M. Kusche and E. Geiger

Kinetics of haze formation in beer – turbidity and flavan-3-ols

Kinetics of haze formation were studied by observing the development of turbidity, the correlation between built aggregates and flavan-3-ols and the reduction of these polyphenols during storage of different stabilised beers at different temperatures. Sample preparation was done by solid phase extraction followed by a HPLC-DAD.
Kinetics of haze formation was influenced by the amount of flavan-3-ols in fresh beer as well as by the storage temperature of bottled beer. Although turbidity showed the same measured value, the reactive amount of flavan-3-ols differed when the beer was stored at different temperatures.

Descriptors: kinetics, haze formation, turbidity, flavan-3-ols, polyphenols

1 Introduction

Beer is an unstable product. Its quality characteristics change from the day of bottling to the day of consumption. For brewers it is important that the product properties should not alter or at least not noticeably for the consumer. In this matter colloidal stability is a significant attribute. Hazy beers will be reclaimed immediately by the clients because of their visual weakness [1, 28].

Much has been learned about the development of chill haze. But aggregation of haze forming particles is a complex process which details are not completely enlightened so far.

Already in 1955 Benough and Harris recognised that tanning substances are involved in haze formation. After this time several authors tried to identify haze relevant substances by measurement of polyphenols and anthocyanogens [4, 20, 22, 28].

Chapon formed the term of tannoids. These are condensed phenolic substances which have the property to aggregate with proteins. He described haze formation in beer with a formula similar to the law of mass action. In this hypothesis proteins and tannins are in equilibrium with a tannin-protein-complex. By adding or reducing one of the involved substances the equilibrium can be shifted to the side of complex or soluble substances. During storage of a bottled beer the structures of the tannin-protein-aggregates get more complex and change into an insoluble state, a permanent turbidity [2, 6, 7, 8].

For Siebert et al. condensed proanthocyanidins like procyanidin B_3 and prodelphinidin B_3 are key substances for haze formation in beverages. McMurrough et al. confirmed this hypothesis for beer. Focal point of McMurrough's work was the flavan-3-ols and in particular catechin, epicatechin, procyanidin B_3 and prodelphinidin B_3. Combining in a formula the analysed amount of flavan-3-ols and haze sensitive proteins measured by tannic acid, the author tried to predict colloidal stability in lager beers [15, 16, 17, 18, 19, 25, 26].

Dr. Marc Kusche, Bitburger Braugruppe GmbH, Römermauer 3, D-54634 Bitburg; e-Mail: dr.marc.kusche@bitburger.de; Prof. Eberhard Geiger, Lehrstuhl für Technologie der Brauerei II, TU München, Alte Akademie 3, D-85350 Freising

Tables and figures see Appendix

Haslam et al. worked on polyphenol-protein–interactions. Flavan-3-ols, especially proanthocyanidins have been detected as substances which are responsible for haze formation in beverages. These substances have the ability to react and aggregate with proteins and polysaccharins. Hydrophobic effects and hydrogen bonds are responsible for the development of reversible complexes. By transformation, e. g. oxidation, of the polyphenols the bonds change into covalent and irreversible types [3, 9, 10, 11, 12].

For other beverages like wine and juice the behaviour of haze active polyphenols during storage have been analysed. The results showed that the concentration of these polyphenols was reduced during aging. The reduction followed a reaction of first order [5, 13, 23, 27, 29].

It is known, that the oxidation of flavan-3-ols to the reactive orthochinon is determining for the reaction rate in haze formation. The intermediate products have the ability to react with a multitude of substances and form visible haze particles [11, 12, 23, 24].

Haze formation in beer is mainly described by a two phase model, divided in a lag- and a log-phase. In the past these phases were analysed separately. McMurrough et al. concentrated their work on the log-phase whereas Leemanns et al. tried to predict colloidal stability of beer by studying the lag-phase [14, 17, 19].

Aim of this work was to describe the reduction of haze active polyphenols of different stabilised beers during storage at different temperatures by reaction kinetics. Hypothesis that haze formation and flavan-3-ols reduction are reactions of first order have been proven. Furthermore the possible correlation between haze formation and flavan-3-ols has been examined.

2 Materials and methods

2.1 Beer treatment

Unfiltered lager beer from a German brewery was treated with no stabiliser, 100 g/hl Xerogel and 30 g/hl Xerogel plus 20 g/hl PVPP (single use) during filtering. The filtered and bottled beers were stored at 4, 9, 20, 30 and 40 °C. For haze measurement (scattered light at 90 ° angle) the samples were cooled down to 0 °C for 24 h. Measurement was done on an analyser from Monitek, Düsseldorf.

After quantifying the turbidity, samples were centrifuged at 0 °C and 13000 rpm for 1 h. The supernatant was decanted carefully and analysed for flavan-3-ols by HPLC.

2.2 Flavan-3-ols by HPLC

Sample preparation was done using a solid phase extraction on polyamide (PA 1000 mg Macherey-Nagel). The column was initially conditioned with 10 ml H_2O. Than 40 ml of the degassed sample was added. Afterwards the column was washed with 10 ml H_2O and dried with N_2. The polyphenols were eluted 4 times with 1 ml of N,N-dimethylformamide solution (85 % v/v). The elute was filled up to 4 ml and filtered through a 0.45 µm filter and then injected into the HPLC system. This method based on a sample preparation of Papagiannopoulos et al., which was modified for beer [21].

The HPLC was a Perkin Elmer automatic sampler, 200 series, with a diode array detector, spectrum 200–400 nm and chromatogram at 275 ± 5 nm. Pre column was a CC 8/4 Lichrospher 100-5 RP-18 ec, column was a Lichrospher 100-5 RP-18 ec, length 250 mm.

HPLC conditions: Injection volume 50 µl, flow rate 0.8 ml/h, temperature 30 °C, solvent A: 1 % acetic acid (v/v), solvent B: 1 % acetic acid in acetonitrile (v/v). The gradient was as follows: 5 min 2.5 % B, in 35 min to 7.5 % B (curve 1), in 60 min to 78 % B (curve 4), 5 min 78 % B.

Standards: (+)-catechin, (+)-epicatechin from Sigma-Aldrich, Taufkirchen, Germany; procyanidin B3 from Leuven Bioproducts, Leuven, Belgium; prodelphinidin B3 from Institut für pharmazeutische Chemie, Universität Münster, Germany. Recovery: (+)-catechin 95 %, (+)-epicatechin 93 %, procyanidin B_3 93 %, prodelphinidin B_3 92 %. All chemicals were HPLC grade.

3 Results and discussion

3.1 Flavan-3-ols and haze formation

Different stabilised beers, and therefore containing different amounts of flavan-3-ols, have been stored at various temperatures (4, 9, 20, 30 and 40 °C).

Trying to predict the colloidal stability of these beers by analysing the flavan-3-ols was not possible. The amount of single substances and the sum of monomers, dimers and all detected flavan-3-ols in the fresh beers (Table 1) did not correlate with the resulting haze formation.

In the next step it was analysed if the formed turbidity correlates to the reduction of flavan-3-ols. Therefore the concentration of these substances which might have reacted during storage was compared to the measured turbidity (scattered light; 90 ° angle). For this reason chill haze had to be separated by centrifugation. The supernatant was analysed for flavan-3-ols. The decrease of substances was calculated with following equation:

$$\Delta c = c_0 - c_t$$

With c_0 was the concentration at the time t = 0 and c_t was the concentration at time > 0.

The results (fig. 1–7) showed a good correlation between the concentration of haze and the sum and single substances of monomeric flavan-3-ols, respectively. In this case the kind of stabilisation was irrelevant. In contrast the correlation of the condensed flavan-3-ols' reduction and the resulted turbidity was influenced by the stabilisation treatment. The coefficient of determination showed a better correlation when the product was not treated with PVPP.

Different temperatures showed different haze development rates and chill haze compositions. At higher temperatures less flavan-3-ols were needed to create the equivalent turbidity, measured in EBC, than at lower temperatures. This suggested that other substances must have an increasing influence on haze formation at higher temperatures.

Haze formation rates and the resulting aggregates were influenced by the starting concentration of flavan-3-ols and the storage temperatures of the bottled beer.

3.2 Mechanisms of haze formation

In the first part of this work the coherence of measured turbidity and analysed flavan-3-ols have be studied. Following the development of haze over the time and the resulting reduction of flavan-3-ols will be examined. First the mechanism of haze formation will be explained by measuring the resulting turbidity over the time. In the second step the decrease of involved substances (flavan-3-ols) over the time will be analysed.

Previously it was described that haze development in beer has two phases, a lag- and log-phase. In the past these phases were analysed separately. By looking at the complete haze formation in products like wine and juice it could have been shown, that development of turbidity follows a first-order reaction. Here it has been tested if chill haze formation in beer also follows a reaction of first order. This reaction can be described by following stoichiometric equation:

$$A \xrightarrow{k} X$$

The concentration change of substrate A per time can be calculated as:

$$a / a_0 = e^{-kt}$$

With a_0 is the concentration at the time t = 0 and a the concentration at t > 0. The variable k is the temperature-sensitive rate constant.

This means for transferring the equation on haze formation in beer:

$$EBC_0 \xrightarrow{k} EBC$$

And for the haze development per time:

$$EBC / EBC_0 = e^{k \cdot t}$$

The rate constant k is here positive because chill haze was formed and not reduced during time. By logarithm of this term the following equation could be formed to:

$$\ln (EBC / EBC_0) = k \cdot t$$

If the hypothesis, that haze formation in beer is following a reaction rate of first order, would be right, all measured values over the time have to result on a straight line with different gradient depending on the storage temperature of the samples.

Looking at the figures 8–10 the temperature-sensitivity of haze formation is well documented. With higher temperature more haze was aggregated in the same time, which was expected.

For untreated beer the assumption, that the development of turbidity follows a first-order reaction, could not be verified. The coefficient of determination for the correlation between turbidity and time was too low to confirm this theory for all temperatures.

For the other cases, beer stabilised with Xerogel or Xerogel and PVPP, the reactions followed a rate of first order. With a coefficient of determination $r^2 > 0.90$ the hypothesis is acceptable.

By measuring the turbidity by photometry, it can only be an overview of mechanism of haze formation. For better results we have to analyse the behaviour of all the participated substances, if it is possible.

3.3 Reaction mechanism of flavan-3-ols during haze formation

Flavan-3-ols are one class of substances which might have an influence on the colloidal stability of lager beers. The decrease of these substances during storage of bottled beer at different temperatures was observed.

First of all an equation was needed which describes haze formation in bottled beer. In Chapon's equation which illustrates the complexation of proteins and tannins, a simple description for the complicate reaction of haze formation was found.

$$P + T \xrightarrow{k} PT$$

Here the reaction depends on the concentration of two substances, polyphenols/tannins and proteins, so this reaction is of second order. The logarithmical form of this reaction is:

$$\ln \frac{T \cdot P_0}{T_0 \cdot P} = (T_0 - P_0) \cdot k \cdot t$$

T_0 and P_0 are the tannin and protein concentrations at the time $t = 0$ and P and T the concentrations at the time > 0.

This formula can be simplified assuming, that the protein concentration is much higher than the concentrations of haze active polyphenols and the amount of these proteins would not noticeably change during haze formation, so $P_0 \approx P$. Or there is a partial reaction which takes place before the complexation, but determines the reaction rate of the protein polyphenol binding.

Both assumptions could be accepted as true. Chapon showed in his work, that only 2 mg of haze active protein in one litre beer are responsible for a turbidity of one EBC. Compared to the whole protein fraction in beer this is a very small part of it [8], although the haze active proteins could not be measured quantitatively until now.

For polyphenols several authors explained that these substances have to be activated before they can react with e.g. proteins. This activation is determining the reaction of haze formation [11, 12, 23, 24]. By these assumptions the equation can be simplified to:

$$\ln \frac{T}{T_0} = -k' \cdot t$$

With:

$$k' = k \cdot [P_0]$$

Here k' was the temperature-sensitive rate constant, because k and (P_0) were also unchangeable variables. Higher values of rate constant k' mean that the reducing of reactant and the reaction rate are faster. In picture 11 a diagram of the correlation between the logarithmical graphs of polyphenol reduction and time is shown. The graphs have to be differentiated by temperature [29].

For untreated and Xerogel stabilised beer the correlation of procyanidin B_3 and prodelphinidin B_3 was with $r^2 > 0.8$ quite high compared to (+)-catechin and (+)-epicatechin. In the stabilised beers the rate constants for monomeric flavan-3-ols were lower than for dimeric. This means that prodelphinidin B_3 and procyandin B_3 reacted faster then catechin and epicatechin. This confirmed other researchers' results which say that polyphenols with a higher degree of polymerisation are more reactive [10, 25].

By comparing the constant rate k' of the different stabilised beers, the highest results have been calculated for untreated beer. Here k' was up to four times higher compared to the stabilised beers. The reduction of flavan-3-ols depended on the amount of the substances in the fresh bottled beer. Higher concentrations of these polyphenols showed also higher reduction rate. But the rate of haze formation did not correlate significantly with the concentration of flavan-3-ols in the fresh beer. Therefore haze formation had to base on different reaction mechanism, because the rate of same reactions is directly proportional to the amounts of reactants.

4 Conclusion – summary

Mechanisms of haze formation in beer were described by reaction kinetics. Therefore influences of different temperatures on the formed agglomerations were analysed.

First of all the formation of haze in combination with the flavan-3-ols was described. The amount of reacting flavan-3-ols was correlated to the turbidity in EBC units. The agglomeration of the particles was temperature-sensitive. At lower temperatures more flavan-3-ols were needed to cause a turbidity which was equivalent to turbidity at higher temperatures. This indicates that the haze had the same quantity but not the same composition.

The kinetic of haze formation for stabilised beer followed a reaction of first order. Distinctive lag- and log-phases were observed for different treated beers. On the other hand untreated beer did not definitely correlate with a reaction system.

The decrease of haze active polyphenols was analysed during beer ageing. To describe the reduction of the flavan-3-ols an equation based on Chapon's model was developed. With this equation the reduction of these substances could be calculated. It was shown that the decrease of these polyphenols was temperature-sensitive and depended on their concentration in the fresh beer. But the reaction rate did not correlate proportional to the content of the flavan-3-ols, so other reaction systems or substances could be involved.

Further improvement of polyphenol analyses, in particular for higher condensed flavan-3-ols, and consideration of other haze active substances, e.g. proteins, polysaccharins, will result in a better understanding of the mechanism of haze formation in beer.

5 Acknowledgment

The financial support for this project was generously provided by the Wissenschaftsförderung der Deutschen Brauwirtschaft e.V..

Many thanks to Prof. Geiger who enabled me to graduate at his professorship.

6 References

1. Bamforth, C. W.: Beer Haze, Journal of The American Society of Brewing Chemists, **57** (1999), pp. 81-90.
2. Batchavarov, V. and Chapon, L.: Vorausbestimmung der kolloidalen Bierhaltbarkeit, Monatsschrift für Brauwissenschaft, **38** (1985), pp. 331-341.
3. Baxter, N.; Lilley T.; Haslam, E. and Williamson, M.: Multiple Interactions between Polyphenols and a Salivary Proline-Rich Protein Repeat Result in Complexation and Precipitation, Biochemistry, **36** (1997), pp. 5566-5577.
4. Bengoudh, W. I. and Harris, G: General Composition of Non-biological Hazes of Beers and some Factors in Their Formation. Part I, Journal of the Institute of Brewing, **61** (1955), pp. 134-145.
5. Cemeroglu, B.; Velioglu, S. and Isik, S.: Degradation Kinetics of Anthocyanins in Sour Cherry Juice and Concentrate, Journal of Food Science, **59** (1994), pp. 1216-1218.
6. Chapon, L.: Der Begriff Tannoide, Monatsschrift für Brauwissenschaft, **46** (1993), pp. 263-279.
7. Chapon, L.: Nephelometry as a method for studying the relations between polyphenols and proteins, Journal of the Institute of Brewing, **99** (1993), pp. 49-56.
8. Chapon, L.: The mechanics of beer stabilization, Brewer's Guardian, **123** (1994), p. 46-50.
9. Haslam, E.: Polyphenol-Protein Interactions, Biochemistry Journal, **139** (1974), pp. 285-288.
10. Haslam, E.: Complexation and oxidative transformation of polyphenols, Polyphenols **94** (1995), INRA, Paris, pp. 45-55.
11. Haslam, E.: Practical Polyphenolics – From Structure to Molecular Recognition and Physical Action, 1998, Cambridge University Press, Cambridge.
12. Haslam, E.; Luck, G.; Liao, H.; Murray, N. J.; Grimmer, H. R.; Warminski, E. E.; Williamson, M. P. and Lilley, T. H.: Polyphenols, astringency and proline-rich proteins, Phytochemistry, **37** (1994), pp. 357-371.
13. Ibarz, A.; Bellmunt, S. and Bota, E., 1992: Unterschiedliche nicht enzymatische Bräunungsprozesse während der Lagerung von Apfelsaftkonzentrat, Flüssiges Obst, **59** (1992), pp. 9-11.
14. Leemans, C.; Pellaud, J.; Mélotte, L. and Dupire, S.: Opportunities for lag phase prediction: a new tool to assess beer colloidal stability, Proceedings of the 29th EBC Congress, (2003).
15. McMurrough, I.: The colloidal stabilisation of beer by treatment with polyvinylpolypyrrolidone, Cerevisia Biotechnology, **23** (1998), pp. 27-34.
16. McMurrough, I. and O'Rourke, T.: New Insight Into the Mechanism of Achieving Colloidal Stability, MBAA Technical Quarterly, **34** (1997), pp. 271-277.
17. McMurrough, I.; Kelly, R. J.; Byrne, J. and O'Brien, M.: Effect of the Removal of Sensitive Proteins and Proanthocyanidins on the Colloidal Stability of Lager Beer, Journal of the American Society of Brewing Chemists, **50** (1992), pp. 67-76.
18. McMurrough, I.; Madigan, D. and Kelly, R. J.: The Role of Flavanoid Polyphenols in Beer Stability, Journal of the American Society of Brewing Chemists, **54** (1996), pp. 141-148.
19. McMurrough, I., Madigan, D. and Kelly, R. J.: Evaluation of Rapid Colloidal Stabilization with Polyvinylpolypyrrolidone (PVPP), Journal of the American Society of Brewing Chemists, **55** (1997), pp. 38-43.
20. Narziss L. and Gromus J.: Stabilisierungsversuche mit polyphenolreichen Bieren, Brauwissenschaft, **35** (1982), pp. 198-203.
21. Papagiannopoulos, M.; Zimmermann, B.; Mellenthin, A.; Krappe, M.; Maio, G. and Galensa, R.: Online coupling of pressurized liquid extraction and high-performance liquid chromatography for automated analysis of proanthocyanidins in malt, Journal of Chromatography A, 958 (2002), pp. 9-16.
22. Posada J.: Anthocyanogenes and head-space air in relation to colloidal stability of beer, Journal of the Institute of Brewing, **75** (1969), pp. 50-54.
23. Rechner, A.: Einfluss der Verarbeitungstechnik auf die Polyphenole und die antioxidative Kapazität von Apfel und Beerenobstsäften, Dissertation, Justus-Liebig-Universität Giessen, 2000.
24. Robards, K.; Prenzler, D.; Tucker, G.; Swatsiang, P. and Glover, W.: Phenolic compounds and their role in oxidative processes in fruits, Food Chemistry, **66** (1999), pp. 401-436.
25. Siebert, K. J.: Effects of Protein-Polyphenol Interactions on Beverage Haze, Stabilization, and Analysis, Journal of Agricultural and Food Chemistry, **47** (1999), pp. 353-362.
26. Siebert, K. J.; Lynn, P. Y. and Carrasco, A.: Formation of Protein-Polyphenol Haze in Beverages, Journal of Agricultural and Food Chemistry, 44 (1996), pp. 1997-2005.
27. Tajchakavit, S.; Boye, J. I.; Bélanger, D. and Couture, R.: Kinetics of haze formation and factors influencing the development of haze in clarified apple juice, Food Research International, **34** (2000), pp. 431-440.
28. Wackerbauer, K. and Anger, H.-M.: Bierstabilisierung unter besonderer Berücksichtigung der Polyphenole, Monatsschrift für Brauwissenschaft, **37** (1984), pp. 153-161.
29. Westphal, G.; Buhr, H. and Otto, H.: Reaktionskinetik in Lebensmitteln, Springer-Verlag, Berlin, Heidelberg, New York, 1996.

Received 13 November, 2006, accepted 16 January, 2007

Appendix

Table 1 Concentration in µMol of flavan-3-ols in fresh beer

Stabilisation with	-	Xerogel	Xerogel + PVPP
Catechin	21.32	18.70	9.61
Epicatechin	4.93	3.49	3.21
Σ Monomer	26.25	22.19	12.82
Procyanidin B_3	14.24	10.93	9.06
Prodelphinidin B_3	25.09	23.91	16.78
Σ Dimer	39.33	34.84	25.84
Σ Flavan-3-ole	65.58	57.03	38.66

Table 2 Coefficient of determination of the correlation between sum of flavan-3-ols and the measured turbidity of different stabilised beers

Temperature [°C]	-	Xerogel	Xerogel + PVPP
4	0.96	0.96	0.88
9	0.81	0.98	0.71
20	0.98	0.96	0.86
30	0.92	0.90	0.66
40	0.97	0.92	0.82

Table 3 Coefficient of determination for the correlation of turbidity formation to time, described by a reaction of first order

Stabilisation with	-	Xerogel	Xerogel + PVPP
4 °C	$r^2 = 0.57$	$r^2 = 0.97$	$r^2 = 0.94$
9 °C	$r^2 = 0.67$	$r^2 = 0.96$	$r^2 = 0.76$
20 °C	$r^2 = 0.77$	$r^2 = 0.93$	$r^2 = 0.95$
30 °C	$r^2 = 0.78$	$r^2 = 0.96$	$r^2 = 0.93$
40 °C	$r^2 = 0.67$	$r^2 = 0.92$	$r^2 = 0.91$

Table 4 Temperature-sensitive rate constant and coefficient of determination for the reduction of flavan-3-ols of an untreated beer

Temperature	Catechin		Epicatechin		Procyanidin B_3		Prodelphinidin B_3		Σ Summe	
[°C]	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2
4	0.044	0.77	0.079	0.44	0.046	0.90	0.060	0.98	0.029	0.95
9	0.056	0.78	0.096	0.40	0.055	0.94	0.060	0.98	0.041	0.93
20	0.059	0.64	0.105	0.57	0.061	0.92	0.067	0.95	0.044	0.95
30	0.063	0.77	0.102	0.35	0.068	0.84	0.080	0.85	0.056	0.86
40	0.056	0.94	0.094	0.69	0.070	0.90	0.088	0.92	0.070	0.86

Table 5 **Temperature-sensitive rate constant and coefficient of determination for the reduction of flavan-3-ols of a beer stabilised with Xerogel**

Temperature	Catechin		Epicatechin		Procyanidin B_3		Prodelphinidin B_3		Σ Summe	
[°C]	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2
4	0.004	0.67	0.008	0.50	0.011	0.90	0.006	0.97	0.007	0.95
9	0.005	0.41	0.011	0.82	0.010	0.88	0.009	0.93	0.007	0.94
20	0.010	0.82	0.015	0.62	0.015	0.85	0.012	0.75	0.011	0.88
30	0.010	0.95	0.013	0.76	0.023	0.97	0.024	0.95	0.017	0.97
40	0.012	0.79	0.015	0.77	0.029	0.98	0.029	0.98	0.021	0.97

Table 6 **Temperature-sensitive rate constant and coefficient of determination for the reduction of flavan-3-ols of a beer stabilised with Xerogel and PVPP**

Temperature	Catechin		Epicatechin		Procyanidin B_3		Prodelphinidin B_3		Σ Summe	
[°C]	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2	k' [D^{-1}]	r^2
4	0.001	0.36	0.005	0.77	0.002	0.58	0.009	0.92	0.005	0.88
9	0.001	0.67	0.003	0.67	0.003	0.42	0.010	0.90	0.005	0.91
20	0.001	0.24	0.008	0.80	0.007	0.73	0.015	0.74	0.008	0.74
30	0.007	0.66	0.012	0.92	0.015	0.85	0.019	0.69	0.014	0.84
40	0.008	0.91	0.011	0.81	0.017	0.90	0.021	0.79	0.015	0.87

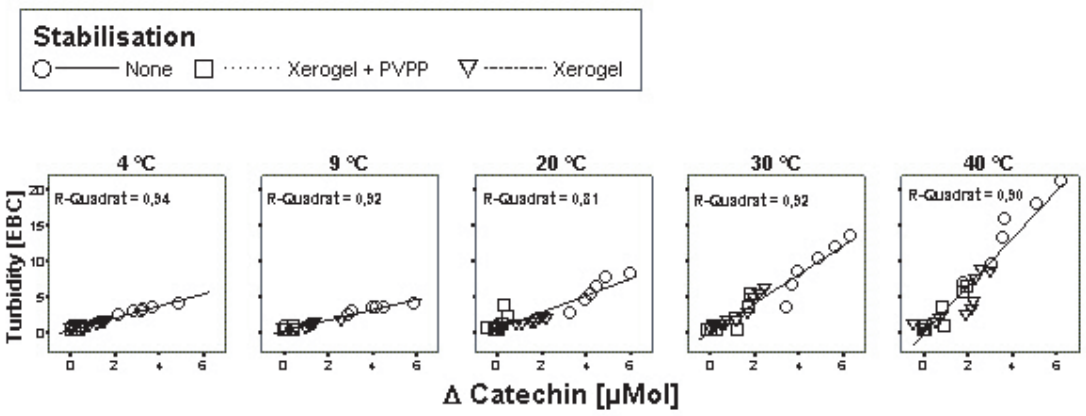

Fig. 1 **Correlation between (+)-catechin reduction and turbidity**

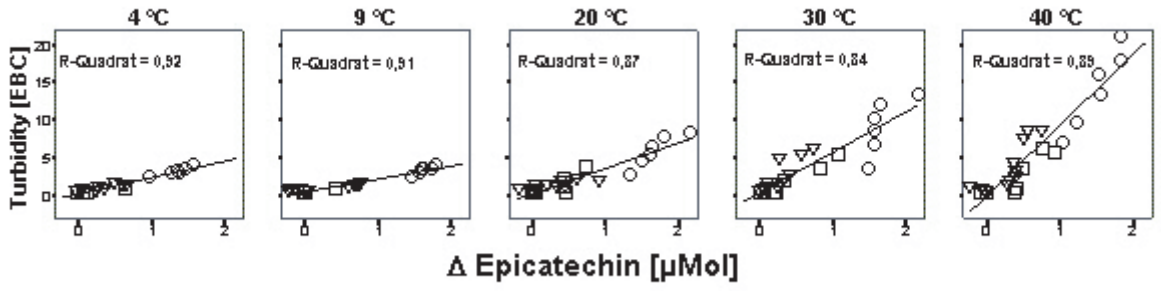

Fig. 2 Correlation between (+)-epicatechin reduction and turbidity

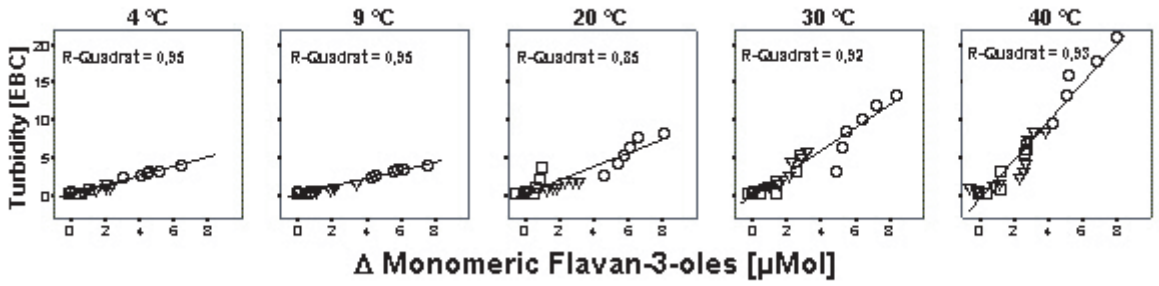

Fig. 3 Correlation between monomeric flavan-3-ols and turbidity

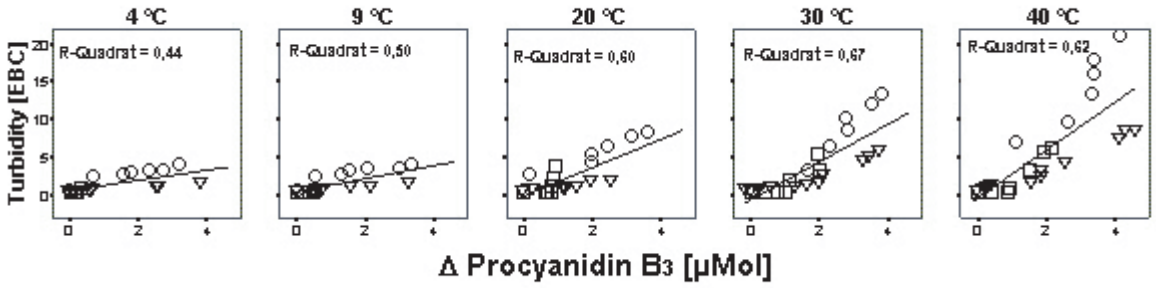

Fig. 4 Correlation between prodelphinidin B_3 and turbidity

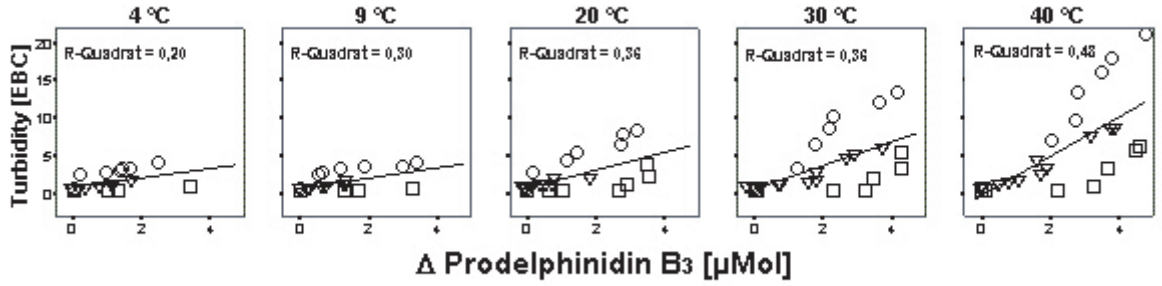

Fig. 5 Correlation between procyanidin B_3 and turbidity

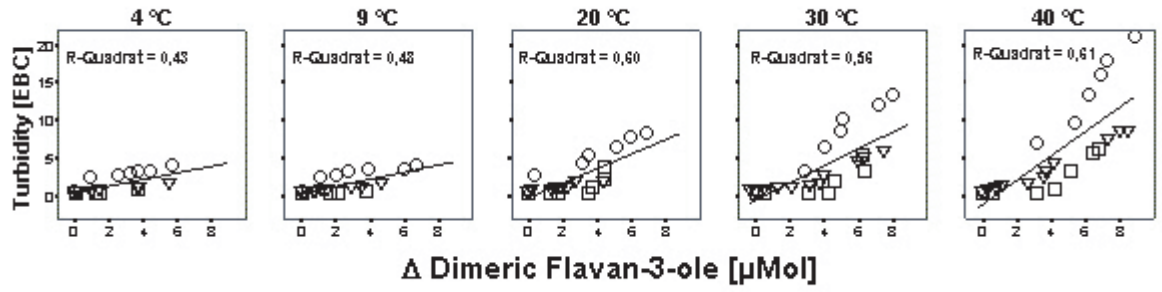

Fig. 6 Correlation between dimeric flavan-3-ols and turbidity

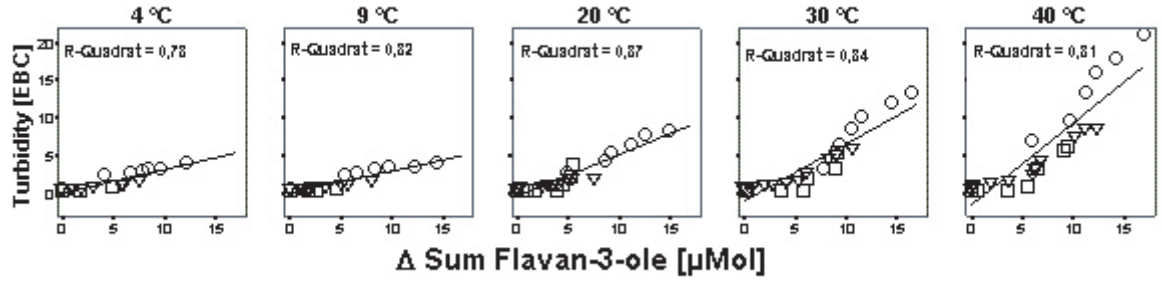

Fig. 7 Correlation between sum of all detected flavan-3-ols and turbidity

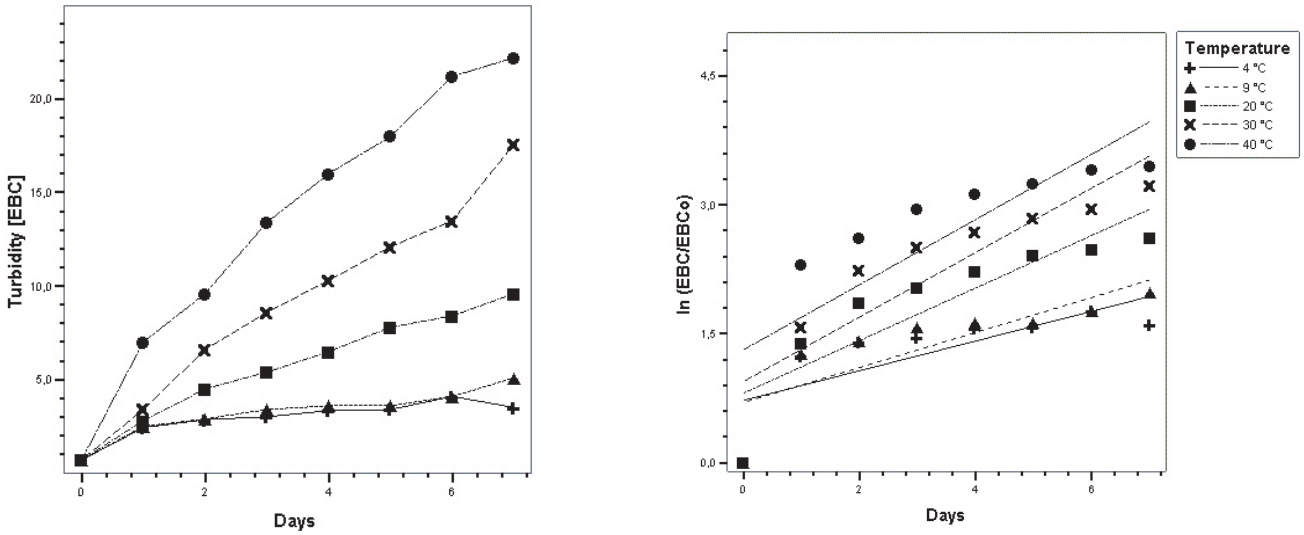

Fig. 8 **Diagram of haze formation and logarithmical graph for an untreated beer**

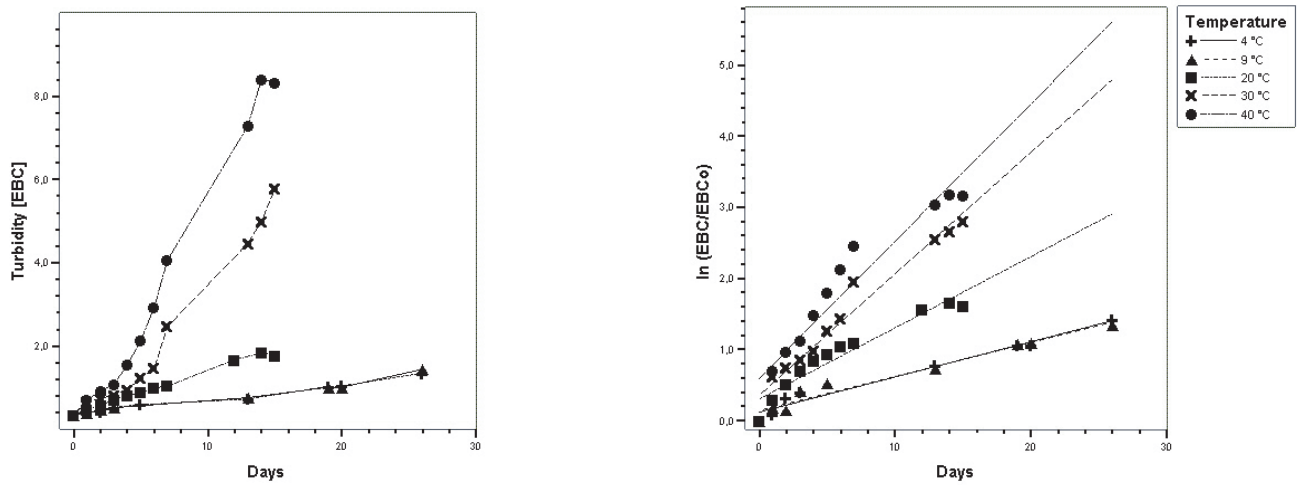

Fig. 9 **Diagram of haze formation and logarithmical graph for a beer stabilised with Xerogel**

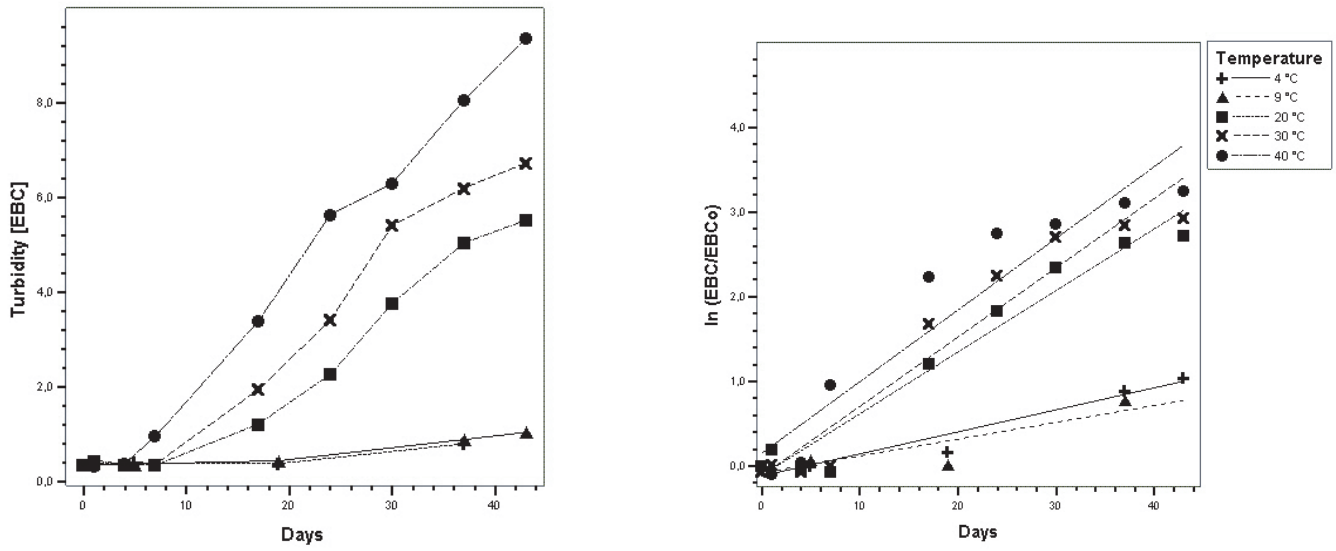

Fig. 10 Diagram of haze formation and logarithmical graph for a beer stabilised with Xerogel and PVPP

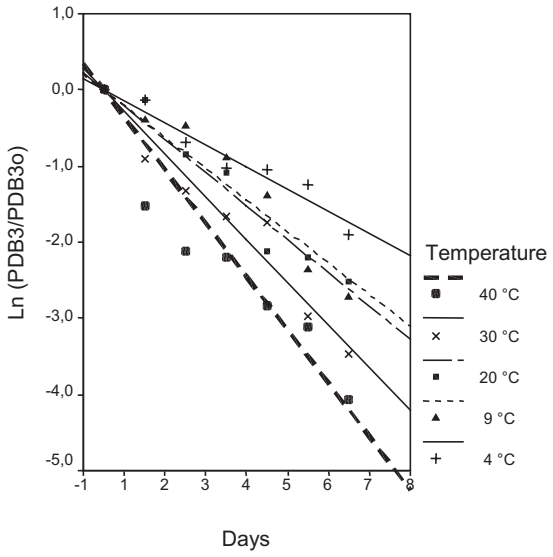

Fig. 11 Correlation between the logarithmical graphs of polyphenol B_3 reduction and time of an untreated beer