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Vaporisation of Aromatic Components during the Beer Production

In a lot of processes and production steps in the Life-Science-Industry liquid semi-finished products are in contact with high temperatures and associated pressures. As a result steaming operations occur which have to be seen as thermodynamic separation processes. Concerning the exhaustion of aromatic components these steps influence intentionally or unintentionally the quality of the final product.
The purport of this article is an overview of the thermodynamical basics concerning the steaming of aromatic components. Therefore the process of vaporisation by vaporescence and the vaporisation by boiling are both explained and defined. Furthermore this theoretical background and the corresponding formulas are tested and proofed by two samples of the sum of all existing experiments.

Descriptors: wort boiling, mashing, vaporisation, boiling, vaporescence, flavours, Dimethylsulphide (DMS)

1 Introduction

Aromatic components are of high importance for the production of food. Their content influences the success and the quality of food and beverages significantly. Actually, a consumer is very interesting in getting naturally produced and pure products. Especially the aromatic profile should consist of natural flavours and shouldn't be artificially created. Considering this customer preference it is important to understand the development of a special aromatic profile during the whole production process. That means that the kinetics of the creation of important flavours must be researched. Furthermore, their expulsion by vaporisation must be made predictable.

A comestible good which is very interesting regarding to this problem is the traditional beverage beer. Especially in Germany, where a brewer has to consider the German purity law, the different aromatic components which create the special character of a beer type have to be of a natural source and must not be added artificially. The multitude of all aromatic substances is divided by an expert in desired and undesired ones. The intention of the production process consists primarily in the advancement of the creation of positive flavours and in the suppression of negative ones. The appropriate tool for the last target is the vaporisation of these flavours.

The vaporisation of a substance describes the phase-change of a molecule out of the liquid phase into the vaporous one. There is one possibility in the process of vaporescence, another one is the procedure of boiling. Related to the brewery especially the wort production in the brew house is interesting concerning the vaporisation and thereby the thermodynamical expulsion of unwanted flavours. The diverse production steps differ in mashing and wort boiling. Mashing means the creation of a suspension of grounded malt and water which is transferred by enzymatic reactions in a sugar containing solution which is called wort. By a separation process, the lautering, the wort is boiled. After this the process is continued by a second separation process in the whirlpool and the last is the pumping of the finished wort into the fermentation cellar. During all these steps vaporisation is an over all occurring separation process which influences the content of important aromatic components.

The target of this published project consists in the finding of a model for the prediction of the content of aromatic components at the end of the mashing process. By combining this model with an existing one describing the vaporisation by boiling [1] a very effective tool is created. This one can be used in every brewery for optimising the boiling process concerning time and energy effort. In this work the aromatic substance Benzaldehyde ais researched. Installing the described method it is possible to change the usual practice of the usage of standard programmes by introducing individually controlled brews. By that way changes in time, energy and finally money can be reached.

2 Basics

Description of the vapour liquid equilibrium

Reducing the content of an aromatic component by vaporescence during mashing or by boiling during wort boiling are vaporisation processes. The impulse for this process is the effort of the two-phase-system for finding the state of equilibrium between the liquid and the vaporous phase.

The vapour-liquid equilibrium state is reached, if all netto flows, like heat and mass-transfer are zero. This formulated mathematically means that the pressure, the temperature and the chemical potential have in both phases the same value.

$$T^V = T^L \quad (1)$$

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$$P^V = P^L \quad (2)$$

$$\mu_i^V = \mu_i^L \quad (3)$$

There is a thermal, mechanical and chemical equilibrium, which summarised is called thermodynamical equilibrium. To depict this state between two phases the vapour and the liquid partial pressure can be used.

$$p_i^V = p_i^L \quad (4)$$

Equation 4 describes the equilibrium between the vapour and the liquid phase if the partial pressures are equal [2].

The partial pressure of the component i in the vapour phase is defined by Dalton in the following way:

$$p^V = y_i \cdot P \quad (5)$$

In this formula y_i describes the concentration of an aromatic component i in the vapour phase. The calculative partial pressure in the liquid phase is formulated by Raoult as follows [3]:

$$p_i^L = x_i \cdot \gamma_i \cdot p_i^S \quad (6)$$

The factor x_i includes the concentration of a component i in the liquid phase. The activity coefficient γ_i means a dimensionless correction factor which is describing the difference between an ideal and a real solution. The formulas of Dalton and Raoult combined lead to the following one [4]:

$$y_i \cdot P = x_i \cdot \gamma_i \cdot p_i^S \quad (7)$$

This equation describes the correlation between the content of a flavour component in a liquid, non ideal mixture to the corresponding concentration in the steam.

Of particular importance for the vaporisation of an unwanted aromatic component during mashing and lautering is the very low concentration area of an aromatic component in water/wort. According to the researched substance the concentration range is between $x_i < 10^{-3}$ to $x_i < 10^{-5}$. Thus this highly diluted solution is called infinite solution. In a homogenous mixture the solute molecules do not interact among each other. There are only interactions between the molecules of water and of the aromatic substance or just between water molecules [5]. The following scheme describes this state.

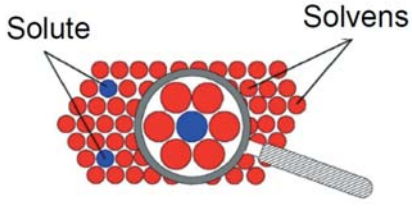

Fig. 1 Concentration range called „infinite solution“ [6]

By using this theory a mixture consisting of one component whose concentration is nearly one and other components whose concentrations are close to zero can be simplified. The activity coefficient loses its dependence to the contribution of a solution. In this concentration range the activity coefficient γ_i^∞ depends only on the temperature [7].

Introducing this simplification and defining a parameter, called distribution factor [2]

$$K_i = \frac{y_i}{x_i} \quad (8)$$

which is an expression for the vapour-liquid-equilibrium, the following modification of the equation above can be obtained [1]:

$$K_i = \gamma_i \cdot \frac{p_i^S}{P} \quad (9)$$

Another name for this parameter is “absolute volatility”. A comparison of two distribution factors of the components i and j, both solute in the same medium, leads to the “relative volatility” $\alpha_{i,j}$.

$$\alpha_{i,j} = \frac{K_i}{K_j} \quad (10)$$

For the condition of an infinite solution of an aromatic component in water/wort equation 10 can be simplified to:

$$\alpha_{i,j}^\infty = \lim_{\substack{x_i \to 0 \\ x_j \to 1}} \left(\frac{y_i / x_i}{y_j / x_j} \right) \approx \lim_{\substack{x_i \to 0 \\ x_j \to 1}} \left(\frac{y_i}{x_i} \right) = K_i^\infty \quad (11)$$

In case of vaporisation by vaporescence this simplification is not valid anymore, because of the fact, the vapour phase is formed by not less than three substances (air, water, flavour). Furthermore the steam content in saturated air under brew house conditions is not high diluted.

Description of vaporisation by vaporescence

The vaporescence of an aromatic component as well as the boiling process are vaporisation procedures. It exists a vapour and a liquid phase which are anxious to reach the state of equilibrium by mass- and heat transfer. The following description of vaporescence is signed by the important fact that the phase change of a molecule is only performed at the phase interface, the surface of the fluid. Therefore the explanation consists in the temperature dependence of a steam pressure. Under atmospheric conditions and in a temperature range lower than the boiling temperature of the fluid, the corresponding steam pressure is to low for creating bubbles.

In the case of pure water molecules of the liquid phase start evaporating by vaporescencce, if the partial pressure of the liquid phase, that means the steam pressure of water, is higher than the partial pressure of the vapour phase. The following expresses this fact:

$$p_{water}^S \geq p_{water}^V \quad (12)$$

The missing bubble creation means that the phase change of a molecule has to be performed in the surface of the liquid phase, the phase interface between steam and fluid. Furthermore it has to be considered that the quality of this way of vaporisation is strongly influenced and controlled by the mass transport to the phase interface and away from it. The basics of the mass transfer can be seen in analogy to the heat transfer. Both describe a resistance against a transport process. Taking into account the different material properties of the steaming aromatic components, the mass transfer can influence the separation quality of the process. Thereby the exhaustion of a flavour can be improved or distinguished. This exercise of influence is dependent on the flow conditions of the vapour and the liquid phase and especially on diffusive properties of a substance.

The following figure describes this factor:

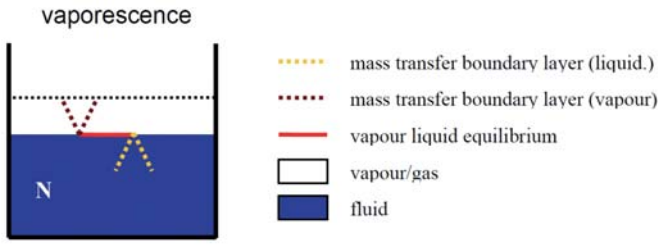

Fig. 2 Illustration of vaporous and liquid concentration gradients

The resulting mass balance describing the process of vaporisation by vaporescence for an aromatic component i is defined as follows [9]:

$$\frac{dN}{N} = \frac{dx_i}{r_i(x_i) - x_i} \qquad (13)$$

For solving this equation the mathematical relation $r_i(x_i)$ has to be known. Therefore the dominant vapour-liquid-equilibrium and the different mass transfers of the substances i and j have to be researched and determined. By introducing two kinetic (K_L, K_G) and one thermodynamic factor ($\alpha_{i,j}$), the process of vaporescence can be calculated. This last factor contains the separation factor of a high diluted aromatic component i compared to the separation factor of a soluting medium j. Of course the explained thermodynamic basics of the vapour liquid equilibrium are valid for this way of vaporisation too.

More complex is the determination of the vaporous and liquid kinetic separation factors. The mass transfer of an unwanted component in both phases has to be looked for.

Calculation of the vaporisation by vaporescence during the mashing production

In the following the process of mashing is modelled concerning the vaporisation by vaporescence. A simplification of the demonstrated calculations is caused by the fact that the mash is stirred homogeneously for a good mixing and for a boosting of the enzymatic reactions [10]. The following figure clarifies this fact.

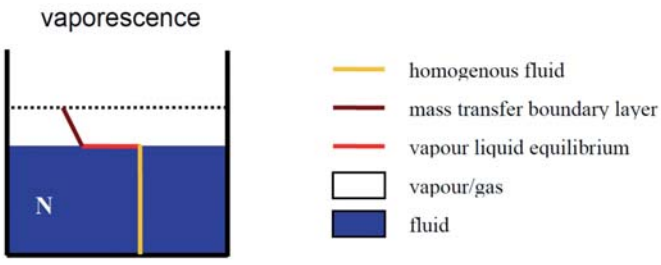

Fig. 3 Illustration of vaporous concentration gradients

For a solution of equation 13, considering the conditions of the mashing process, a thermodynamic and a kinetic separation factor has to be researched and defined. The kinetic factor describing the mass transfer in the vapour phase can be calculated by using following equation [9]:

$$K_G = \frac{NTU_{Gj}}{1 + NTU_{Gj}} \cdot \frac{1 + NTU_{Gi}}{NTU_{Gi}} \qquad (14)$$

The parameter NTU_{Gi} (number of transfer units) of a component i in the vapour phase (G) soluted in a medium j describes the influence of the velocity on the mass transfer, the seize of the surface and the flow speed of the surrounding medium. The corresponding definition is:

$$NTU_{Gi} = \frac{\beta_{Gi} \cdot A}{\dot{V}_G} \qquad (15)$$

Of high importance is the included mass transfer coefficient. This factor can be understood as a velocity, composed out of the diffusive constant of the substance i and the thickness of the vaporous boundary layer l. Therefore the definition is:

$$\beta_{Gi} = \frac{D_i}{l} \qquad (16)$$

By using the first law of Fick this factor can be described by the loss of the mass of component i and the belonging vaporous partial pressure of this substance. With some simplifications of this equation like the ideal gas law and the supposition of a vaporous partial pressure of zero of component i in the incoming inert gas, the following variation of Fick`s law can be defined [11]:

$$\dot{m}_i = x_i \cdot \gamma_i \cdot \frac{p_i^S}{R_i \cdot T_V} \cdot \beta_i \cdot A \cdot M_i \qquad (17)$$

This equation means a possibility to determine the needed mass transport coefficient adapted to different processes and aggregates by performing experiments in laboratory scale. For scaling up these results to practical systems, the experiments must include varying conditions like changing vessels, raising flows of inert gas and different temperatures. By the resulting data a Sherwood relation can be formulated, which is needed for finding different mass transfer coefficients of flavours in air [12].

These premises are the basis for the prediction of the vaporisation by vaporescence of aromatic components in infinite dilution during the mashing process. The following equation has to be used:

$$D_N = 1 - \left(\frac{x_i}{x_{i0}} \right)^{\frac{K_{ig}}{\alpha_i^{\infty} - K_{ig}}} \quad (18)$$

It is obvious that the thermodynamic and the kinetic separation factors are needed for solving equation 18. By that way a prediction of the vaporisation of an unwanted aromatic component is possible.

Description of vaporisation by boiling

The process of boiling is characterized by steam bubbles which exist in the boiling fluid. This statement seems to be nearly trivial but in fact it includes both possibilities for the process of vaporisation by boiling. Related to pure water this fluid is boiling if the steam pressure is equal to the ambient pressure. Following equation is valid:

$$p^S_{water} = P_{atmospheric} \quad (19)$$

In this equation both methods of boiling can be identified. One principle is given by influencing the temperature dependent steam pressure of a substance. By heating a fluid directly its steam pressure is raising. If substance specific vaporisation energy is reached a molecule evaporates by leaving the liquid phase and going to the vaporous one.

Another principle is given by the flash evaporation. This method means vaporisation by boiling by influencing the ambient pressure. It is reduced to the temperature dependent steam pressure of a substance. In the whole liquid steam bubbles are raising and the phase change of the molecules is reached. The intensity of boiling by this method depends on the difference in pressure and temperature. All existing wort boiling systems can be explained by these two principles. There are differences concerning the process control (continuous, discontinuous), the way of heating, the position of the vessel and the heating system (internal, external) and the special process parameter like the pressure and the temperature. But without any exception all possible systems can be reduced to the described two possibilities of boiling.

Calculation of the vaporisation by boiling using direct heating

The relation of the content of an aromatic component in the liquid phase to the concentration in the vaporous one is described for this way of boiling by the thermodynamic factor. That means that there is always a functional relation between the liquid aromatic content in both phases at every moment of the boiling process by which the vaporisation of a component can be calculated. Figure 4 describes the vapour-liquid-equilibrium in the case of boiling by direct heating.

The describing mass balance for this process of vaporisation by boiling is given as follows [13]:

$$\frac{dL}{L} = \frac{dx_i}{y_i - x_i} \quad (20)$$

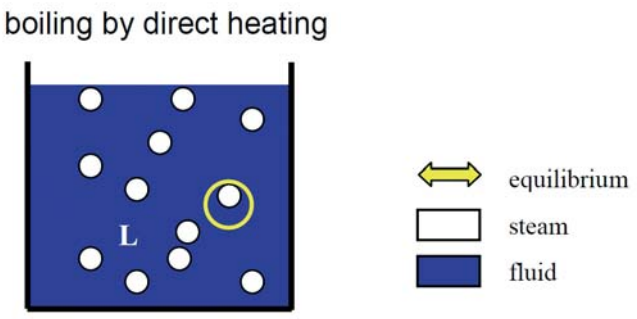

Fig. 4 Illustration of the vapour-liquid-equilibrium in the case of boiling by direct heating

This equation can be solved by using equation 8 and by introducing the standardized over all evaporation.

$$D_N = 1 - L_N \quad (21)$$

The resulting expression is formed as follows:

$$D_N = 1 - e^{\int_{x_{i0}}^{x_{ie}} \frac{dx_i}{y_i(x_i) - x_i}} \quad (22)$$

For solving this equation the described knowledge concerning the vapour-liquid equilibrium is required. By that way the steaming of an aromatic component during the process of boiling by direct heating is possible.

Calculation of the vaporisation by boiling using flash evaporation

This way of boiling is characterized by another vapour-liquid-equilibrium contrary to the method of boiling by direct heating. Of course there is a relation between the fluid at the beginning of the boiling process and the rising steam at the end. But this relation can be described by the equilibrium. Following figure expresses this problem:

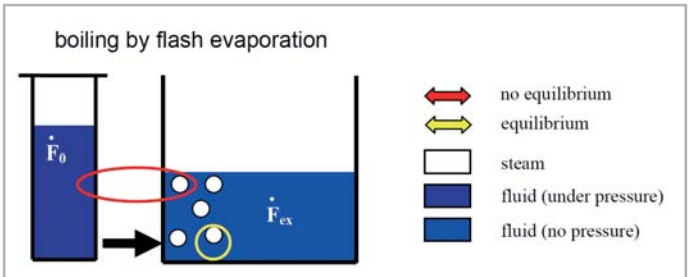

Fig. 5 Illustration of the vapour-liquid-equilibrium in the case of boiling by flash evaporation

For this process the relation between the concentration of an aromatic component in the vaporous phase and its content in the pressurized liquid phase which are not in a state of equilibrium must be looked for. In this case there is a vapour-liquid-equilibrium between the steam and the non pressurized liquid phase. This fact can be proven by equations 1, 2, 3. The temperatures and pressure

do not achieve the conditions of a thermodynamic equilibrium. This vaporisation process cannot be calculated using equation 22. Another mass balance describing vaporisation by boiling has to be defined. The following equation describes the process flash evaporation:

$$\frac{\dot{F}_{ex}}{\dot{D}} = \frac{y_i - x_{i_0}}{x_{i_0} - x_{i_{ent}}} \tag{23}$$

By some simplifications this form of equation 23 can be obtained

$$x_{i_{Nex}} = \frac{1}{\dot{D}_N \cdot \left(K_{i_\alpha}^{\infty} - 1\right) + 1} \tag{24}$$

For solving this equation the temperature determined vapour-liquid-equilibrium of the flash vessel has to be known. Furthermore, the over all evaporation during the step of expansion has to be determined. By measuring the temperature difference ($T_0 - T_{ex}$), inserting the vaporisation energy (r_{ex}) and using the effective heat capacity (c_w) the following equation can be obtained:

$$D_N = \frac{c_W \cdot (T_0 - T_{ex})}{r_{ex}} \tag{25}$$

Using this equation it is possible to calculate and to predict the vaporisation process of a continuous controlled flash vaporisation.

Combination of both boiling principles

The explained principles of boiling by direct heating and boiling by flash evaporation cannot be found very often in the described, practical constructions. Very often combinations of both systems are used. The most popular aggregates are internal and external boilers, which work by using the principal of a flash evaporation in a discontinuous procedural method. Therefore wort is superheated in a boiling system and hence the pressure in of the fluid is higher than the atmospheric ambient pressure. By leading back and gathering overheated wort in the wort kettle, the fluid is expanded to atmospheric pressure. As a result steam bubbles are arising and the wort is boiling. Thereby unwanted aromatic components are vaporised.

Summarising these explanations, a description of the boiling process by an internal or external boiler is given in two steps. Number one consists in the superheating of the fluid and number two is the expanding process in the wort kettle. A qualitative variation between internal and external boiler is given in the intensity of boiling. Dependent on the temperature difference of superheated and expanded wort the vaporisation quality is influenced and the needed over all evaporation for reaching a special aromatic concentration level is changing. The rule of thumb is valid that with a rising temperature difference between boiling and expanded wort the separation effect of a boiling system is further away from the optimum of a direct heated boiling vessel.

For calculating and predicting the content of a flavour at the end of an external or internal boiling process, the conditions of a flash evaporation have to be combined with a discontinuous process control. For this purpose equation 22 has to be modified using following relation:

$$y_i = \omega_i \cdot K_{i_{ex}}^{\infty} \cdot x_{i_0} \tag{26}$$

The parameter ω_i is explained by the fact that between the non expanded liquid phase and the expanded steam phase no vapour-liquid-equilibrium is existing. As a consequence of that a relation between both concentrations can only be formulated by defining and introducing the factor ω_i. This parameter is defined as follows:

$$\omega_i = \frac{x_{i_{ent}}}{x_{i_0}} \tag{27}$$

It is obvious that the relation factor ω_i is always smaller than one, caused by the aromatic content in the unexpanded fluid and the related, lower concentrated aromatic content in the expanded wort

In the case of a discontinuous, directly heated boiling process equation 8 describes the vapour-liquid-equilibrium. The relation between the concentration of an aromatic component in the vapour and the liquid phase is different for an indirectly heated boiling process using an internal or external boiler. The additional parameter ω_i has to be determined and combined with the thermodynamic factor. Because of the fact the parameter ω_i is always smaller than one, the quality of exhaustion of unwanted aromatic components in not directly heating systems is always worse than in directly heating ones. Regarding to these conditions the following equation can be defined for calculating the vaporisation concerning unwanted aromatic substances:

$$D_N = 1 - L_N = 1 - e^{\int_{x_{i_0}}^{x_{i_e}} \frac{dx_i}{\varpi_i \cdot y_i(x_i) - x_i}} \tag{28}$$

By using this equation the content of a special component can be predicted.

A special variation of a discontinuous boiling system using external heaters is to be seen in atmospherically boiling aggregates. One possible construction is given by a thin layer evaporator. In this case the boiling process is performed by direct heating under ambient pressure. That means wort flowing back to the wort kettle is not expanded. For this method equation 28 is not valid, but equation 22 can be used for predicting the boiling process.

3 Results

The following figures are excerpts of already proceeded results [1, 15, 16].

The mashing experiments are performed in laboratory scale. A mashing apparatus was constructed which allows to define various conditions like the temperature in the liquid and the gaseous phase, the volume flow of air and the Reynolds number in the liquid phase. Furthermore the influence of different mash tune geometries was researched.

The boiling experiments are performed in technical scale. A thin layer evaporater used as an external heater was researched.

More detailed information concerning the used materials and methods can be found in literature [1, 15, 16].

The schemes contain the calculated residue curves for boiling and vaporescence and the related confidences, the experimental founded residue values and their confidence belt. The ordinate describes the standardized content of the aromatic substance Benzaldehyde in the fluid, the abscissa contains the parameter time (mashing) or the relative over all evaporation (boiling). Furthermore in Figure 6 the mashing programme with temperature data in Kelvin is illustrated.

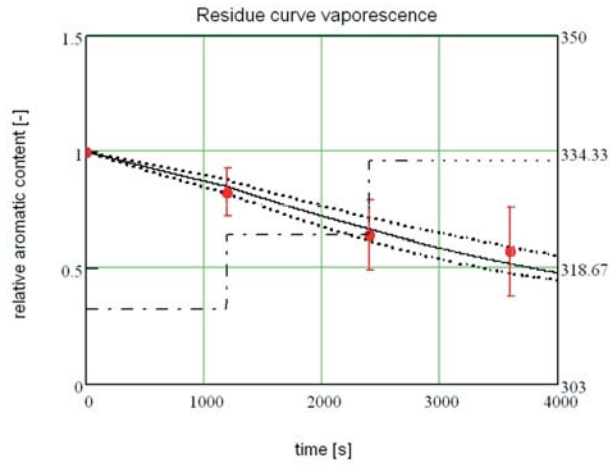

Fig. 6 Vaporescence during mashing (30°C, $\dot{V}_{Luft} = 0{,}06 m^3/h$)

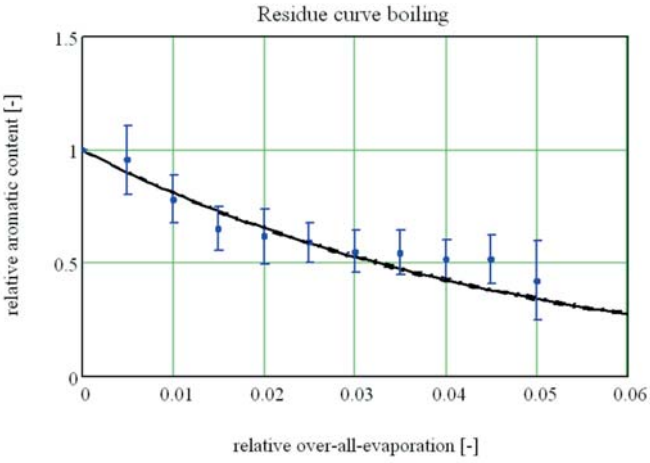

Fig. 7 Vaporisation during boiling

It is obvious, that in both systems the experimental values confirm the calculated residue curves. That means the vaporisation by boiling and vaporescence during the wort production can be calculated and predicted. More results can be found in literature.

4 Summary and Perspectives

The aim of the presented work consists in the finding and determining of a model for the prediction of the vaporisation of aromatic components during the processes of the brew house.

Actually the equations describing the vaporisation by boiling during the wort boiling process are tested in laboratory and in practical scale. The vaporisation by vaporescence during the mashing process is tested in laboratory scale and the underlying model is actually advanced to systems in industrial scale. Therefore the dependence of the vaporous kinetic factor to the differences in the geometry of a mashing vessel and the used mashing programme and the process control have to be modelled. Using special process engineering tools this problem was solved.

The presented models will be used for creating an over all predicting model describing the vaporisation of aromatic components during the whole wort production in the brew house. This result will be used for optimising the wort production of every brewery. One possibility consists in reducing the over all evaporation by predicting the aromatic profile, a second one is given thereby that the processes of mashing and lautering can be seen as new tools for influencing aromatic profile by using the advantages of temperature dependent thermodynamic factors. Savings in time, energy and finally money can be reached without any technical modification or improvement of the brew house.

5 Literature

1. Hertel, M.: Das Ausdampfverhalten von Aromastoffen während der Würzekochung, dissertation, TU München, Germany, 2007.

2. Gmehling, J. and Kolbe, B.: Thermodynamik, 2nd ed., Georg Thieme Verlag, Stuttgart, Germany, 1992.

3. Langenheinecke, K.; Jany, P. and Sapper, E.: Thermodynamik für Ingenieure, Friedr. Vieweg & Sohn Verlag\GWV Fachverlage GmbH, Wiesbaden, Germany, 2001.

4. Gmehling, J.: Phasengleichgewichtsmodelle zur Synthese und Auslegung von Trennprozessen, Chem. Ing. Tech., VCH Verlagsgesellschaft, Weinheim, Germany, **66**, no.6, 1994.

5. Grisher, D.: The Determination of Activity Coefficients at Infinite Dilution with the Help of the Dilutor Technique (Inert Gas Stripping), Chemical Engineering & Technology, **22**, 1999.

6. Krummen, M.: Experimentelle Untersuchung des Aktivitätskoeffizienten bei unendlicher Verdünnung in ausgewählten Lösungsmitteln und Lösungsmittelgemischen als Grundlage für die Synthese thermischer Trennprozesse, dissertation, University Oldenbourg, Germany 2002.

7. Alessi, P.; Fermeglia, M. and Kikic, I.: Significance of Dilute Regions, Fluid Phase Euqilibria, Elsevier Science Publishers, Amsterdam, Netherlands, 1991.

8. Dohnal, V. and Fenclova, D.: Air-Water Partioning and Aqueous Solubility of Phenols, Chemical Engeneering Data, American Chemical Society, **40**, 1995.

9. Schlünder, E.U.: Über den Einfluss der Stoffübertragung auf die Selektivität der thermischen Trennverfahren – dargestellt am Bei-

spiel der Schleppmitteldestillation, VT Verfahrenstechnik, **11**, no. 11, 1977.

10. Narziß, L.: Abriß der Bierbrauerei, 6th ed., Wiley-VCH, 2001.

11. Weidlich, U. and Gmehling, J.: Expositionsabschätzung, Schriftenreihe der Bundesanstalt für Arbeitsschutz, Wirtschaftsverlag NW, Germany, 1986.

12. Gmehling, J.: Grundoperationen – Lehrbuch der Technischen Chemie, **2**, Georg Thieme Verlag, Stuttgart, Germany, 1996.

13. VDI, VDI – Wärmeatlas, Springer, Berlin, Germany, 2003.

14. Mersmann, A.; Kind, M. and Stichlmair, J.: Thermische Verfahrenstechnik Grundlagen und Methoden, 2nd ed., Springer, Berlin, Heidelberg, Germany, 2005.

15. Scheuren, H.; Heinemann, S.; Hertel, M.; Dauth, H. and Sommer, K.: Vorhersage und experimentelle Bestätigung des Ausdampfverhaltens gängiger Würzekochsysteme, Brauwelt, **14**, Fachverlag Hans Carl, Nürnberg, Germany, 2008.

16. Scheuren, H. and Sommer, K.: Vaporescence versus boiling – Expulsion of aromatic compounds during the whole wort production, World Brewing Convention Hawaii, 2008.

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