn rate improves DMS evaporation due to an optimized evaporation. Still the optimization prevails the worsened formation which leads to both principles operating rather on a par. The optimized process goes together with reduced energy cost due to a lower evaporation but higher energy cost for the pump around. For a calculation of overall savings both have to be regarded.

Flash evaporation stands for the principle of boiling via calandria (internal/external boiler) as both of them perform a flash evaporation. Calandria which do not operate with forced flows (internal boilers) can easily be optimized by retrofit of a pump. Then the variation of pump around velocity as new influencing parameter enables the mentioned optimization.

Concluding the results' part some simplifications are worth to be pointed out as they might occur for both principles and the corresponding calculations. These simplifications are derived from the ratio between formation and evaporation. Depending on how strong or weak the velocities of formation and evaporation differ from each other three borderline cases can be remarked:

Case A: Evaporation Prevails Formation

The following applies:

$$\frac{dx_i}{dt} >> \frac{dc_i}{dt} \qquad \text{eq. 18}$$

For this particular case the process can be described only with equations 4 (kettle boil) and 10 (flash evaporation) while neglecting the formation.

Case B: Evaporation is Up To Formation

The following applies:

$$\frac{dx_i}{dt} = \frac{dc_i}{dt} \qquad \text{eq. 19}$$

In this particular case no concentration change will occur throughout the process. Thus no calculation for this steady-state has to be carried out.

Case C: Evaporation is Inferior to Formation

The following applies:

$$\frac{dx_i}{dt} << \frac{dc_i}{dt} \qquad \text{eq. 20}$$

In this particular case the considered compound's fugacity (DMS) out of the solvent (water) is very low. The dominating action is the formation of compound (i), so that the influence on concentration can be described with good approximation by merely regarding the increase caused by the formation. Then only the formation has to be calculated according to equation 1 for a kettle boil or rather equation 2 for a flash evaporation.

6 Summary and Perspectives

Considering evaporation and formation of DMS for separately both kettle boil and flash evaporation delivers interesting results. A first answer to the initial question whether flash evaporation is better, equal or worse in term of DMS reduction in comparison to a kettle boil is that every system is better than the other but only regarding one particular operation.

Interpreting only this result it has to be stated that a possible domination strongly depends on particular process conditions. Thus, a certain potential for optimization can be suspected for nearly every brewery equipped with internal or external boiler.

This potential is clarified calculating the simultaneous evaporation and formation of DMS for both kettle boil and flash evaporation. A second answer to the initial question is given:

With equal and continuous evaporation rates at higher turn rates of wort (higher pump around velocity) flash evaporation approaches the kettle boil. Both systems are then rather on par. For breweries performing low wort turn rates a possible optimization strategy is to increase wort volume flow through the boiler while keeping the other parameters. This will lead to a reduction of the needed overall evaporation. Nevertheless it is recommended to have the entire wort preparation calculated prior to the modification due to the numerous actions and reactions that have to be regarded besides cleavage of DMSP and evaporation of DMS.

In particular, it has to be stated that shown calculations can be simplified with different ratios of DMS to DMSP. Depending on the simplification and the investigated boiling principle the shown equations for merely regarding evaporation of formation have to be considered.

These statements of comparison 2 add to the remarks of comparison 1. However, it has to be mentioned additionally that not only the turn rate (pump around velocity) but also the ratio of evaporation rate to turn rate has to be attended. The latter gives another huge potential for optimization by variation throughout the entire boiling process which will be subject to the following article.

7 Literature

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