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Predicting Haze Stability in Wheat Beer using Light Scattering Analysis Techniques

Visible and intense turbidity is seen as a defining characteristic of German and Belgian wheat beers. To date, no reliable method has been established for predicting the haze stability of wheat beer. It would be very beneficial for breweries to be able to predict haze stability so as to ensure that the beer retained a satisfactory level of haze during its shelf life. To predict wheat beer haze, trials were undertaken, in which light scattering analysis techniques and particle size distribution measurements were made, for the purpose of characterizing the haze stability of wheat beer. The wheat beer samples assessed had substantial differences in haze stability durability, from 19 days up to more than 160 days, as judged by when 90° scatter light intensity drops below 30 EBC units. Interestingly, the classification of all samples by the 90°:25° ratio of scatter light intensity showed values from 0.5 up to 1.0 and it was observed that as haze stability increases, the ratio expressing the intensity of light scattering at 90°:25° also increases. Particle size distribution measurements showed for samples with high 90°:25° ratios of scatter light intensity (> 0.9) had monomodal distributions with high ratios of particles < 1 µm which was favourable indicator of beer haze durability*.

Descriptors: wheat beer, haze, haze measurement

1 Introduction

A pronounced amount of haze is typical for German and Belgian wheat beer styles and therefore represents an important quality attribute. This is quite the opposite that brewers require for their bright or non-turbid beer styles that conventionally make up the majority of the beer market [1]. The rising popularity of these naturally cloudy beer styles has necessitated that they possess an extended shelf life as well as prolonged haze stability. This is to ensure that when a customer purchases the beer that at least a satisfactory level of haze is evident on dispense. However, predicting the haze stability of wheat beer is still difficult, because reliable method has yet to be developed. As part of these trials, bottled wheat beers were tested using light scattering analysis techniques and particle size distribution measurements.

1.1 The principles of light scattering analysis and turbidity measurements in beer

The intensity of scattered light at fixed angles by spherical particles can be expressed using the dimensionless parameter x based on the MIE theory [2]:

$$x = \frac{\pi d}{\lambda} \quad (1)$$

where d is the diameter of the particle and λ the wavelength of the light. The parameter x for particles between 0.1–1 µm at a wavelength of 500 nm is between 0.62–6.2, and for particles with a diameter of 5 µm (e.g. yeast cells), it is approximately 31. For all MIE parameters, forward scattering (< 90°) generally increases as the angle decreases. The absolute intensity of scattering increases with particle diameter [3].

Light scattering analysis is a state-of-the-art technique that is used by the brewing industry. For instance, it is used for in-line monitoring of lautering and filtration processes, measuring centrifuge performance, as well as for monitoring the colloidal stability of the finished beer after packaging [4–16]. Primarily haze is not a physical quantity but human visual perception. Haze meters are calibrated with a formazin standard according to ISO 7027 (DIN 38404, part 2). Although calibration with a formazin standard is an approved method, it is also common knowledge that haze meters do not express absolute values for particle size distribution [15, 17]. *Carrasco and Siebert* [18] investigated the human visual perception of haze and found a correlation between the intensity that light was scattered at 90° and the human perception of turbidity up to 50 EBC units.

Brandl [19] also carried out inquiries into wheat beer haze stability using light scattering analysis techniques and was able to establish a relationship between a ratio of the light scattered at 90°:12° and increased haze stability. He attributed better haze stability at a ratio > 0.6 and to higher concentrations of particles less than 0.5 µm in size. Light scattering analysis at 90° is a technique that is more suited to measuring particles smaller than 0.5 µm which remain in suspension. He defined the desired haze stability for wheat beers as the time period from packaging to the point at which the 12° measurements for the intensity of scattered light drop below 15 EBC units.

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Tables and figures see Appendix

1.2 Sedimentation in mono- and polydisperse suspensions and its influence on haze

The calculation for the velocity at which sedimentation of particles occurs according to Navier-Stokes is limited to parameters like laminar flow (Reynolds number < 0.25), low particle concentration ($< 1\%$ by volume) and a general lack of particle interactions, e.g. van der Waals forces [20, 21]. According to Navier-Stokes (Eq. 2), sedimentation velocity u of a spherical particle is:

$$u = \frac{gr^2(\rho_D - \rho_T)}{18\eta} \quad (2)$$

where g is gravity, r the radius of a spherical particle, ρ_D the density of the particle, ρ_T the density of the fluid and η the viscosity of the fluid. Sedimentation velocity u is strongly affected by the particle diameter. If one of these parameters for Navier-Stokes is not present, then sedimentation behavior can only be determined through experimentation, for example with a sedimentation scale [20] or by centrifugation [22]. Sedimentation behavior of a suspension is related to the concentration of particles and whether their distribution is mono- or polydisperse [23]. *Bickert and Stahl* [23] carried out trials investigating the influence of particle concentration and how it affects the sedimentation behavior of mono- and polydisperse particle suspensions with particles of SiO_2 . In trials with SiO_2 particles of a diameter of $1\ \mu\text{m}$, already a very low solid concentration of $10^{-4}\%$ ($= 1\ \text{ppm}$) by volume affected an increased medial sedimentation velocity, caused by repulsive particle interactions. This effect was reduced with increasing particle concentrations. The results of *Bickert and Stahl* corroborate the results reported by *Ekdawi and Hunter* [24] and *Vesaratchanon et al.* [25] for monomodal particle suspensions. This is also the case for polydisperse particle solutions where sedimentation behavior is dependent on particle concentration. Furthermore, small particles in suspension cause an overall slowing in the sedimentation rate of the larger particles due to the increased suspension density and viscosity, whereas larger particles at lower ratios accelerate the settling rate of smaller particles due to the effects of wake. However, as total particle concentration increases, coupled with a higher ratio of larger particles, this leads to a general slowing in the sedimentation rate of the smaller particles. In strongly flocculating suspensions, all particles sediment with equal velocity due to strong attractive particle interactions [22]. *Weikl* [26] investigated the sedimentation of particles in wheat beer and determined that the critical particle size for sedimentation was $1\ \mu\text{m}$. Particles of a diameter less than $1\ \mu\text{m}$ are subject to Brownian motion and therefore remain in suspension, while those greater than $1\ \mu\text{m}$ are prone to sediment. These experiments showed that yeast cells with a mean diameter of $5\ \mu\text{m}$ sediment out at a velocity of approximately $1.5\ \text{cm/day}$, thus producing not a stable level of cloudiness in the beer. The results of both *Weikl and Delvaux* [27] are mutually corroborative, the latter of whom compared the particle size distributions of different worts adjusted to a pH of 4.2 and an ethanol concentration of 5.2% by volume to emulate the conditions in beer. He found that increased haze stability was achieved for the samples with the highest number of particles smaller than $1.03\ \mu\text{m}$ in diameter. Furthermore *Delvaux* [28–31] investigated the haze stability of Belgium wheat beers with the focus on raw materials and haze components.

The goal of this study was to better understand how the wheat beer turbidity changes over time for so that a method could be developed to predict the duration of haze stability of finished wheat beer.

2 Materials and methods

Twenty eight commercial and pilot-scale bottled German style wheat beers were analyzed using light scattering analysis and particle size distribution measurements. Turbidity was measured using a LAB SCAT 2-angle ($90^\circ:25^\circ$) laboratory light scattering analysis system from Sigrist-Photometer AG/Switzerland (0–200 EBC units). Particle size distribution was measured with the HELOS laser diffraction system with Sucell dispersion unit from Sympatec/Germany and Sympatec WINDOX 5 software.

The samples for the turbidity and particle size distribution measurements were prepared as follows:

Wheat beer bottles were stored at $20\text{--}22\ ^\circ\text{C}$ and cooled to $10\text{--}12\ ^\circ\text{C}$ before sample preparation. Turbidity and particle size distribution were measured with $500\ \text{ml}$ ($2 \times 250\ \text{ml}$ supernatant of $0.5\ \text{liter}$ NRW-type bottles) of beer at a temperature of $12\ ^\circ\text{C}$, in order to simulate serving conditions. The supernatant was transferred into a two liter receiving bottle from Brand/Germany by vacuum suction to achieve degasification and to avoid any transfer of sediment, e.g. yeast cells. The sample volume was decanted from the receiving bottle to a $500\ \text{ml}$ NRW-type clear glass bottle and tempered to $12\ ^\circ\text{C}$ in a water bath. After completing the turbidity measurement, the samples were conditioned again to $12\ ^\circ\text{C}$ and also used for the particle size measurement. Particle size measurements were done in a cooled room with a room temperature $< 14\ ^\circ\text{C}$ to avoid condensation of parts of the Helos particle measurement system. The initial measurements for turbidity and particle size distribution were done 7–14 days after packaging primarily for the purpose of detecting those particles, which are slow to sediment out.

3 Results and discussion

3.1 The perception of haze intensity and a definition for haze stability

A comparison of wheat beer samples at various levels of turbidity showed a 90° light scatter value of greater than 30 EBC units constituted a satisfactory amount of haze in a dispensed beer. Due to this experience of the authors, haze stability was defined in this paper as the time required after packaging until the turbidity measured at 90° drops below a value of 30 EBC units at a temperature of $12\ ^\circ\text{C}$. Turbidity and particle size measurements were carried out at $12\ ^\circ\text{C}$ to simulate a typical serving temperature. According to corporate preferences, every brewery must determine for itself what level of turbidity will produce the haze intensity it requires either at the point of sale or during consumption.

3.2 The relationship of haze stability to the ratio of the intensity of 90°:25° scattered light

The change in the intensity of the 90° and 25° readings for 28 bottled wheat beer samples was measured over time. Over the duration of the trials, all of the samples except for P 34, P 49 and P 51 showed a permanent decrease in the intensity of the scattered light at 90° and 25°. The samples were classified by the R 90°:25° ratio the first time measurements were taken, which was 7–14 days after packaging. R 90°:25° was in the range of 0.5–1 for all of the samples at this point of time. Samples with a ratio less than 0.45, greater than 1.1 or within the range of 0.8–0.9 have not been observed. Table 1 shows the number of samples classified according to their R 90°:25° values.

The change in the values for intensity at 90° scatter are given in figures 1–4 and classified according to their R 90°:25° ratios as follows: 0.5–0.6, 0.6–0.7, 0.7–0.8 and 0.9–1. The minimum haze stability of the analyzed wheat beer samples increased with higher values for R 90°:25°. The distribution of maximum haze stability values showed no clear correlation between R 90°:25° and haze stability. Samples P 18 (R 90°:25° = 0.5–0.6; Fig. 1), P 49 and P 51 (R 90°:25° = 0.6–0.7; Fig. 2 b) exhibited very high haze stability compared to the other samples with equivalent R 90°:25° values. A similar change in turbidity was observed in samples with a ratio of 0.7–0.8; however, they possessed low maximum values. The distribution of the interpolated minimum and maximum values for haze stability is given in table 2.

These results do not completely substantiate the conclusions of *Brandl* [19] that ratios of > 0.6 for side and forward scattering (90°:12°) led to higher haze stability. In this study only the general trend shows that higher values for R 90°:25° lead to better haze stability, which especially applies to the absolute minimum values for haze stability.

With regard to the fundamental concepts of light scattering, a ratio of the intensity for 90°:25° of 0.9, for instance, was not possible, because the forward scattering was more intense than the light scattered at 90° for all particle sizes. This phenomenon is related to calibration with formazin and is well known, for example, in beer filtration, where the intensity of 90° scattering is usually higher than that at 25° or 12°.

In addition to light scattering analysis, particle size distributions were measured. The particle size distributions for the samples of wheat beer with 90°:25° ratios of 0.5–0.6 and 0.9–1 are presented in figures 5 and 6. All of the samples with values less than 0.8 for R 90°:25° had a bimodal density distribution, except for sample P 2. Substantial differences between samples with values less than 0.8 and between 0.9 and 1 for R 90°:25° were observed. All of the samples with a ratio greater than 0.9 possessed a monomodal particle size distribution as well as a substantially higher ratio of particles less than 1 µm. It appears that wheat beers with a bimodal particle distribution have a higher potential for agglomeration and also have a higher amount of larger particles with an increased rate of sedimentation. Furthermore, particles with a diameter less than 1 µm that sediment out very slowly or simply remain in suspension

will be influenced by larger particles, due to the effects of wake. This results in particles of this size being sedimented out thus reducing haze stability. Conversely wheat beers with monodisperse particle size distributions seem to exhibit a lower tendency towards agglomeration, resulting in more desirable and durable haze stability. Due to the complexity of agglomeration and sedimentation phenomena, an absolute prediction of haze stability using light scattering analysis techniques does not appear practical at this time. Similar to the forced aging test for colloidal stability of filtered beers in MEBAK [32], a prediction of haze stability in practice has to be determined empirically by comparing values for R 90°:25° and the change in the intensity of the turbidity in bottled samples.

4 Summary

An increased ratio for the intensity of light scattered at 90°:25° tends to lead to an increase in haze stability; the minimum values for haze stability and the 90°:25° ratio showed strong correlation. The likelihood that a method for predicting the precise shelf life duration of haze stability by only using light scattering analysis techniques does not appear to be practical due to the complexity of the sedimentation and agglomeration kinetics occurring in beer. However, light scattering techniques were a practical tool for quality assurance based on empirical data that evaluated changes in the 90°:25° ratio as a means for predicting the haze stability of wheat beer.

Footnote

- * Parts of the results were presented in 2009 at the 42. Technologisches Seminar Weihenstephan

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Appendix

Table 1 Classification of the samples analysed according to the ratio of 90°:25° scatter light intensity

R 90°:25°	Number of samples per class
0.5-0.6	5
0.6-0.7	10
0.7-0.8	4
0.9-1	9
	$\Sigma = 28$

Table 2 Minimum and maximum values for haze stability according to the ratio of 90°:25° scatter light intensity

R 90°:25°	Range of haze stability (min.–max.) [days]
0.5–0.6	19–38 (> 80)
0.6–0.7	26–78 (> 90)
0.7–0.8	32–48
0.9–1	37–>160

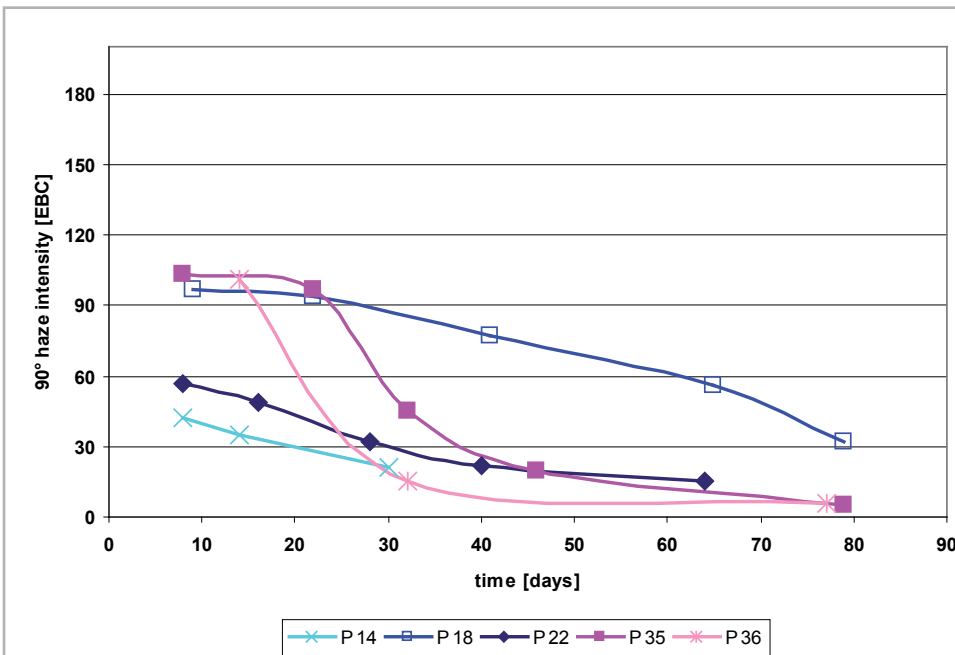


Fig. 1 Change in the scatter light intensity at 90° for wheat beers with a 90°:25° ratio of 0.5–0.6 measured at 12 °C

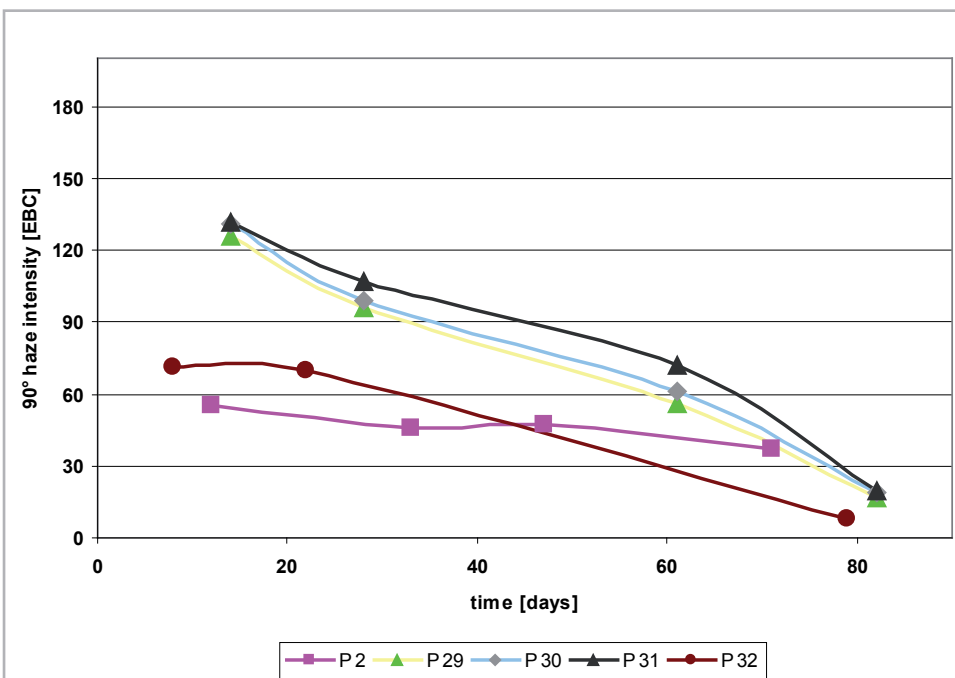


Fig. 2 a Change in the scatter light intensity at 90° for wheat beers with a 90°:25° ratio of 0.6–0.7 measured at 12 °C

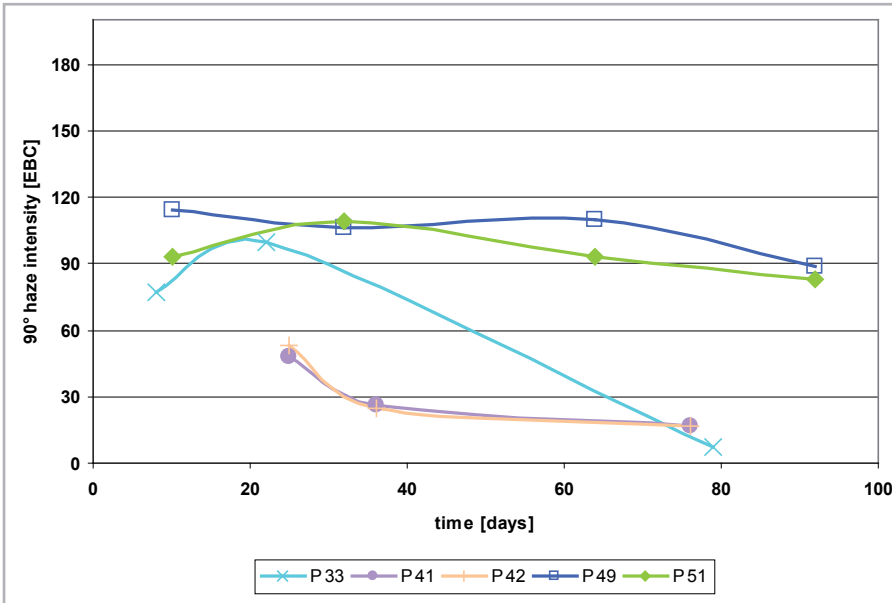


Fig. 2 b Change in the intensity at 90° for turbidity for wheat beers with a 90°:25° ratio of 0.6–0.7 measured at 12 °C

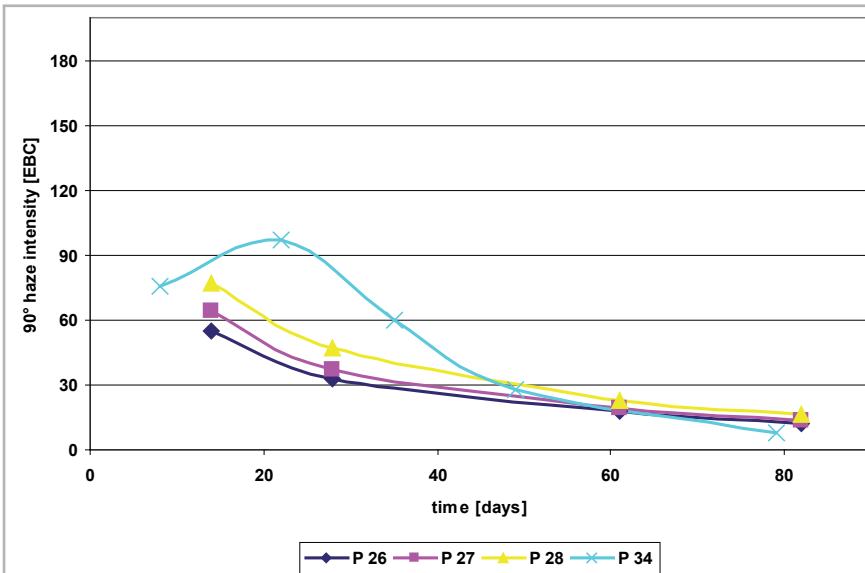


Fig. 3 Change in the scatter light intensity at 90° EBC for wheat beers with a 90°:25° ratio of 0.7–0.8 measured at 12°C

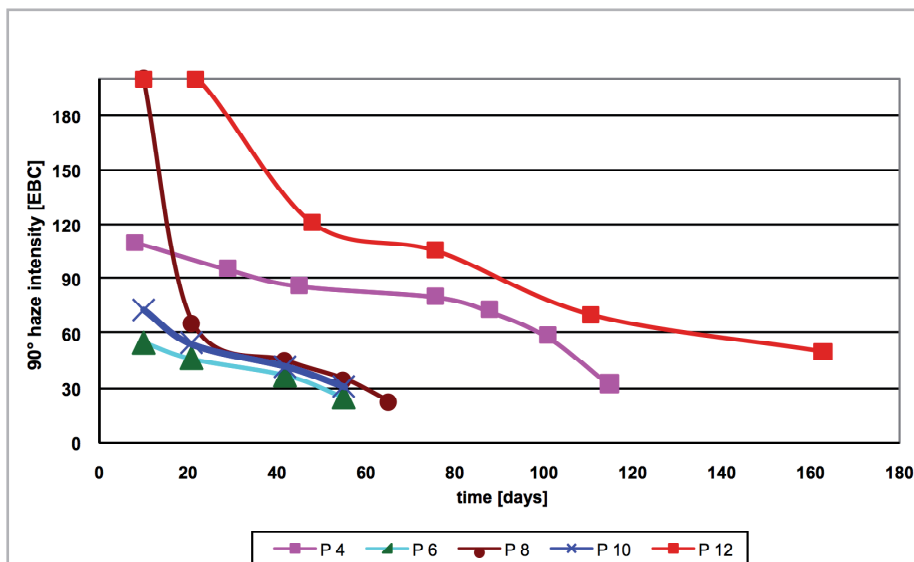


Fig. 4 a Change in the scatter light intensity at 90° for wheat beers with a 90°:25° ratio of 0.9–1 measured at 12 °C

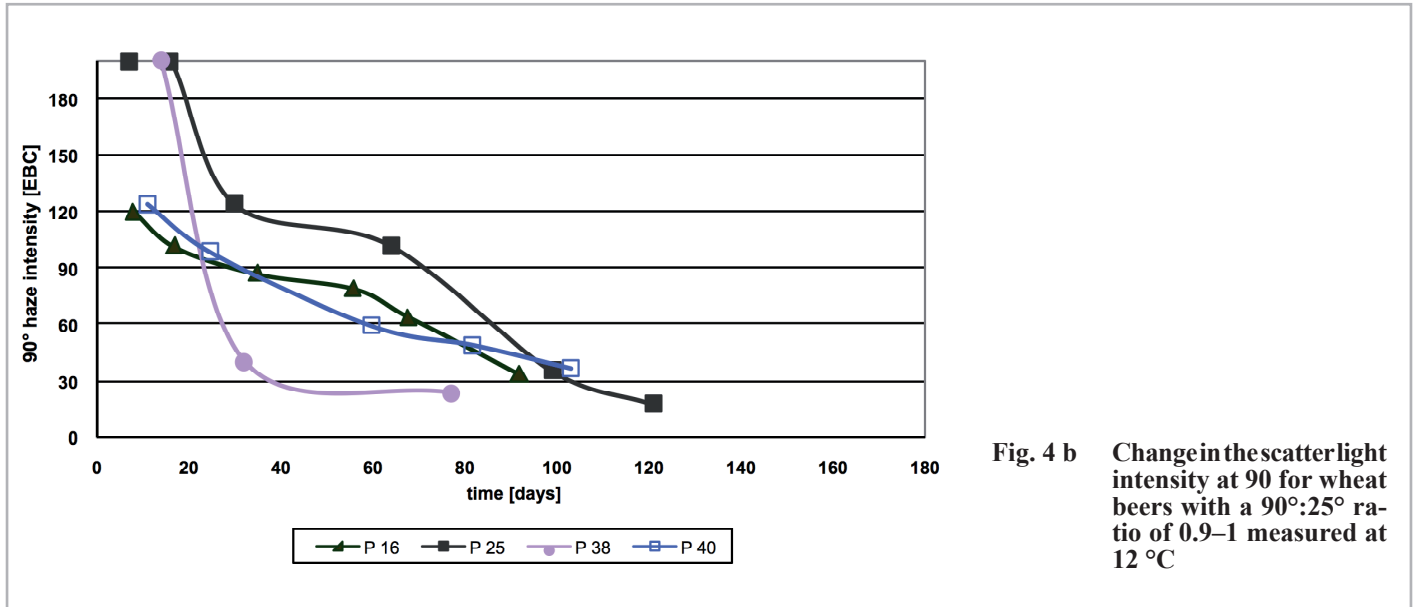


Fig. 4 b Change in the scatter light intensity at 90° for wheat beers with a 90°:25° ratio of 0.9–1 measured at 12 °C

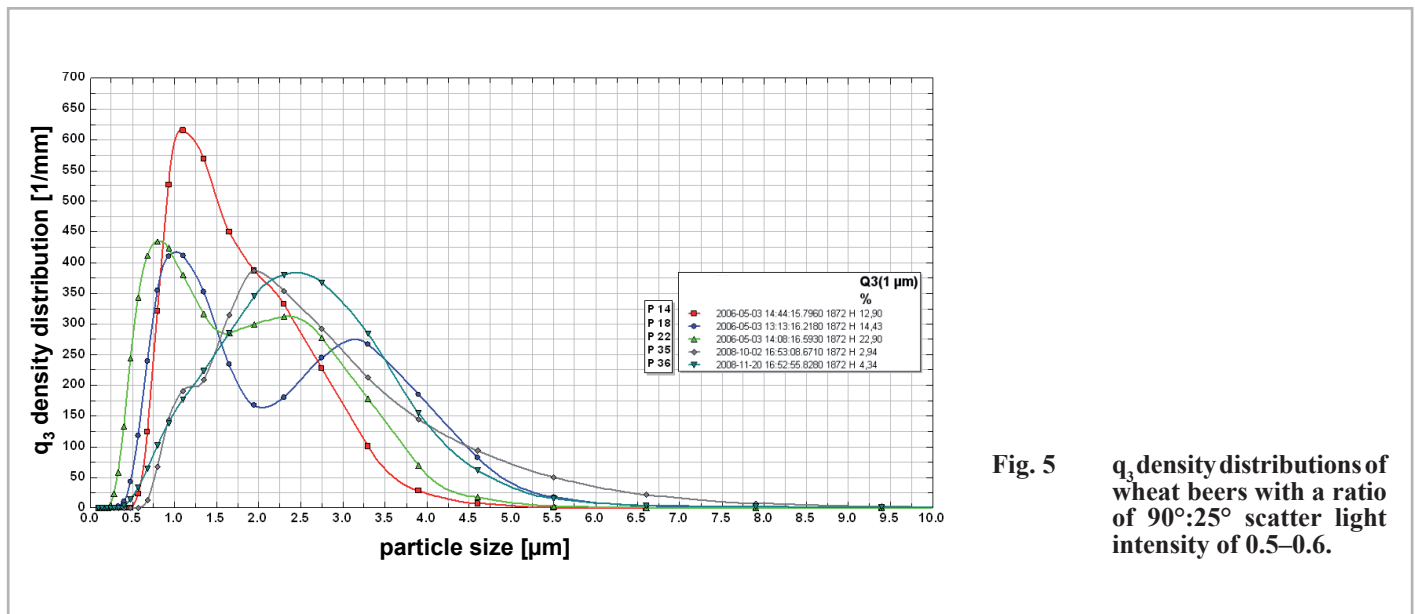


Fig. 5 q_3 density distributions of wheat beers with a ratio of 90°:25° scatter light intensity of 0.5–0.6.

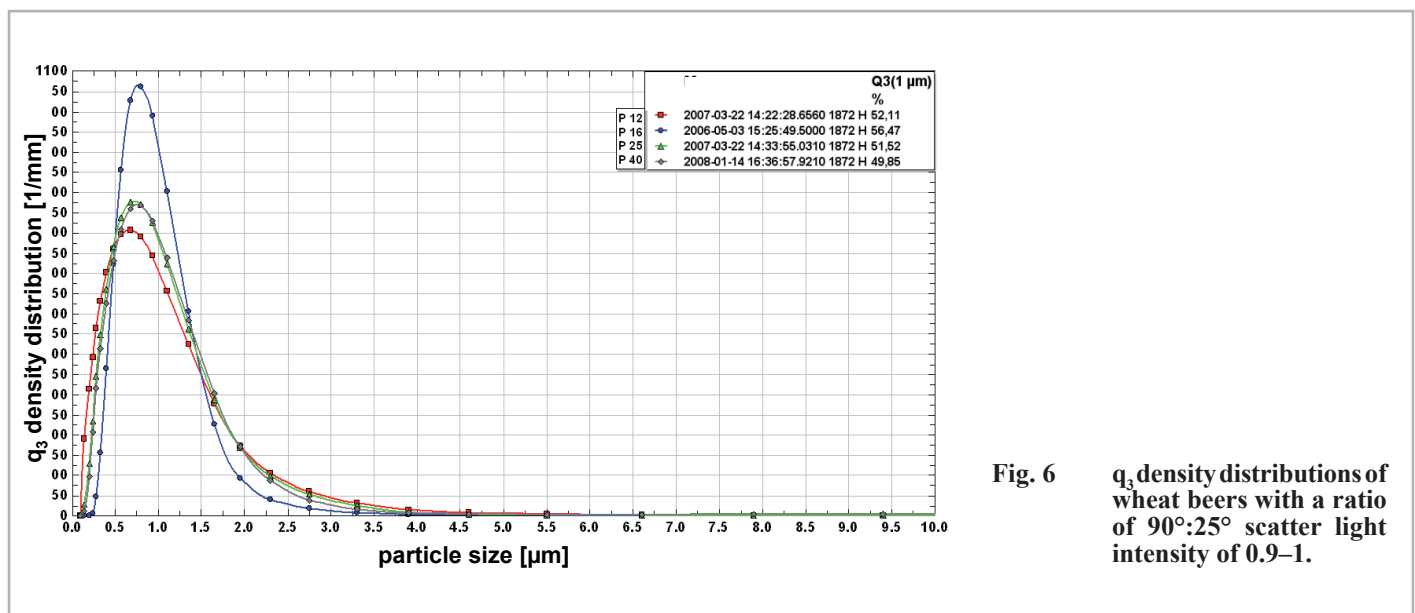


Fig. 6 q_3 density distributions of wheat beers with a ratio of 90°:25° scatter light intensity of 0.9–1.