Pulverization of Highly Viscous Barley Malt Extract Using a Supercritical Fluid Spray Process

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INTRODUCTION

Malt extract is a highly viscous, rich in sugars, water-based solution. It is produced by means of vacuum evaporation of a sugar solution (mash) in the brewing industry. It is a natural flavor and colorant and is widely used in baking, confectionery, breakfast cereals, malt beverages, dairy products, sauces and as a caramel substitute. The difficult handling and dosing of that viscous liquid product can be simplified when the product is pulverized. Commercially available malt extract powders are usually produced by spray-drying. Unfortunately the heat treatment during this process decreases the quality of the original product.

The principal chemical reaction that occurs during heating is the Maillard reaction, also called non-enzymatic browning. The reaction takes place between an amino acid and a reducing sugar. The reactive carbonyl group of the sugar reacts with the nucleophilic amino group of the amino acid and forms a variety of molecules responsible for odors and flavors [1]. During Maillard reaction the formation of intermediate compounds such as 5-Hydroxymethyl furfural and brown pigments occurs [2], thus the color of the product changes. Hence color measurement is a good indicator of heat stress and has been used successfully to calculate the rate constants and activation energies for nonenzymatic color development [3, 4].

In the present work, a high pressure method has been used to dry and pulverize malt extract. The method is based on a high-pressure spray technique called Particles from Gas Saturated Solutions (PGSS). Several foodstuffs and derived products like chocolate, cacao butter, and soy lecithin were already pulverized by PGSS [5]. This technique has been recently used for a gentle drying of aqueous green tea extracts [6]. Purpose of the present work is to analyze the influence of process parameters on product properties and quality (via change of color).

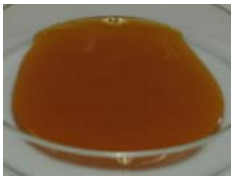
MATERIALS AND METHODS

Materials

Malt extract “Bavarian Pilsner unhopped” was supplied by company Weyermann (Bamberg, Germany). Its chemical composition is detailed in Table 1. Sugars were determined by HPLC, protein was analyzed by Kjeldahl and water was measured by Karl-Fischer titration.

Table 1: Composition of liquid malt extract and picture

Compound	Percentage (wt.-%)	Compound	Percentage (wt.-%)
Water	25,5	Glucose	6,4
Protein	5,8	Fructose	1,6
Maltose	39,3	Saccharose	1,9
Maltotriose	18,0	Salts, Vitamins	1,5



Color change due to thermal treatment

The evaluation of the influence of thermal treatment on the color of malt extract was carried out in a closed system. Malt extract was filled in stainless steel tubes using a syringe. The

tubes have an external diameter of 6 mm and wall thickness of 1 mm (Figure 1). They can be hermetically closed at both ends with threaded caps. The tubes were immersed in a temperature controlled and stirred oil bath at the selected temperature for a certain time according to the experimental design (Table 2). After thermal treatment, the tubes were submerged immediately in ice-water to stop chemical reaction (thermal shock). It can be assumed from transient heat transfer calculations, that malt extract right in the center of the tube does 90 % of the temperature change within 3 minutes. Thus, the required time for sample warm up can be neglected in comparison to the total experimental time of at least 30 minutes. The treated malt extract was taken out from the tubes and its color was determined according to 2.3. Thermal treatment and determination of color were carried out twice. Mean values were used to calculate color degradation reaction rates as a function of temperature. Reaction rates for higher temperatures were calculated using Arrhenius transformation.

Figure 1: Stainless steel tubes used for the analysis of the thermal treatment

Determination of the color

Color determination of the liquid and pulverized malt-extract was made according to the International Method for the determination of the color of beer and malt, which was approved by the Committee of the European Brewery Convention (EBC). It is a spectrophotometric determination at a wave length of 430 nm.

Four grams of malt extract (liquid or powder) were dissolved in distilled water to reach a concentration of 12 % of soluble solids. The obtained solution was filtrated twice; first, through a Sartorius filter paper no. 288 and afterwards through a PTFE membrane (0,45 µm). The filtrated solution was measured at 430 nm using a Shimadzu spectrophotometer. The obtained absorbance value multiplied by 25 gives the color EBC value.

Characterization of the powder

- Moisture content of the samples was measured by Karl Fischer titration (Mettler Toledo)
- Particle morphology was characterized using Scanning Electron Microscopy (SEM)

Principles of PGSS drying procedure

Figure 2 shows the flow scheme of the PGSS drying pilot plant. Maximum operating pressure of the plant is 200 bars and maximum temperature is 250°C.

Malt extract is pumped by a high-pressure pump to a static mixer, where compressed and preheated carbon dioxide (CO_2) is added. Both substances are mixed together intensively at high pressure during a short residence time of some seconds. Afterwards the mixture is sprayed through a single path nozzle into a spray tower, operated at ambient pressure. The expanding gas contributes to the formation of fine droplets. Due to the Joule-Thomson effect the gas cools rapidly down and depending on the conditions before expansion, the temperature in the spray tower decreases. Fine particles, CO_2 and water are exhausted by a blower through a cyclone, where the powder is separated from the gas. The produced powder is collected in a vessel. The design of the mixing elements (right side of Figure 2) facilitates the intensive mixture of malt extract and supercritical carbon dioxide under high pressure and elevated temperatures. During the mixing, supercritical carbon dioxide is partly dissolved in the malt extract, causing a decrease of the viscosity. Simultaneously, some high volatile

components of the multi-component system malt extract are also partially dissolved in the dense carbon dioxide. Thus, water is extracted from the malt extract.

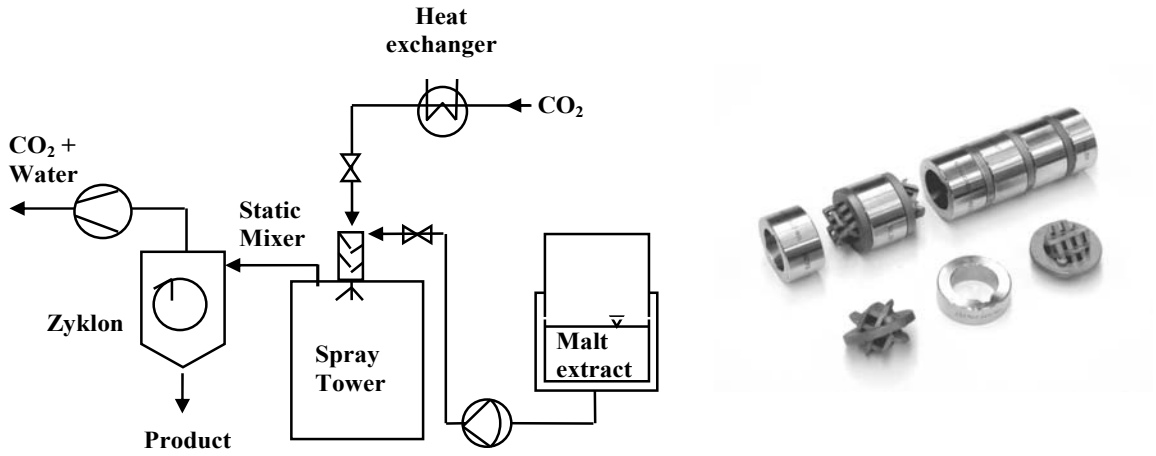


Figure 2: (left) Flow Scheme of the PGSS pilot plant (right) static mixer

The success of a pulverization experiment depends on the amount of extracted water and the relative humidity in spray tower respectively in cyclone. Due to the fact, that the solubility of gaseous water in carbon dioxide depends on the temperature, it should be assured that the extracted water at the spray tower/cyclone temperature is completely solved in carbon dioxide. Figure 3 shows the temperature-composition diagram of CO_2 and water at a pressure of 1 bar. According to the diagram, the process has to be operated in the spray tower at compositions above the dew point line (shaded area of Figure 3). In order to get free-flowable malt extract powders the working area is even smaller because the stability of the powder depends on the relative humidity.

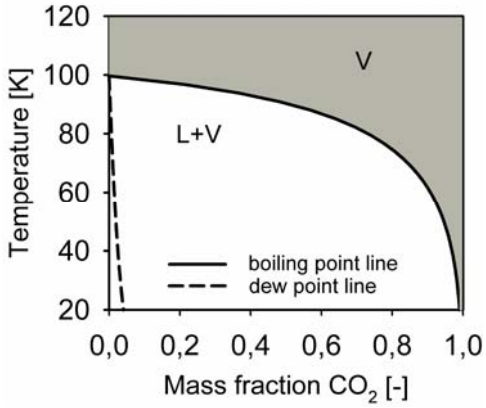


Figure 3: Calculated temperature-composition diagram for water and carbon dioxide (ideal calculation)

There are two ways to set a low relative humidity (~15 %) in the spray tower/cyclone. First, a high specific gas amount can be used ($kg_{CO2}/kg_{malt\ extract}$) in order to work at lower temperatures and to decrease the heat stress of the product. Second, high temperatures and lower specific gas amount ($kg_{CO2}/kg_{malt\ extract}$) can be used. This reduces costs, but the residence time at these temperatures should be carefully controlled to avoid an unwanted heating treatment.

RESULTS

Analysis of the thermal treatment

Table 2 shows the mean of the color EBC value and the standard deviation (δ) for each thermal treatment. Figure 4 (top) shows the obtained color EBC values, which depend on the temperature and time. High regression coefficients (R2=0,99) indicate that color degradation follows a kinetic order of zero. The reaction rates at each evaluated temperature are given by the slope. The dependency of the reaction rates (kT) with temperature was calculated by means of Arrhenius transformation (Figure 4- bottom). Thus, reaction rates at elevated temperatures can be calculated.

Table 2: Obtained color EBC value for malt extract after thermal treatment

Temp.(°C)	60°C		80°C		90°C		100°C	
time (min)	EBC value	δ	EBC value	Δ	EBC value	δ	EBC value	δ
0	22,89	1,08	22,79	1,03	22,33	1,01	23,05	1,31
30	23,01	0,90	24,28	0,68	26,53	0,58	32,61	0,44
60	23,19	1,01	25,31	0,38	29,90	0,65	46,68	0,11
90	23,40	0,90	27,08	1,20	35,28	0,82	63,90	0,57
120	23,55	0,99	28,04	1,59	39,30	0,92	77,09	1,86
180	23,83	0,99	31,41	0,86	50,50	1,10	103,90	6,51

$$\Delta EBC = k_T * time(\text{min})$$ **Equation 1**

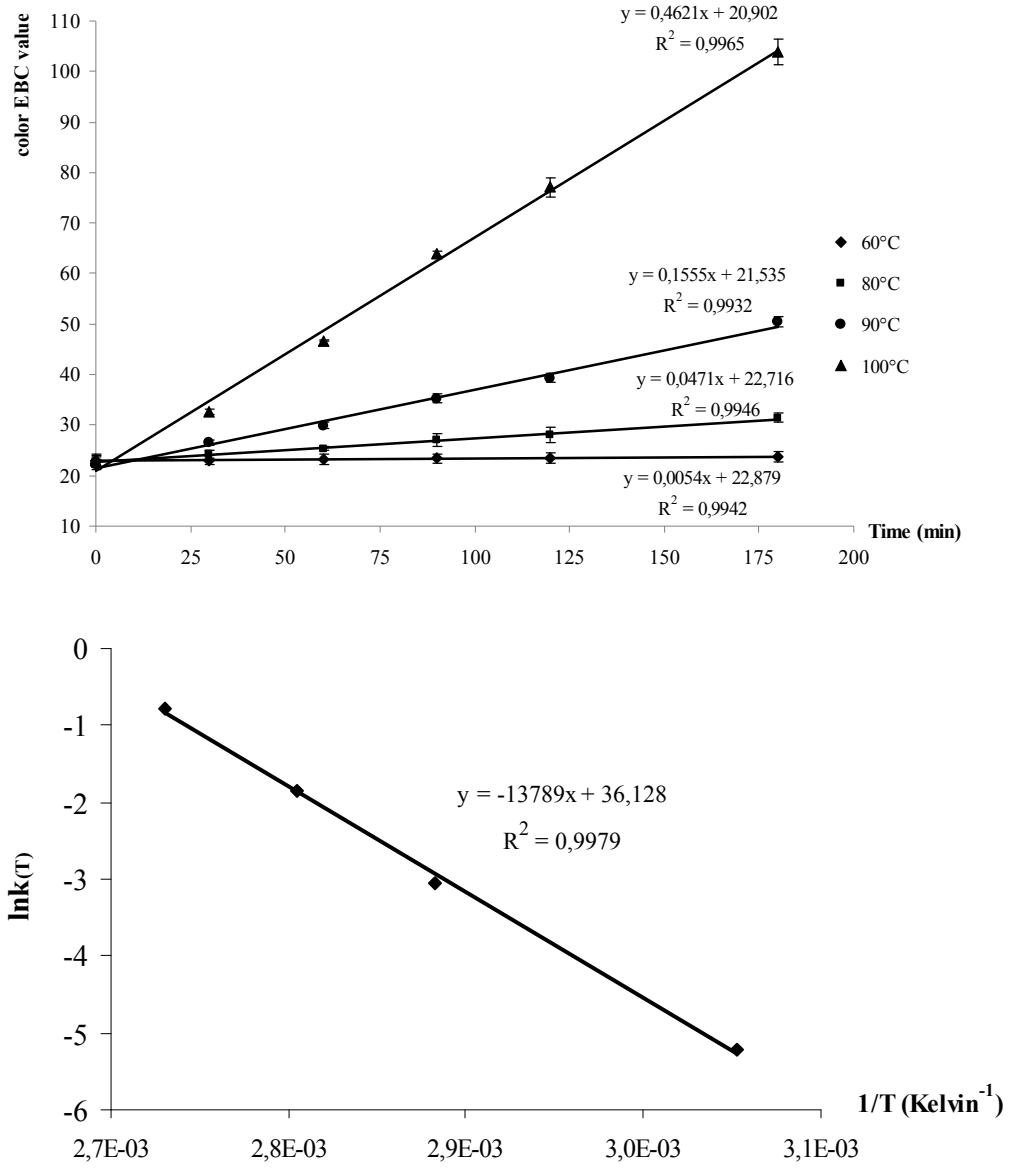


Figure 4 : (top) EBC Color value of malt extract vs. temperature and time, (bottom) reaction rate depending on temperature (Arrhenius transformation)

In Table 3 reaction rates of the color degradation at different temperatures are given. According to the results, malt extract can be stored at 60°C during 180 min without changing the color significantly ($p \leq 0,05$). At higher temperatures malt extract changes its color with increasing treatment time dramatically. For instance at 140 °C, the color changes 0,52 EBC in only two seconds.

Table 3 : Color degradation reaction rates (k_T) at different temperatures

T(°C)	k_T *10 (min^{-1})	T(°C)	k_T *10 (min^{-1})	T(°C)	k_T *10 (min^{-1})	T(°C)	k_T *10 (min^{-1})
60	0,05	90	1,56	110	11,34	130	67,67
80	0,47	100	4,62	120	28,33	140	154,96

Drying with PGSS drying process

Two runs of PGSS experiments are shown in Table 4**.** Indicated variations result from error of measurement and parameter fluctuations during experiments (typical duration 30 min per trial). Vessel and pipelines (Fig. 2) of the pilot plant were heated to 50°C in order to facilitate the flow of malt extract, which has a very high viscosity of 8 Pas at room temperature. At this temperature, malt extract is not suffering any color degradation (see 3.1) during the trial. Experiments of run I (1, 2, 3 and 4) were carried out using 12 mixing elements of 12 mm diameter, similar pressure before expansion and similar specific gas amount (mass flow of carbon dioxide in kgh^{-1} divided by mass flow of malt extract in kgh^{-1}). Experiments of run II (5, 6 and 7) were carried out using 16 mixing elements of 6 mm diameter and with a similar pressure before expansion as well as with similar specific gas amount. In all trials the mixing section was 96 mm long. To adjust the temperature before expansion the carbon dioxide was heated at 190-215°C and the mixing line was insulated. Spray tower temperature resulted from the conditions before expansion.

The color of the initial liquid malt extract and of the obtained powder was determined for each experiment. Figure 5 shows the change of color as a function of temperature for the two experimental runs. The residence time of malt extract in the mixing section (static mixer) at the temperature before expansion was calculated by using Equation 1 and the reaction rates determined in 3.1. Residence time in the mixing section can be controlled by the specific gas amount and the diameter of the static mixer. For instance, color variations in the experiments of run I are bigger than in run II due to a prolonged residence time (11 vs. 3 seconds). Using smaller static mixers and a lower specific gas amount, the residence time in the mixing section can be minimized. Therefore it is possible to pulverize malt extract at 138°C without causing a significantly change of color (experiment No. 7).

Table 4 : Conditions and results of pulverization experiments

Run	**I**				**II**		
Experiment	**1**	**2**	**3**	**4**	**5**	**6**	**7**
specific gas amount* ± 3	14	14	15	16	11	12	12
temp. before expansion (°C) ± 3 °C	**127**	**137**	**143**	**149**	**127**	**131**	**138**
pressure before expansion (bar) ± 5 bar	89	94	97	102	98	98	103
spray tower temp. (°C) ± 3 °C	62	72	79	85	60	63	70
diameter of static mixer (mm)	8	8	8	8	6	6	6
powder moisture (wt.-%) ± 0,25%	6,8	6,6	5,3	5,1	6,9	6,3	5,5
powder color (EBC) ± 0,25	25,1	26,08	27,86	30,41	22,15	22,4	23
color variation (EBC)	1,1	2,0	3,8	6,4	0,2	0,4	1,0
residence time (s)	11,9	10,3	11,9	12,1	2,1	3,2	4,4

*specific gas amount = mass flow of Carbon dioxide in kg/h / mass flow of malt extract in kg/h

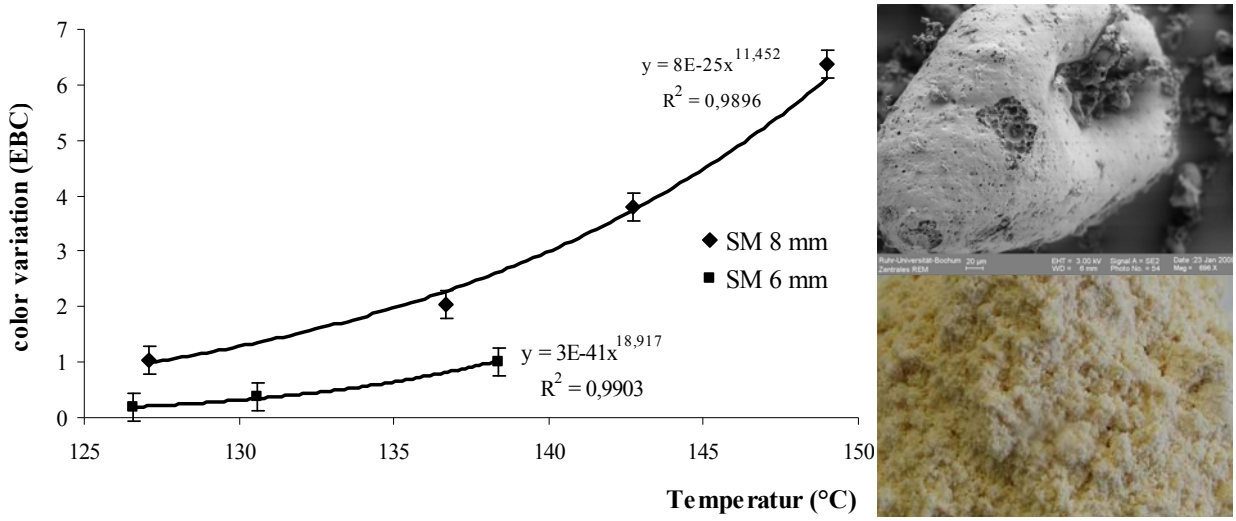


Figure 5 : (left) color variation during the high pressure spraying in function of the temperature before expansion and the diameter of the static mixer, (right top) SEM picture of powder of experiment No.3., (right bottom) picture of malt extract powder.

It can be also observed that the higher the before expansion temperature, the lower is the moisture of the produced powder. Therefore, higher temperatures facilitate water separation but the residence time should be carefully controlled to avoid a change of the powder's color. Figure 5 shows that color variation as well as reaction rates are connected to temperature by an exponential correlation. Typically, the morphology of the powders produced by PGSS drying is porous (Figure 5).

CONCLUSIONS

Color degradation of the malt extract follows a kinetic order of zero. Malt extract can be stored at 60°C or lower during 180 min without suffering a significantly ($p \leq 0,05$) color change. At higher temperatures (≥140°C) significant color degradation occurs in a few seconds.

The intensity of thermal treatment in PGSS drying process can be controlled by the residence time in the mixing section (static mixer). Residence time is adjusted by the specific gas amount and the dimension of the mixing elements. It can be minimized using small mixing elements and low specific gas amounts. The effect of thermal treatment in the PGSS drying process is adjustable. The process is appropriate to dry highly viscous and thermal susceptible substances.

REFERENCES :

[1] BALTES, W., Lebensmittelchemie, 5th. Edition, Springer Editorial, **2000**, p. 93.
[2] BOSKURT, H., GÖGÜS, F., EREN, S., Non-enzymatic browning reactions in boiled grape juice and its models during storage, Food Chemistry, Vol. 64, **1999**, p, 89-93.
[3] LOPEZ, A., et. al., Influence of drying conditions on the Hazelnut quality: III. Browning, Drying Technology, Vol.15, **1997**, p. 989-1002.
[4] TOSI, E., CIAPPINI, M., Re, E., LUCERO, H. Honey thermal treatment effects on hydroxymethylfurfural content, Food chemistry, Vol. 77, **2002**, p. 71-74
[5] METERC, D., PETERMANN, M., WEIDNER, E., Drying of aqueous green tea extract using a supercritical fluid spray process, The journal of supercritical fluids, Volume 45, Issue 2, June **2008**, p 253-259.
[6] WEIDNER, E., High pressure micronization for food applications, The Journal of Supercritical Fluids, **2008**, doi:10.1016/j.supflu.2008.11.009.