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Article *in* BrewingScience · July 2008

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D. P. De Schutter, M.-R. De Meester, D. Saison, F. Delvaux, G. Derdelinckx, J.-M. Rock, H. Neven and F. R. Delvaux

Characterization and Quantification of Thermal Load during Wort Boiling

Thermal load is often considered as a vague and obscure burden for brewers. In order to clarify the concept of thermal load, this paper aimed to characterize and quantify thermal load during wort boiling. Thermal processing of wort was found to cause the accumulation of Maillard intermediates, which might lead to the generation of off-flavours during beer ageing. The amount of intermediates could be quantified in terms of HMF-equivalents. A part of these intermediates was reduced by yeast during fermentation. The remaining non-reducible intermediates in beer can therefore be considered as the chemical memory of thermal load on wort.

In order to quantify thermal load in wort, the kinetic behaviour was examined and a pseudo 0th order kinetics was established. The quantification of thermal load was then captured in a formula, which consisted of two terms. The first is a specific wort term, which evaluates the susceptibility of a particular wort to applied thermal load. This tool could be used by every brewer to predict the effect of boiling process changes on the wort. In addition, a boiling system term was created. Although the latter term is highly theoretical, it provides insights in the impact of differences in boiling intensity on thermal load of wort.

Descriptors: wort boiling, thermal load, TBA, HMF, Maillard reaction, Maillard intermediates

1   Introduction

Thermal load in the brewhouse is known for a long time as one of the main factors causing flavour instability of beer [1, 2]. Accordingly, many new wort boiling systems have been developed that tried to diminish wort thermal stress [3] besides an overall reduction in evaporation rate and consequently, energy savings. These developments were inspired by many different strategies, like forced convection [4], wort boiling with thin-film evaporation [5], dynamic low-pressure boiling [6, 7], gentle boiling with flash evaporation [8, 9], and vacuum boiling [10]. Without any doubt, energy savings are the main driving factor for every innovation arising in the field of boiling technology. However, reduction of thermal load remains an asset and is highly desired by brewers today.

At present, research concerning the boiling process is mainly focused on volatile flavour compounds and how they are evaporated [11, 12]. Recently, *Hertel* and coworkers delivered excellent insights into the physics of evaporation [13] and the evaporation efficiency of various boiling systems [14]. For some flavour compounds created during the wort boiling process, the relationship with flavour stability has indeed been established. The famous (E)-2-nonenal, by *Jamieson* and *Van Gheluwe* [15] first linked to the cardboard flavour, is known to form imine-adducts in the boiling kettle. In this imine linkage it is protected against yeast reduction and can subsequently be released during beer aging [16, 17]. In high-alcohol specialty beers, furfuryl ethyl ether is known as an important staling flavour as well [18] and its formation is highly influenced by the boiling process, where its precursors furfuryl alcohol and furfural are generated [19]. However, most other flavour compounds have an aldehyde function, which can be reduced by yeast [20]. Common volatile heat load indicators are also known to be reduced during fermentation, like furfural [21] and 5-hydroxymethylfurfural (HMF) [22]. Therefore it does not make much sense to over-investigate the behaviour of all flavour compounds during boiling, except for DMS and other non-reducible potent flavour compounds.

Moreover, in previous work it became clear that no unambiguous relation between volatile compounds and heat load on wort can be established. It was thus concluded that no volatile compound is suitable enough to bear the role of heat load indicator and that rather the non-volatile fraction of wort should be taken into account [23]. This non-volatile fraction comprises intermediates of the Maillard reactions, like Amadori rearrangement products, imines, enaminols, dicarbonyl compounds etc. The presence of these compounds can be measured by the thiobarbituric acid (TBA) method (or TBN/TBI), which was first used by *Grigsby* and *Palamand* [24], and since then widely used to quantify thermal load of wort, without reflecting about the actual chemical meaning of

Authors: Ir. David De Schutter, Ir. Marie-Rose De Meester, Ir. Daan Saison, Dr. Ir. Filip Delvaux, Prof. Dr. Ir. Guy Derdelinckx and Prof. Dr. Ir. Freddy Delvaux: Centre for Malting and Brewing Science, Faculty of Bioscience Engineering, Katholieke Universiteit Leuven, Kasteelpark Arenberg 22, 3001 Heverlee, Belgium;
Jean-Marie Rock, Brasserie d'Orval S.A., 6823 Villers-devant-Orval, Belgium;
Dr. Ir. Hedwig Neven, Brewery Duvel Moortgat N.V., Breendonkdorp 58, 2870 Puurs, Belgium

Tables and Figures see Appendix.

this method. *Schwill-Miedaner* found that the TBA value proceeds following a pseudo 0th order reaction, with an activation energy of 107 kJ/mol [25]. However, this observation and calculation was based on one wort and it was not taken into account that each individual wort might display another activation energy, since the rate of Maillard reactions is highly determined by the concentration of reactants (sugars, amino acids) and the pH [26].

Therefore the objective of this study was to clarify the chemical significance of the TBA value, to explain how the boiling process can influence the TBA-value and to provide a predictive tool that determines the heat load susceptibility of every single kind of wort. This tool could be used to evaluate the impact of changes in the boiling process on the heat load of wort.

2   Materials and methods

2.1   Wort production

Wort production was performed in the pilot scale (5 hl) brewery of the Centre for Malting and Brewing Science (Heverlee, Belgium). An amount of 80 kg milled pilsner malt (Dingemans, Stabroek, Belgium) was added to 220 L of water at 55 °C. The pH was adjusted to 5.5 with lactic acid and the mash was subjected to a rest of 10 min. Next, the temperature was raised to 63 °C (35 min of rest) and the saccharification temperature of 72 °C (20 min). After the saccharification rest, the mash was heated up to 78 °C and subsequently transferred to the lauter tun, in which the separation of spent grains and sweet wort takes place. The filtered sweet wort was collected in the boiling kettle, where it was heated up to 90 °C. At 90 °C, the wort was collected in 1.5 l containers and immediately cooled down to room temperature. Hereafter the containers with sweet wort were frozen at –25 °C. Prior to the boiling experiments, the wort was defrosted; the density (originally 17.2 °P) was adjusted to 12° P with deionised water and the pH was adjusted to the appropriate pH with sulfuric acid (20 %). Where needed sodium hydroxide (20 %) was used to increase the pH. When the effect of wort density was studied, the wort was adjusted to the appropriate density.

2.2   Boiling of wort in sealed pyrex tubes

Pyrex tubes were filled with 25 ml of wort and incubated in a boiling water bath. Each experiment was conducted in duplicate. After holding the samples in the water bath for the predetermined time, they were immediately cooled down on ice and prepared for analysis.

2.3   TBA procedure

The procedure was adapted from *Coghe et al.* [27]. Five ml of a TBA solution (288 mg of thiobarbituric acid in 100 ml acetic acid (90 %)) was added to 10 ml of wort in sealed pyrex tubes (in duplicate). The mixtures were kept in a water bath at 70 °C for 70 minutes. Hereafter the samples were cooled on ice. Absorptions were measured spectrophotometrically at 448 nm, the maximum absorption of the HMF-TBA complex. If necessary, the samples were diluted in order to obtain a value in the linear range of the

spectrophotometer. As blank measurement, untreated wort with TBA solution was measured at the same wavelength. Subsequently, the TBA value was calculated as follows (D = dilution factor):

$$TBA = 10 \text{ x } (D \text{ x } A_{448} - A_{blank})$$

3   Results and discussion

Before developing a method that evaluates the susceptibility of a certain kind of wort to thermal load, it is worthwhile to dig deeper into the Maillard reaction and find out what kind of information the TBA value actually delivers. Therefore the chemical background and the influence of certain wort parameters of the Maillard reaction will be discussed. Then the actual application of the TBA procedure to wort boiling procedures will be calculated and a tool can be created in order to evaluate the impact of different boiling procedures on the thermal load of wort.

3.1   Initial stages of the Maillard reaction

In Figure 1, a schematic is given from the early stages of the Maillard reaction towards the formation of HMF. This furan compound is able to bind TBA, resulting in a chromophore with a maximal absorption at 448 nm. In Figure 1, glucose is taken as an example, although other reducing sugars can also be involved in this reaction. The Maillard reaction initiates when a reducing sugar in open chain form and an amino compound in non-protonated form condense to an imine, by a nucleophilic addition to the carbonyl group of the reducing sugar [26]. This initiation is facilitated at high pH values, since the pKa of such amino groups is situated around pH 9. Thus, the Maillard reaction initiation will be retarded at lower pH values and at wort pH the ratio of non-protonated relative to protonated amino acids is about 1/10 000. Once the Maillard reaction is initiated, it will proceed towards the formation of ARP. On the other hand, all subsequent reactions, like the protonation of the Schiff base, the formation of the enaminol and the generation of the Amadori Rearrangement Product (ARP), can be either acid or base catalyzed. Nevertheless, pH has a tremendous impact on the direction of the Maillard reaction pathway starting from ARP. The ARP can undergo 2,3-enolization and react towards 1-deoxyglucosone and further to furanones (not show in Fig. 1), or the ARP can lead to the formation of 3-deoxyglucosone via 1,2-enolization. Interestingly, the formation of 3-deoxyglucosone (3-DG) is not really affected by pH, while the formation of 1-deoxyglucosone decreases strongly at lower pH [26]. After cyclization of 3-DG and subsequent dehydration reactions, HMF is formed.

Since the initial stages of the Maillard reaction pathway comprise a cascade of reactions, it is not uncommon to encounter all intermediates together in wort and beer. Moreover, *Martins* and *Van Boekel* [26] observed a steady build up of ARPs during heating of glucose in presence of glycine at pH values 4.8 and 5.5. Since these pH values situate themselves around the wort boiling pH, ARPs will build up in wort as well. When these ARPs are present in increasing concentrations, all the downstream reactions will be accelerated, resulting in increasing amounts of reaction products. The authors indeed encountered an ever increasing formation rate of furfural and furfuryl alcohol with boiling time during 8 hours of boiling [23]. Thus, it might be expected that after boiling the

amount of Maillard reaction intermediates as well as end products will be present in higher levels.

3.2   The meaning of TBA value

The peculiar and interesting feature of the TBA procedure is as follows. Under strong acidic conditions (pH~2), the initiation of the Maillard reaction will be largely inhibited, especially at 70 °C. The already present intermediates will undergo acid-catalyzed reactions and due to the inhibition of the 2,3-enolization pathway towards 1-deoxyglucosone, the reactants will mainly follow the 1,2-enolization route towards 3-DG and further to HMF. After binding with TBA, the total amount of bound HMF can be measured at 448 nm. However, it must be noted that the yield of this procedure is not 100 % [28]. There will still be some intermediates left in the wort. Nevertheless, the reproducibility of the procedure is high and the TBA method gives a good impression of the Maillard intermediates in wort. Correspondingly, the TBA procedure is widely used in the brewing world.

The TBA-value can also be considered as the HMF-potential [23] of wort, analogous to the (E)-2-nonenal potential proposed by *Drost et al.* [29]. In other words, during the TBA procedure all the intermediates that are able to be converted to HMF are taken into account, going from Amadori compounds to dicarbonyl compounds. In order to have an idea of the quantitative relevance of the TBA-value in terms of HMF equivalents, HMF was added to wort in increasing amounts by the standard addition method. The supplemented wort samples were subjected to the TBA procedure and the TBA values were expressed in function of the added HMF as shown in Figure 2. The slope of the graphic indicates the increase of 0.59 TBA units per ppm HMF added to the wort. In other words, an increase of 1 TBA unit during boiling is equal to 1.7 ppm equivalents of HMF and precursor compounds.

Brewer's yeast was able to reduce some of the TBA-reactive compounds during fermentation, leading to a decreased TBA value in fresh beer. In Figure 3, the TBA values of 2 different treated worts and their respective beers are depicted. The first wort was boiled for 1 hour; the second wort was boiled for 3 hours. Remarkably, the TBA value of the first wort decreased with only 9 units during fermentation, while the other TBA value decreased with 17 units. Accordingly, it can be stated that when the boiling process proceeded, the amount of reducible Maillard intermediates increased more than the non-reducible Maillard intermediates. Nevertheless, the absolute amount of non-reducible Maillard intermediates remained higher in the beer with the highest thermal load. It is already known that yeast is able to reduce some dicarbonyl compounds, like methylglyoxal and 3-DG [30] or HMF [22]. Presumably, the 2 non-volatile intermediates arising from the cyclization and dehydration of 3-DG leading to HMF, can be reduced as well since they have a very susceptible aldehyde group (Fig. 4).

3.3   Influence of pH and density

In order to evaluate whether wort pH plays a crucial role in the development of Maillard reactive intermediates during boiling, wort ranging from pH 2 until pH 10 was boiled for one hour and the TBA increase (ΔTBA) was measured. The results are depicted

in Figure 5. The lowest ΔTBA was obtained in a range between pH 5 and 6.

Although the Maillard reaction initiation is inhibited at lower pH values, the ΔTBA increased with decreasing pH starting from pH 5. Possibly the already present Maillard intermediates (created during malting) reacted towards HMF in a higher yield with decreasing pH. In previous work, a higher furfural (the pentose-derived equivalent of HMF) formation was already observed with decreasing pH [23]. Martins and Van Boekel also observed the inhibition of several other reaction routes of 3-DG at pH values as low as 4.8 [26], which enables the Maillard reactions to proceed towards HMF and equivalent furan compounds with a higher yield. Instead, a serious increase was observed with increasing pH above pH 7. This was no surprise, as the Maillard initiation is greatly enhanced at pH values around the pKa of the amino groups.

Schwill-Miedaner observed that the development of Maillard reaction products, as measured by TBA, followed a 0th order reaction [25]. However, this implicates that the reaction proceeds independently of the concentration of reactants. In order to investigate this, lautered wort of 20.6 °P was diluted in a range from 10 °P to 20 °P and subsequently boiled for one hour at pH 5.2. After the boiling process, the ΔTBA was measured for all samples as depicted in Figure 6. Overall, ΔTBA increased with increasing density, suggesting that the formation of Maillard reaction intermediates did not follow a pure 0th order relationship but a pseudo 0th order relationship. It was also suggested by Van Boekel [31] that in some cases the cascade of Maillard reactions can be approximated by a pseudo 0th order reaction, provided it is used as an engineering tool for a specific medium with a unique composition. Creating this engineering tool is one of the aims of this study.

3.4   Kinetics of ΔTBA in relation to the wort composition and boiling system

Thermal energy and consequently, thermal load can be applied in different ways. First, wort can be maintained at a defined temperature for a certain time interval. This will result in a ΔTBA that corresponds to the susceptibility of the wort for that amount of thermal load. However, the added amount of thermal load can also differ with boiling system and boiling intensity. Accordingly, it is crucial to split these two distinct phenomena in different terms when examining the kinetics of ΔTBA.

3.4.1   Wort composition

The pseudo 0th order relation of the creation of TBA-reactive substances means that the TBA value increases linearly with time (dTBA/dt=k). After integration in a certain time interval it can be written as

$$\Delta TBA = k \ x \ \Delta t \tag{1}$$

The constant k is the rate constant of the reaction and is a function of the temperature (Arrhenius formula):

$$k = k_0 \ x \ e^{(-E_a/RT)} \tag{2}$$

In equation 2, k_0 is the rate constant of the reaction, E_a the activation energy of the overall reaction in J/mol, R the universal gas constant (8,314 J/mol.K), and T the temperature in Kelvin. Schwill-Miedaner determined that the activation energy of wort was equal to 107 kJ/mol. However, it might be possible that the activation energy of every single wort differs from another, due to differences in wort composition, pH, and density. Therefore, equation 2 might be considered as the term describing the characteristics of particular wort. In this opinion, k_0 can be considered as the specific wort constant and E_a, the specific wort activation energy.

Although equation 1 & 2 describe very well the wort specifications, it remains a crude approximation since it only considers the wort temperature in the bulk phase (T_0). The temperature at the interface of a heating device and wort is always more elevated than the bulk temperature (Fig. 7). Therefore chemical reactions at the interface will proceed faster, which gives an additional amount of ΔTBA during boiling. It was also observed in previous work that the ΔTBA increased with increasing heating intensity [23]. The temperature of the wort at the interface with the heating device is a function of the steam temperature at the interface steam/stainless steel, conduction through the stainless steel wall, surface area of the heating device, fouling on the heating surface and convection in the wort kettle. The convection also determines the thickness of the boundary layer at elevated temperature. Roughly, the average temperature between wortbulk and wortwall can be taken as T_1 in the extended equation:

$$k = k' + k'' = k_0 \times (e^{(-E_a/RT_0)} + k_1 \times e^{(-E_a/RT_1)}) \tag{3}$$

In equation 3, k_1 is the boiling system constant, taking in consideration the volumetric contribution of the boundary layer at elevated temperature (defined as (thickness of boundary layer x area)/(total wort volume)). The first part ($k_0.e^{(-E_a/RT_0)}$, 4) of the equation is 'the specific wort term'; the second part is 'the boiling system term' ($k_0.k_1.e^{(-E_a/RT_1)}$, 5). Equation 3 takes into account the additional thermal load given by the specifications of the boiling system (due to high steam temperature, size of boiling equipment), regardless of the boiling temperature.

In order to calculate the specific wort term, the procedure of Schwill-Miedaner [25] was used. Pilsner wort was produced on pilot scale, adjusted to 12 °P and subsequently held at 80 °C, 90 °C, 95 °C and 98.5 °C for 75 minutes. The TBA values in function of temperature are depicted in Figure 8 (A). The slope of each temperature corresponded with the k-value for that temperature. In order to calculate the activation energy E_a and k_0, equation 4 had to be solved:

$$\ln k = \ln k_0 - E_a/RT_0 \tag{6}$$

When ln k was plotted against $1/RT_0$ (Fig. 8 B), Ea was the slope of the curve and found to be 79269 J/mol. Ln k_0 is equal to the intercept, resulting in k_0 equal to 3.9E8. The specific wort term could then be written as:

$$k = 3.9E8 \times e^{(-79269(J/mol)/R.T_0)} \tag{7}$$

In order to confirm this result, wort was held at 2 additional temperatures (85 and 92.5 °C) and the results were compared to the predicted values. All measured values were found in the 99 % confidence interval of the predicted values (results not shown).

In order to prove that the wort specific term is unique for every single kind of wort, the obtained results were compared with two distinct industrial worts. Wort was taken from 2 different breweries and subjected to the same procedure as described above. The ln k values were also plotted against 1/RT, as depicted in Figure 9. The specific wort term for Industrial wort I is as follows:

$$k = 4.86E10 \times e^{(-93496(J/mol)/R.T_0)} \tag{8}$$

The specific wort term for Industrial wort II is:

$$k = 9.64E8 \times e^{(-81849(J/mol)/R.T_0)} \tag{9}$$

Clearly Industrial wort I had the highest Ea and consequently the highest temperature dependency. Correspondingly, if the wort temperature rises, the relative ΔTBA increase will be higher in comparison with the standard wort and Industrial wort II. Equally when wort temperature decreases, the ΔTBA decrease will be more pronounced. The reason for this difference could be an increased wort density, a different mashing procedure (amount of amino acids, sugar composition), different malt parameters (such as kilning temperature, as suggested by *Back et al.* [32]) or a different wort pH.

When equation 7 is put into equation 1, a tool is created to predict how a particular kind of wort would react if specific wort boiling parameters were altered that affect boiling time and temperature.

$$\Delta TBA = k' \Delta t = 3.9E8 \times e^{(-79269(J/mol)/R.T_0)} \times \Delta t \tag{10}$$

With equation 10 for example, it is possible to evaluate to what extent the TBA value will increase during the whirlpool rest, or what amount of thermal load is added when boiling at 103 °C. Equally, when boiling at a different temperature than 100 °C, one can calculate the time needed for exact the same thermal load (iso-TBA boiling). In Table 1, a comparison is calculated between different boiling strategies and a reference boil of 60 minutes at 100 °C. In all cases the effect of temperature variation is more pronounced with Industrial wort I, since it has the highest activation energy. Raising the boiling temperature to 103 °C (under pressure) causes a more dramatic ΔTBA increase than in the other worts. However, the same observation counts for a temperature decrease. In Table 1 it can be seen that the effect of wort precooling on the ΔTBA value is more pronounced for the wort with the highest activation energy.

However, if one desires to adjust the steam pressure during the boiling process, the boiling system term needs to be calculated in order to gain insight in the chemical effect of the changes in boiling intensity. This can be done by a theoretical approximation using knowledge concerning heat transfer processes. This will be discussed in the theoretical development of the boiling system term.

3.4.2   Theoretical development of the boiling system term

The boiling intensity can be considered as the total amount of heat transferred during a boiling process. The easiest way to calculate the heat transfer Q is to measure the evaporation rate and multiply this with the evaporation enthalpy.

$$Q = \dot{m} \text{ x } \Delta H_{vap} \tag{11}$$

The amount of evaporated water per second is given by $\dot{m}$, and ΔH_{vap} is the evaporation enthalpy of water (2676 kJ/kg at 100 °C). If we assume steady state conditions the heat transfer of boiling systems is the result of convection at the interface steam/wall, conduction through the wall, and convection at the interface wort/wall (Fig. 10). There can only be steady state conditions when the heat transfer by convection and conduction are equal. The temperature of the steam at the exit of the boiler can be considered as T_{steam}. Generally, the heat transfer can be written as the total temperature difference ($T_{steam} - T_0$), divided by the total thermal resistance $R_{thermal}$ (12):

$$Q = (T_{steam} - T_0)/R_{thermal} \tag{12}$$

Energy transfer by conduction can be written as:

$$Q = k_c \text{ x } A \text{ x } (T_{steam} - T_{int})/d \tag{13}$$

The constant k_c in equation 13 is the thermal conductivity of the wall, A the total surface area of the heating device, and d the thickness of the wall. The thermal conductivity is a material constant and varies between 10 and 73 W/mK for stainless steel [33].

Heat transfer by convection is given by:

$$Q = h \text{ x } A \text{ x } (T_{int} - T_0) \tag{14}$$

The convective heat transfer coefficient h (W/m²K) in equation 14 is a function of wort viscosity and flow rate (laminar/turbulent). The overall heat transfer is then given by:

$$Q = \frac{T_{steam} - T_0}{\dfrac{d}{k_c.A} + \dfrac{1}{h.A}} \tag{15}$$

With this equation, the only unknown is h, while Q can be found using equation 11. When a boiling system uses natural convection, h is highly variable with the steam temperature. The constant h can be calculated by the Nu(Re,Pr) function, which is rather complex [33]. However, in a system with forced convection, h can be considered as a constant when the same pump speed is applied. In this dissertation, h is treated as a constant in order to simplify calculations.

When characterizing the impact of a particular boiling system, one must start with the characterization of the wort specific term (10). Subsequently, wort must be boiled at the same boiling intensity in order to keep T_{steam} constant throughout the entire boiling process. The ΔTBA additive effect of the boiling intensity (boiling system term) can then be determined following equation 3.

$$\Delta TBA = k'\Delta t + k''\Delta t \Rightarrow k_1 = \frac{k}{3.9E8 \times e^{-79629/RT_1}} \tag{16}$$

The only unknown is then T_1, which can be determined by combining equation 13 and 14 and solving towards Tint (Q is equal in both equations). Then T_1 can be approximated with ($T_{int} + T_0$)/2. Combining equation 13 & 14 gives:

$$\frac{k_c \times A \times (T_{steam} - T_{nt})}{d} = h \times A \times (T_{nt} - T_0) \tag{17}$$

Solving towards Tint gives:

$$T_{nt} = \frac{k_c \times T_{steam} + h \times d \times T_0}{h \times d + k_c} \tag{18}$$

The remaining unknown k_1 can then be solved with 16 resulting in a general predictive term for the TBA increase during boiling with forced convection, using the values of the standard wort.

$$\Delta TBA = 3.9E8 \times (e^{\frac{-79629\,J/mol}{R.T_0}} + k_1 \times e^{\frac{-79629\,J/mol}{R.\left(\frac{T_{nt}-T_0}{2}\right)}}) \times \Delta t \tag{19}$$

The values of T_{int} and k_1 are obtained from 18 and 16, respectively.

It is obvious that equation 19 is very complex and not easy to use. Moreover, it requires a lot of additional information in order to solve this equation (thickness of heating wall, total surface area, steam temperature at the exit of the boiler, etc…). Only the wort specific term (10) is a practical engineering tool. It requires a short procedure of heating wort at 4 different temperatures and subsequently measuring the TBA value.

Although equations 16, 18 and 19 are not easy to solve, they can provide additional interesting information when deciding to alter the boiling process. In order to reduce the thermal load as affected by the boiling system, k_1 and T_{int} must be reduced as much as possible (19). In equation 16, it becomes clear that k_1 decreases with decreasing T_1 and thus, T_{int}. It is also obvious (18), that Tint is directly proportional to T_{steam}. The reduction of T_{steam} will therefore result in a lower T_{int} and consequently in a lower ΔTBA. Equation 18 can also be regarded as a function of the linear relation of T_{int} and T_{steam}. An increase in T_{steam} with 1K will result in an increase of T_{int} with k/(h.d + k) K. Another interesting conclusion can be made when observing equation 17. If the convective heat transfer coefficient is increased by a more efficient mass transfer, the corresponding T_{int} will decrease as well, resulting in a lower ΔTBA. Thus, forced convection can help to reduce the thermal load on wort.

When fouling occurs on the heating surface, an additional insulation layer is added, with a high impact on heat transfer (Fig.11). Equation 15 must then be extended with an additional term of resistance:

$$Q = \frac{T_{steam} - T_0}{\dfrac{d_1}{k_c \times A} + \dfrac{d_2}{k_{fo\,1} \times A} + \dfrac{1}{h \times A}} \tag{20}$$

The mass transfer Q in equation 20 is always smaller than in equation 15. Therefore the total heat transfer will be reduced due

to the insulating capacity of the fouling layer. In the brewhouse less evaporation will be obtained and correspondingly, T_{int} will be lower as well. However, the effect of fouling on thermal load is ambiguous, since the raised temperature in the fouling layer (Fig.11) causes severe burning and consequently increased thermal damage.

4   Conclusions

The aim of this study was to explain the chemical relevance of thermal load and to provide a quantification tool for thermal load in the brewhouse, represented by ΔTBA.

It was discussed how thermal load during boiling could lead to the accumulation of intermediates and end products of the Maillard reaction, hereby generating a so-called HMF-potential. In addition, the TBA-value of 2 different treated worts decreased considerably during fermentation, due to the reduction of susceptible intermediates like HMF and its precursor compounds. It can be expected that the TBA value of a beer after fermentation corresponds with the remaining content of Maillard intermediates, representing the chemical memory of heat load in the beer. These Maillard intermediates can then further react during beer ageing towards flavour active compounds that affect the flavour stability of beer.

The pH and wort density clearly influenced the ΔTBA during boiling. This suggests that the ΔTBA will evolve differently in each kind of wort. This was confirmed by the comparison of the standard wort with 2 industrial worts, which were all different from each other.

In addition, an engineering tool was created in order to quantify and predict thermal load on wort, consisting of 2 terms: a specific wort term and a boiling system term. The specific wort term is a simple equation that reveals how wort will respond on variations in time and temperature during wort boiling. The procedure to obtain this term is very straightforward and easy to use. Using this tool, predictions can be made of the heat load impact of different wort boiling procedures. The boiling system term is a function of steam temperature, convection and conduction and is rather complicated to calculate. However, it provides insight in how the steam temperature and the convective heat transfer coefficient could be determining factors in the impact of the boiling intensity and boiling systems on the thermal load of wort.

5   List of abbreviations and symbols

3-DG	3-deoxyglucosone
A	surface area of heating wall
ARP	Amadori Rearrangement Product
ΔH_{vap}	evaporation enthalpy of water (2676 kJ/kg)
Δt	time interval of boiling period
d	thickness of heating wall
E_a	activation energy (J/mol)
h	onvection coefficient (W/m²K)
HMF	5-hydroxymethylfurfural
k	overall reaction rate constant
k_0	reaction rate constant
k_1	ratio of boundary layer volume to total wort volume
k_c	thermal conductivity of heating wall (W/mK)
k_{foul}	thermal conductivity of fouling layer (W/mK)
$\dot{m}$	mass transfer rate (kg/s)
Q	heat transfer (W)
R	universal gas constant (8.314 J/molK)
$R_{thermal}$	overall thermal resistance
T_0	boiling temperature of wort in boiling kettle
T_1	average temperature of wort in boundary layer
T_{int}	temperature at the interface wort/heating wall
T_{steam}	temperature of heating medium (steam)
TBA	thiobarbituric acid

6   References

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Acknowledgements

Appendix

Table 1 **Top: Comparison of different boiling procedures with a reference boil of 60 min at 100 °C**
Bottom: comparison of a convetional whirlpool rest with precooling

Boiling procedure	ΔTBA					
	Standard wort	Δ	**Industrial wort I**	Δ	Industrial wort II	Δ
Reference (60 min, 100°C)	**11.2**		**14.3**		**12.1**	
60 min, 103°C	13.8	**2.5**	18.1	**3.9**	14.9	**2.8**
60 min, 98°C	9.8	**−1.4**	12.1	**−2.1**	10.5	**−1.6**
50 min, 103°C	11.5	**0.2**	15.1	**0.9**	12.4	**0.3**
40 min, 103°C	9.2	**−2.1**	12.1	**−2.2**	10.0	**−2.2**
Whirlpool rest (20 min)						
without precooling (98°C)	3.3		4.0		3.5	
precooling (89°C)	1.7	**−1.6**	1.9	**−2.1**	1.8	**−1.7**
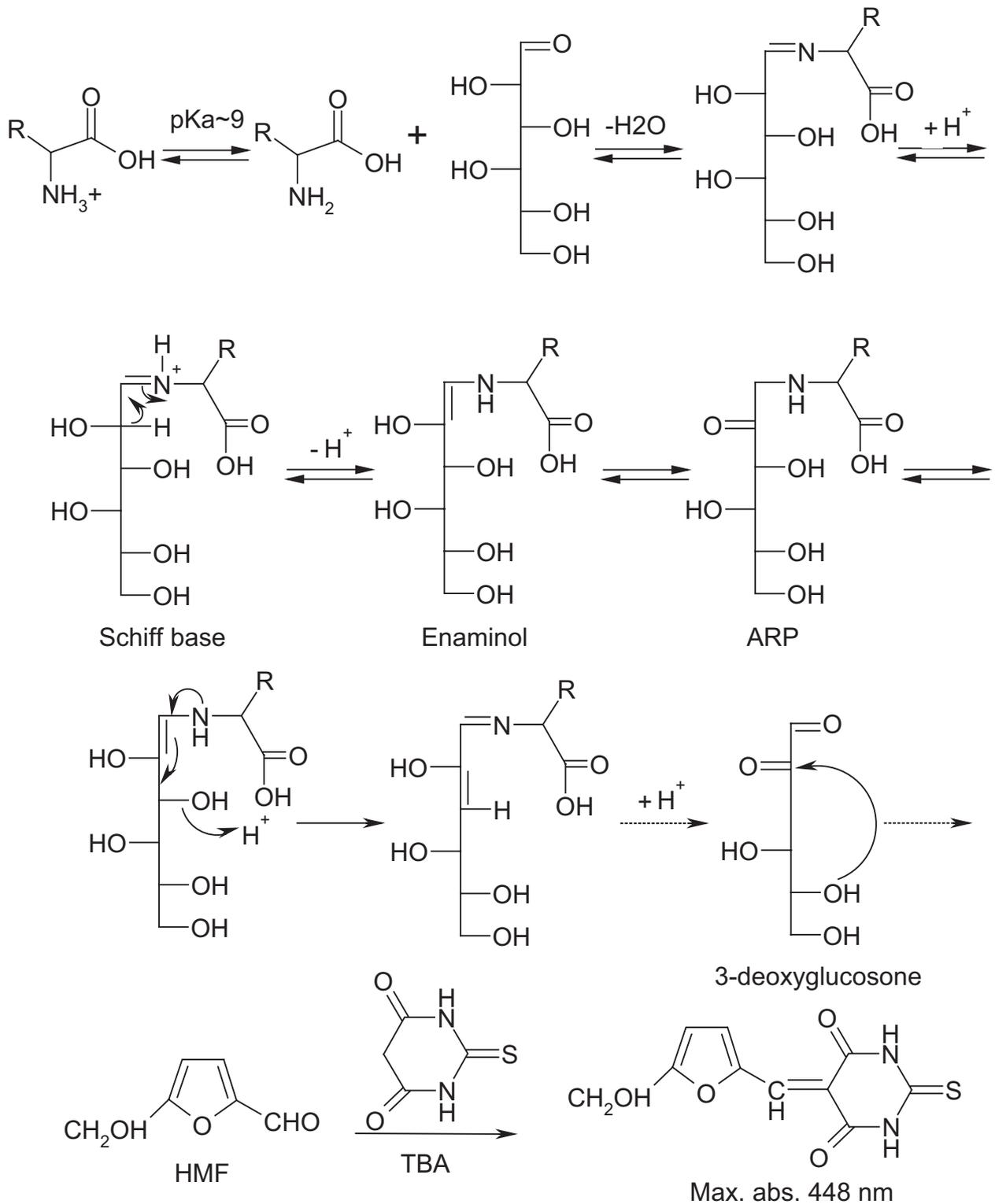
Fig. 1   Maillard reaction leading to the formation of HMF and the subsequent reaction with TBA (ARP: Amadori Rearrangement Product; HMF: 5-hydroxymethylfurfural)
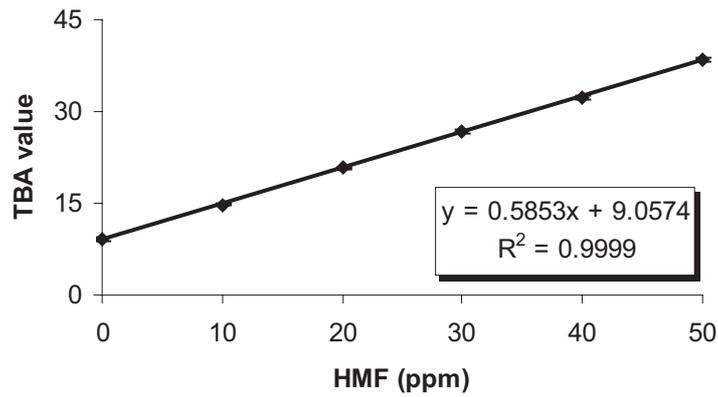
Fig. 2   The relation between the TBA value and HMF equivalents. For each data point the standard deviation (SD) is given (n = 4)
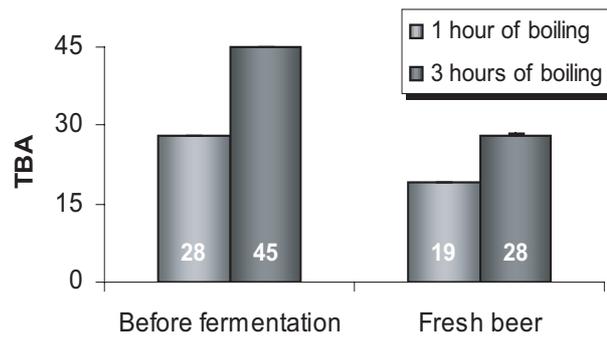
Fig.3   Reduction of the TBA value due to fermentation. For each data point, the SD is given (n = 2)
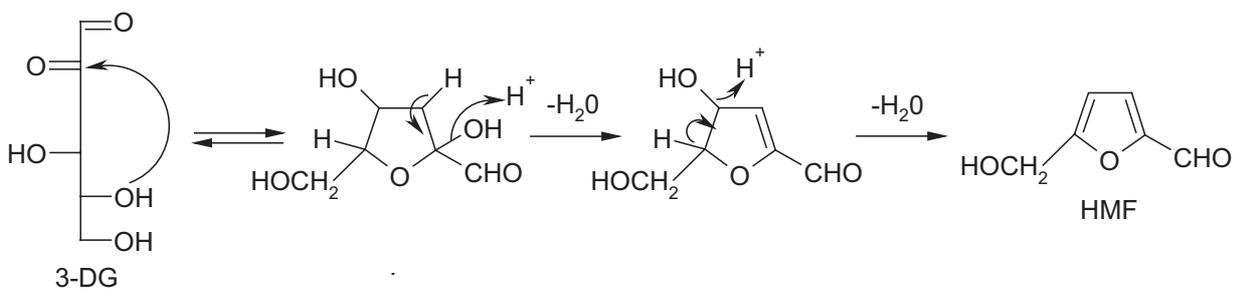

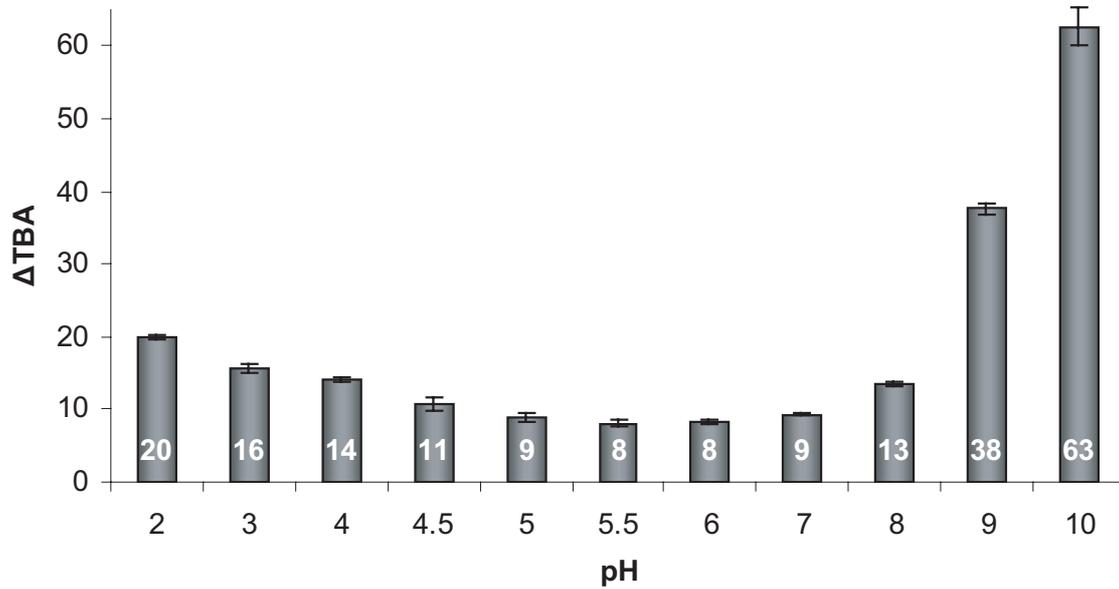**Fig. 4**   Detail of the cyclization of 3-DG and subsequent dehydration reactions leading to HMF

Fig. 5   The TBA increase (ΔTBA) after 60 min boiling of wort at different pH. For each data point, the SD is given (n = 2)
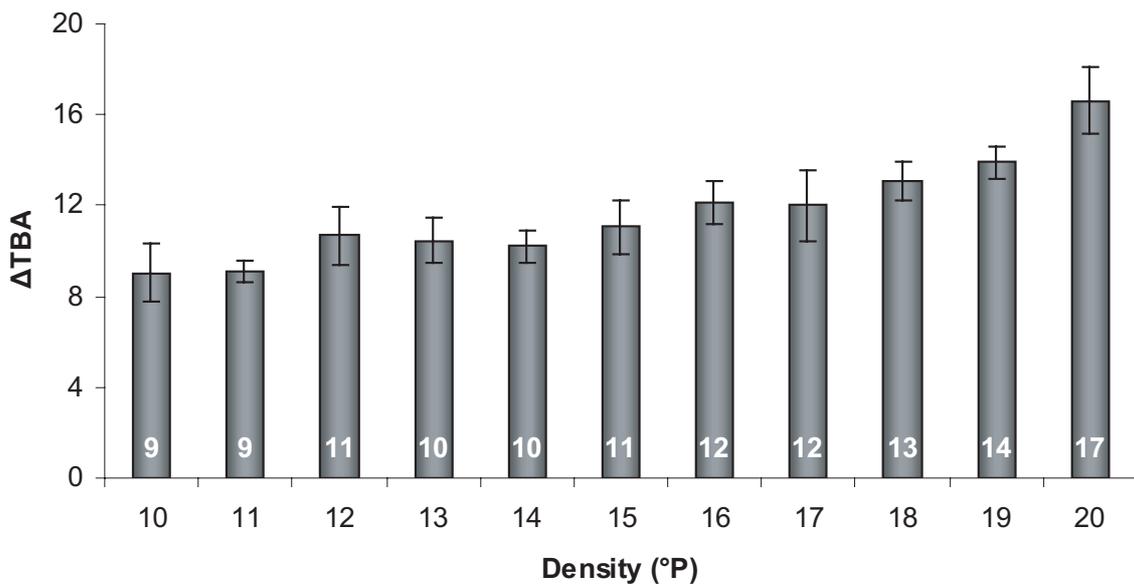
Fig. 6   ΔTBA after boiling of wort with increasing density. For each data point, the SD is given (n = 2)
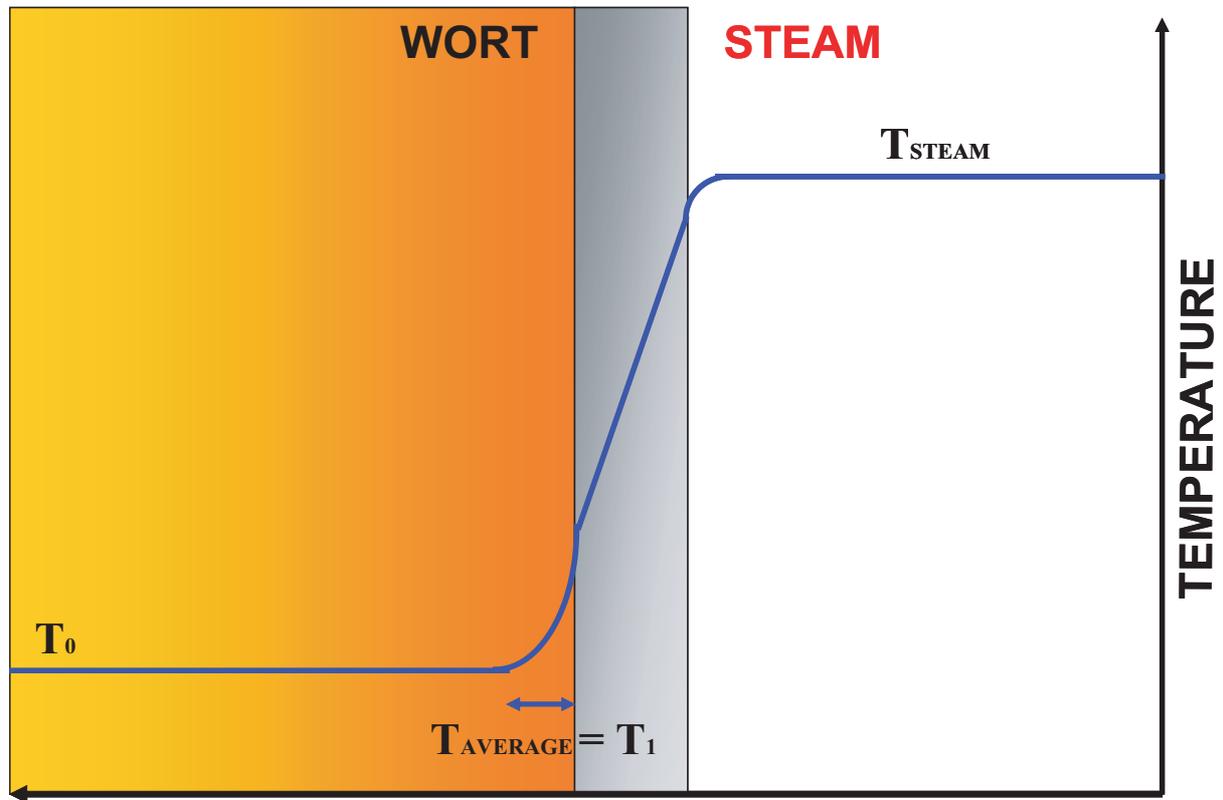
Fig. 7   Temperature distribution at the interface of a heating device and wort
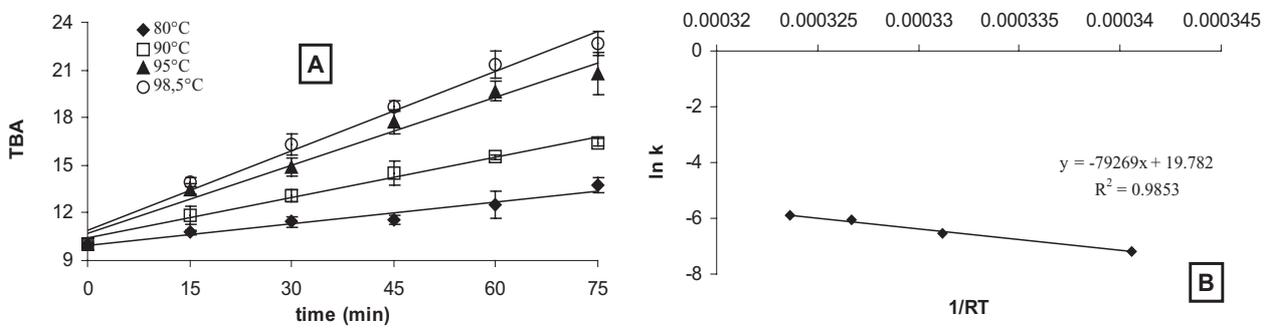

Fig. 8   Increase of TBA at different temperatures in order to find k (A). For each data point, the SD is given (n = 4); n k vs. 1/RT delivers E_a and k_0 (B).
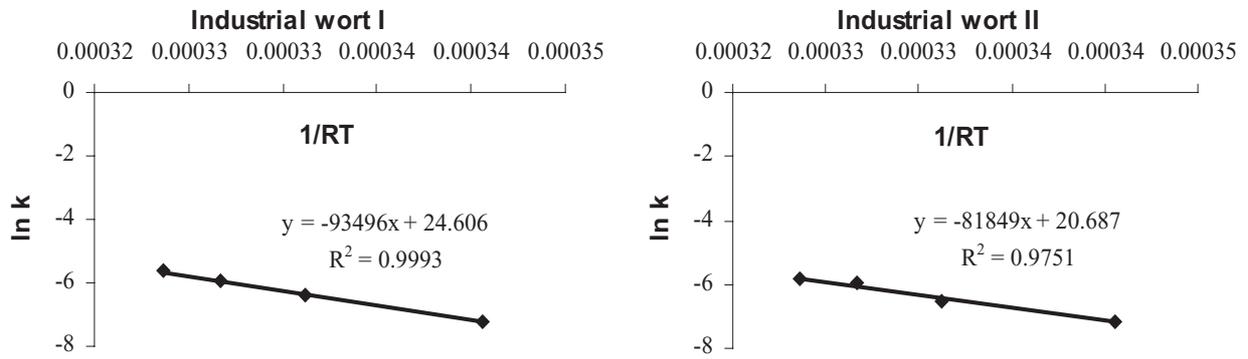
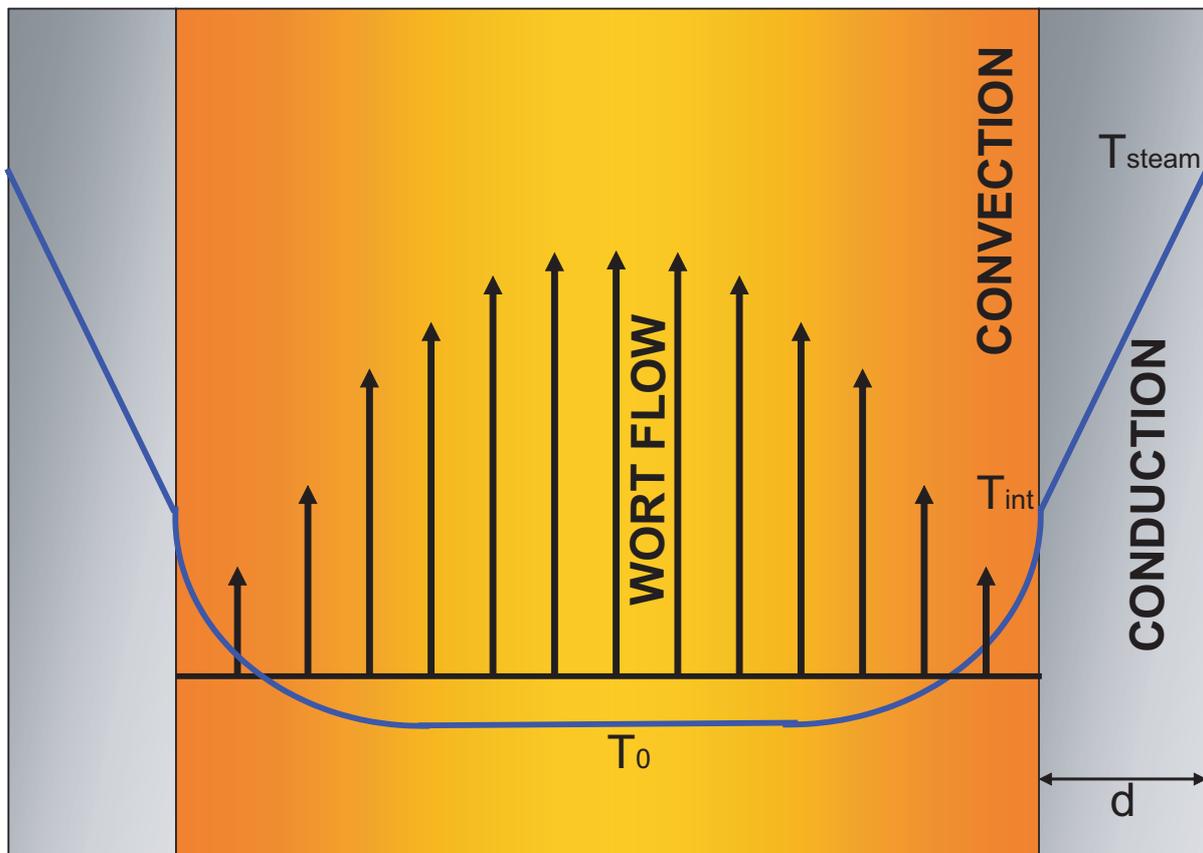**Fig. 9   ln k vs. 1/RT for 2 different industrial worts**

Fig. 10   Heat transfer by conduction and convection in a boiling system (T_{steam} = temperature at the outlet of steam unit; T_{int} = temperature at the interface wort/wall; T_0 = boiling temperature of the wort)
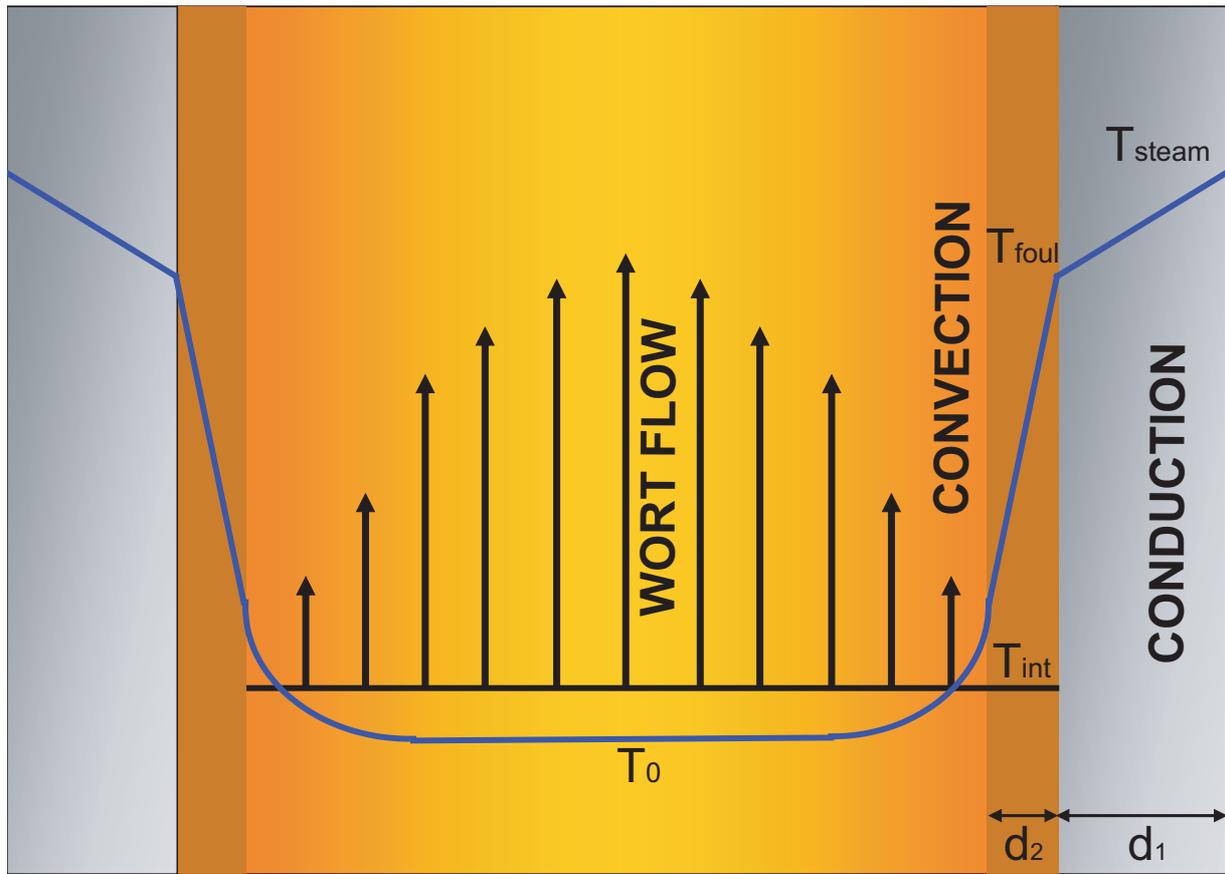
Fig. 11   Heat transfer by conduction and convection in a boiling system, whit an additional conduction/insulation due to fouling (T_{steam} = temperature at the outlet of steam unit; T_{foul} = temperature at the interface wall/fouling layer T_{int} = temperature at the interface wort/fouling layer; T_0 = boiling temperature of the wort)