THE ROLE OF THE PVPP IN THE REMOVAL OF POLYPHENOLS FROM BEER.

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Abstract

Haze of beer in the first sequence is presented as the cause of the formation of complexes between proteins and polyphenols in the composition of beer. To decrease the sensitivity to the formation of the haze can be achieved by decreasing the content of protein and polyphenols, or reduce the size of molecules to proteins and polyphenols. In the experimental part of this work are examined changes in sustainability among the beer completely without sustainable, beer stabilized with different amounts of PVPP, and combinations with silica gel and PVPP. Time stability is determined by the methods of force Test (0/60). Testing with force test (0/60) was used as a method of determining shelf life of beer. Besides checking the changes are the primary parameters of beer such as: extract, alcohol foam, acridity, turbidity, color and pH value. Combined treatment as is expected has shown a high level of stability of beer. Selective Removal of part of polyphenols and protein fractions, with the balance located between these factors, it is possible to regulate the length of the beer be a long lasting.

Key words: *beer, polyphenols, haze, protein, PVPP, stabilization.*

When we discuss about the quality of the beer, it is a clouding of the main parameters of quality. Currently, brewers have offered the length of beer from 6-12 months and frequent cases to guarantee stability even 18 months. To explain the problem should be mentioned that proteins, carbohydrates and polyphenols metal ions are mainly responsible for the formation of fog in beer. Phenol compounds have come from malt and beer Lupo and their content in beer depends on the technological process involved. Depending on the structure and molecular size they affect us, taste, color and foam. Polyphenols most important included are anthocyanogene, catechins and flavones (1).

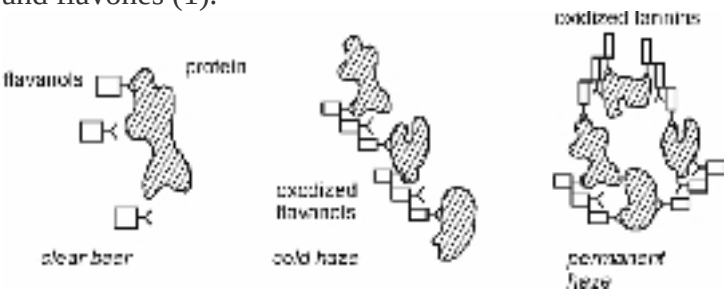

Fig. 1. Compounds influencing formation of haze of various types (2)

Hydrogen bridges between molecules of polyphenols and polypeptides are formed by hydroxyl groups of polyphenols and oxygen atom of the peptide group. If the temperatureis in the range from +5 to – 2°C, the reaction of phenol and protein compounds produces haze (Fig. 1). The formation of this, so-called cold haze, represents a reversible process and it disappears at +20°C. While low-molecular flavanols in the reaction with tannins do not influence haze, irreversible haze is formed in the reaction with oxidized tannins (3).

In order to improve the colloidal stability of beer it is necessary to remove both proteinand polyphenolic fractions. In the present-day technology this is carried out with hydroand xerogels, polyvinylpolypirrolidone (PVPP), as well as with combined agents. Besides,

in a number of countries it is allowed to use enzymes, ascorbic acid, and other preparations.Whether the agents applied produce desired effects it is usually established using thehaze forcing test (0/40/0°C or 0/60/0°C). Although being reliable, this method is also connected with analytical errors, it is time-consuming, and does not allow a timelyintervention, i.e. the adjustement of stability parameters in the course of beer filtration. Beer haze is measured using process and laboratory photometers with two absorptionangles (25° and 90°). It should be noticed that neither filtration nor stabilization are conceived as measures for correcting mistakes made in the production process. Hence, from the very beginning, it is necessary to perform stringent control of the quality of all techno5 logical factors that influence beer quality, and especially of those that influence stability of its sensory parameters (2): To make more legible documentation, these parameters can be followed using special forms, as presented in Table 1 (4).

Table 1. Control form for monitoring quality of stabilization process with recoverable PVPP.

Sample for analysis	Type of analysis	Frequency	Limit value	Test/Comment
PVPP	Swelling volume	Each batch	< 60 ml	Acc. to test method and specification
PVPP suspension from dosing vessel	Concentration	After each regeneration	not limited	Not later than the 5th regeneration
PVPP suspension from dosing vessel	ash	Once a year	< 0.4 %	Acc. to test method and specification
PVPP suspension from dosing vessel	Control of regeneration	Once a year	Absorption capacity the same as with single-use PVPP	Adsorption steady state after regeneration must be achieved in full

The stabilization agents are added together with kieselguhr, i.e. at the stage of precoat filtration. These agents can improve quality of filtration and at the same time reduce the amount of kieselguhr. However, one must not forget that their addition increases the load of filtration surface (in kg/m2), irrespective of filter type (5). Often, stabilization is made with silica gels. Silica gels represent a group of highly porous adsorption means composed of colloidal silica. Silica gels serve for the removal of protein fractions and beer haze,
i.e. for achieving optimal physico-chemical stability. Silica gel can be added at the different stages of production process. The moment and amount depend on the product quality, technology applied, and technical facilities of the brewery. In Fig. 2 is sketched one of the possibilities of using silica gel. Silica gel can also be added in the course of pumping green beer from the fermentation tank to maturation tank, to the buffer tank, after beer maturation prior to kieselguhr filtration. Most often, silica gel is added together with kieselguhr or with single-use PVPP. When adding silica gel between the fermentation and maturation tank it is practiced to add 1/3 of the total amount via special dosage pump, the remaining 2/3 being added as usual at filtration. We distinguish essentially two types of silica gels – hydrogels with total water content <60% and xerogels with <10%. Depending on beer characteristics and desired shelf life, the recommended amounts are 40-100 g/hl for hydrogel and 30-70 g/hl for xerogel (6).

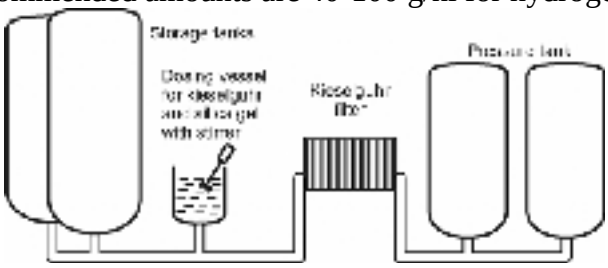

Fig. 2. Technological scheme of the system for removal of protein fractionwith silica gel, dosed together with kieselguhr (6)

Use of enzymes in the process of beer production is not allowed in all countries. For this purpose it is possible to use, for example, the enzyme obtained from the skin of papaya fruit (*Carica papaya*), whose enzymatic activity is due to two peptide hydrolases, papain and chymopapain. The enzymes do not remove haze fractions but reduce them to products that do not influence haze formation. They cleave high-molecular proteinaceous fraction to medium-molecular proteins (molar mass <103), peptides and amino acids. The addition
of 2-4 ml/hl of enzyme preparation directly to maturation tank it is possible to achieve a high degree of enzymatic degradation (6).
Beer stabilization can also be achieved with the aid of ascorbic acid; however, its usage is not allowed in some countries. Ascorbic acid improves colloidal stability of beer but does not solve the problem of excessive exposure to air in the course of packiging. A dose of 2-8 g/hl is added directly to beer, and in no case before or during filtration. Iron from the kieselguhr has an adverse effect on the reduction capacity of ascorbic acid (6). In addition to beer, PVPP is presently used for stabilization of wines and juices. There are two groups of PVPPs: for single and multiple use (recoverable PVPPs). In both cases unhindered adsorption of PVPP is achieved by its soaking in water before use. Beer stabilization with PVPP is carried out immediatelly after filtration and the amounts vary from 10 to 50 g/hl (2).

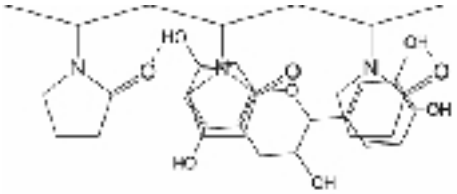

Fig. 3. Adsorption mechanism of PVPP (2)

The reaction of PVPP is based on the formation of hydrogen bridges between the carbonyl group of polyamides and phenolic group of polyphenols (Fig. 3). This bond yields 7 adsorption of polyphenols on insoluble stabilization agent (2). The amount of PVPP used for beer stabilization is limited by its physical properties. PVPP can be compressed, which, at a higher dosage can bring about an uncontrolled increase in pressure during filtration and filter clogging. For adding PVPP to a beer stream it is necessary to prepare first its m10% solution in warm water. Depending on the filter type, the precoat values vary between 175 and 225 g/m2. The allowed surface load of the filter must not be exceeded. With the single stabilization, the sum of all amounts used must not exceed the amount prescribed maybe the producer of the filtration equipment. The water-absorption capacity of PVPP is 6 l/kg. While maximal load of filtration elements can be easily calculated on the basis of the nominal parameters, the actual dosage of PVPP depends on the quality of filtration raw material and technological procedure. A usual dose is in the range of 20-50 g/hl (5). In addition to single-use PVPP large breweries have also systems for beer stabilization using recoverable PVPP, and stabilization process is carried out on a separate filter with horizontal sieves or filter candles. Stabilization process is stopped at the moment when the filtration cake on circular horizontal sieves fills all the free space between the sieves. Regeneration is carried out with hot alkali (NaOH 1.2-1.6%, 65°<T<85°C), which removes the polyphenols adsorbed on PVPP. Hot water (50°<t<70°C) is used to remove the excess of alkali from the stabilization cake, while cold, acidic washing (0.5-1% phosphoric acid) lowers pH value to below 7. Final rinsing with clean cold carbonized waterremoves the mineral residues. After completing regeneration PVPP is removed from the sieves by rotating the filter element, whereby it falls down to the filter bottom. Then, it is pumped to a receiver, to be dosed in the next stabilization operation (5). In previous sections we have seen that a balanced adsorption of proteins and polyphenols is more desirable than either removal of polyphenols or proteins alone for enhancing colloidal stability of beer. Therefore, the industry has developed various products which can be used in different production stages for beer stabilization. The addition of a new composition of a selected carrageenan and micronized PVPP improves the wort clarity and gives brighter wort colors. The use of this new product (Figs. 4 and 5) increases yield and throughput through the remainder of the downstream brewing process. It also allows minimizing of trub which is comprised of spent hops, precipitated proteins and other insoluble materials including tannoids. This experiment should show that the inadequate use of stabilization aids, lack of industrial equipment just as reliable and a fast determination method for prediction of shelf life result in negative influence on beer stability and fast creation of beer haze.

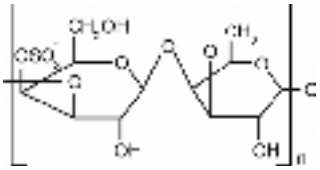

Fig. 4. κ-carrageenan

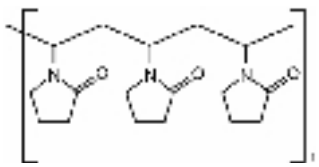

Fig. 5. Cross-linked polyvinylpyrollidone

EXPERIMENTAL WORK

The experiment and laboratory tests were carried out in an Austrian brewery. The stabilisation and filtration aids were obtained at this site. The new product “Brewbrite” was supplied from ISP and added (15 g/hl) during the last 10 minutes of the kettle boil, hence shortly prior to second (aroma) hoping. Subject of experiment was in all cases a “Lager” type beer with parameters shown in Table 2.

Filtered beer loses its clarity during maturing, and especially at low temperatures when it becomes opaque, i.e. when a precipitate is formed. To determine beer quality in the shortest time use is made of the accelerated haze forcing test, described in the MEBAK
methods of analysis (7). Result can be obtained already after several days upon beer packaging, and is expressed in “warm days”.

Analytical methods for extract, alcohol, bitterness, color, pH, foam, haze and shelf life of beer are described in MEBAK (7).

There is a whole range of the so-called global methods for the determination of polyphenolic compounds based on the characteristics of particular compounds for the determination. For this purpose use is made of EBC Method for the determination of total polyphenols. The analysis is based on the reaction of Fe2+ ions, forming in alkaline solution the colored complexes that can be measured spectrophotometrically (7). Beer bitterness was determined via *iso*-alpha-acids that are extracted with *iso*-octane. The method is also described in MEBAK (7).

Swelling volume was determined on the basis of the known amount of PVPP that is soaked in water and measured after 24 h. To 10 g of PVPP in a vessel of 250 ml, 50 ml of water were added and stirred for several minutes. The suspension was then transferred to a measuring cylinder and filled with water to 100 ml. Direct volume reading is carried out after 24 h. Ash was determined after soaking PVPP in 2 ml of sulfuric acid (1:1) in a weighed vessel. The vessel with PVPP was placed on a heater and incinerated mildly to the disappearance of white smokes. After that it was heated at T = 800°C ± 25°C and, upon cooling, weighed to calculate percentage with respect to the blank (4). Control of PVPP regeneration was carried out by the method of Harris and Rocketts described in MEBAK (7). Concentrations of anthocyanogens and tannins of the PVPP from the dossage vessel are compared after regeneration with those of pure, unused PVPP.

RESULTS AND DISCUSSION

In the experimental part of this study, we examined the life changing completely the free beer in beer stabilized stabilized with various doses of PVPP, and using silicate gel and combining new agents for beer stabilization after treatment with PVPP. In Fig. 6 illustrated the effect of different doses of PVPP on stability, long life in beer. Value of 2 units facts, EBC is a value limit of "acceptable" to the market.

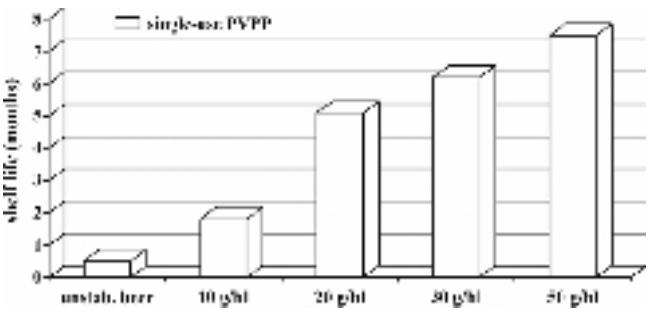

Fig. 6. Effect of different doses of single-use PVPP on beer stability.

With beer exports, is expected to blur will not exceed 2 EBC in 12 months time. As the deadline for unstable beer is only two weeks, with a dose of 20 g / hl of beer PVPP expectancy shows a strong increase. To achieve the 6 month period, it is necessary to use 40-50 g / hl PVPP for use in practice often leads to suffocating the filter. Recoverable PVPP has smaller volume of swelling, so that higher doses are possible. The effect of the above agents for the stability of beer is shown in Table 2.

Table 2. Comparison of unstabilized beer and beer treated with single-use PVPP.

Beer analysis	Blank unstab. beer	50 g/hl PVPP irrecov.
Extract (% mas)	10	10
Alcool (% vol)	4.3	4.3
Bitterness (BE)	19	20
Color (EBC)	8.0	7.5
pH	4.2	4.2
Foam (s) accord. to NIBEM	105	112
Initial haze (EBC) in bottle	0.72	0.64
Haze forcing test (0/60°C) (warm days)	0.4	9.5
Haze forcing test 1 week (0/60°C) (EBC)	13	1.1

In the test shown in Fig.7, stability was monitored by sampling multiple filtered beer that after every 60 minutes of filtration. Life beer is determined by test forcir (0/60 ° C). The highest rate of colloidal stability of beer showed that the combination of stabilized using silicate gel (xerogel) and the free recoverable PVPP. Beer was not stabilized, only in samples from the first hour of filtration showed a stability of 5 days warm, and soon thereafter was reduced to zero values. A linear decrease was observed in the colloidal stability of beer is only Silika stabilized gel. In contrast, only stabilize beer PVPP lost viability after hours before filtration, and then the level of colloidal stability has remained constant.

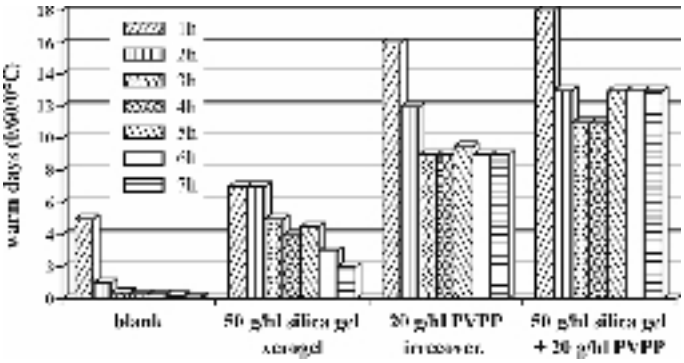

Fig. 7. Comparison of the effect of silica gel (xerogel) and PVPP (irrecover.) and filtration duration on colloidal stability of beer.

CONCLUSION

To achieve colloidal stability of beer is necessary to remove proteins-polyfenolice complex, or to prevent their formation. The process of stabilization should not have negative effects on the sensory characteristics such as beer, smell, taste, sight and foam. Combined treatment with PVPP Silica gel and has become a standard procedure that results in a product of very high quality. On the basis of the tests described it can be concluded that for obtaining optimal results, a dynamic regime of dosage should be conceived.. This regime will take time in adjusting the dose as agent in proportion to the absorptive capacity, which is subject to change in the course of filtration. Besides technological qualifications of the staff responsible for process control, efficient stabilization requires adequate processing equipment. The main parts of the equipment are: the PVPP-filters with coating to regenerate regeneration station, dosing valves and vessels, dosing pumps, filters for clarification, haze measurement equipment and a modern control system. Analytical problem stems from the fact that it is very difficult to predict what will be the effect of stabilization after using a selected agent.

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