Comparison of PGSS-Drying Process with Classical Techniques for Drying and Pulverization of Viscous Barley Malt Extract

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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 flavour 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 is simplified when the product is pulverized.

Nowadays, the demand of malt extract in powder form is increasing in the market, due to its dosing and handling properties. Nonetheless, some properties like high hygroscopicity, tendency to compaction, intensity of colour (due to thermal stress) or bad solubility of the malt extract powder sold in the market (typically spray dried) are not desirable and should be overcome by investigating other pulverization methods.

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

In the present work, a high-pressure method was 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 was recently used for a gentle drying of aqueous green tea extracts, also [6].

Aim of the present work, is to determine the working area using PGSS-drying in order to obtain dry and free flowing malt extract powder; to analyze the influence of process parameters on product properties and quality (via change of colour), and finally to compare the properties, advantages and disadvantages of malt extract powder generated by means of the high pressure spray process and the classical techniques (like spray drying and freeze drying).

MATERIALS AND METHODS

Materials

CO_2 (99.9%) was supplied by YARA (Bad Hoenningen, Germany).
Weyermann (Bamberg, Germany) supplied malt extract "Bavarian Pilsner unhopped". Its chemical composition is detailed in Table 1. Sugars were determined by HPLC, protein was analyzed by Kjeldahl-method and water was measured by Karl-Fischer titration.

Table 1. Composition of liquid malt extract

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

Methods

PGSS-drying. Malt extract was dried and pulverized using a PGSS drying pilot plant, with a maximum operating pressure of 200 bars and maximum operating temperature of 250°C (Fig. 1).

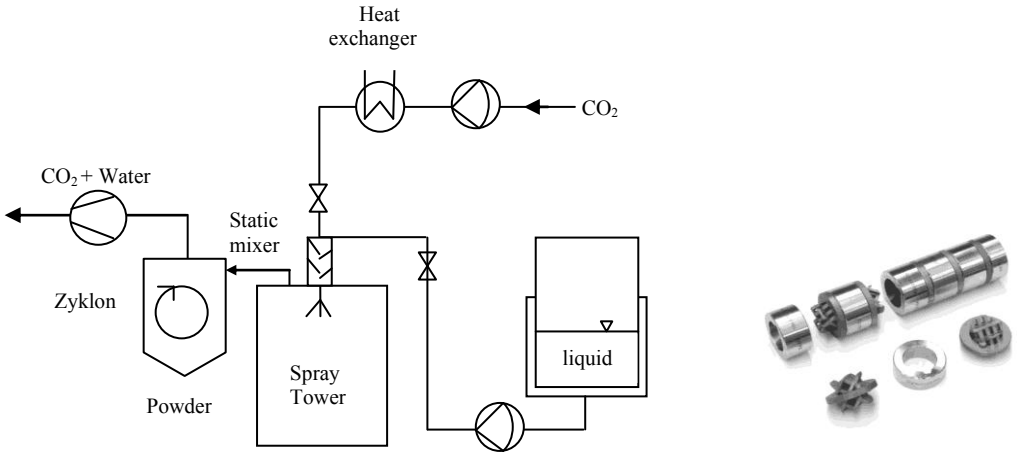

Fig. 1. Simplified flow scheme of the PGSS pilot plant (left), static mixer (right)

A high-pressure pump doses malt extract to a static mixer. There, 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. A blower exhausts fine particles, CO_2 and gaseous water. Subsequently, a cyclone separates the powder from the gas. The produced powder is collected in a vessel.

The design of the mixing elements (right side of Fig. 1) facilitates the intensive mixture of malt extract and supercritical carbon dioxide under high pressure and at elevated temperatures. The ratio of CO_2 mass flow and malt extract mass flow is named specific gas

amount (SGA). The pre-expansion conditions are called pre-expansion temperature and pre-expansion pressure. These are the adjustable process parameters; simultaneously, the post-expansion temperature is the systems response and is a result of the mass and energy balance at the spray tower. During the mixing in static mixer, supercritical carbon dioxide dissolves partly in the malt extract, causing a decrease of viscosity. At the same time, water and some high volatile components of the multi-component system malt extract dissolve also partially in the dense carbon dioxide. Thus, water is extracted from the malt extract.

The success of a drying experiment depends on the amount of extracted water and the relative humidity in spray tower. 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 spray tower temperature is completely soluble in carbon dioxide. Fig. 2 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 Fig. 2), in order to avoid a condensing water phase.

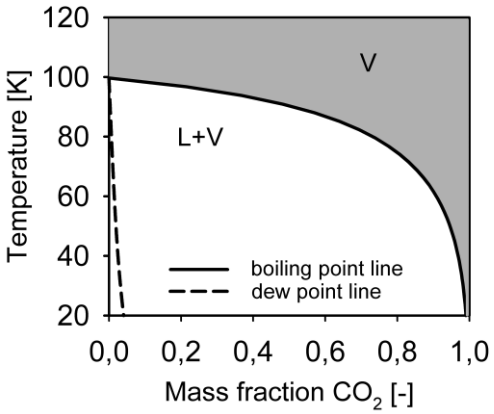

Fig. 2. Calculated temperature-composition diagram for water and carbon dioxide at 1 bar (ideal calculation)

Characterization of powder. The produced malt extract powders were analyzed as follows:

- Moisture content was measured by Karl Fischer titration (Mettler Toledo); as solvent Methanol dry and Formamide dry (50:50) provided by Sigma Aldrich were used.
- Particle morphology was characterized using Scanning Electron Microscopy (SEM)
- Particle size distribution was determined using a laser diffraction method (Malvern Instruments); powders were dispersed in dry state with a dispersion pressure of 2 bars [7]
- Apparent densities were measured by DIN ISO 697 [8]
- Colour of the liquid and pulverized malt-extract was measured according to the International Method for the determination of the colour of beer and malt, Committee of the European Brewery Convention (EBC) (MEBAK II 2.16.2) [9]. It is a spectrophotometric determination at a wavelength 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 colour EBC value.

- Flowing index was measured using a Ring shear tester (Schulze, 2006). Flow properties were indicated by means of fcc values; 0 <fcc ≤2 means very cohesive, 2 <fcc ≤4 cohesive, 4 <fcc ≤10 easy flowable and fcc >10 free flowable.

- Tendency to compaction was evaluated qualitatively and quantitatively: 50 g of powder was put into a metallic cylinder and pressed with a weight of 1500 g. The system was stored under a relative humidity (RH) of 45 % and a temperature of 25°C. After 1 week, the pressed cake was evaluated qualitatively (categories: no compaction, low compaction, strong compacted) and after 2 weeks the force which was required to destroy the cake was measured.

- Absorption of moisture was investigated by gravimetric method. The weight of a powder sample (starting weight 5 g) stored at 45% RH and 25°C was determined after 15, 30, 45, 60, 120, 180, 240 min and after 24, 48 and 72 hours (until equilibrium was reached).

RESULTS AND DISCUSSION

PGSS-drying – Working area

As mentioned before, the formation of dry powder in a drying experiment depends on the amount of extracted water in the static mixer and of the relative humidity in spray tower. According to the diagram (Fig. 2), the process has to be operated in the spray tower at compositions above the dew point line; additionally, working area is also limited by the substances properties (e.g. melting point in case of some polymers) and its behaviour in the presence of moist (relative humidity).

In order to identify an adequate working area to dry malt extract by means of PGSS drying, more than 50 experiments were carried out at different conditions. The spraying pressure was set between 75 and 170 bar, the pre-expansion temperature was varied from 118 to 160°C, the specific gas amount was adjusted between 9 and 29, and the post-expansion temperature was in the range of 41 to 97°C.

A heat and mass balance was prepared in order to calculate the amount of removed water from the malt extract and the mass fraction of carbon dioxide in the spray tower [10]. The obtained values were plotted in dependency of the spray tower temperature in the temperature-composition diagram for water and carbon dioxide. The temperature-composition diagram for water and carbon dioxide at 1 bar was calculated assuming an “ideal calculation” using the software Aspen tech 2006.5.

Fig. 3 shows that the success (powder formation) of the experiments depends on the relative humidity and the spray tower temperature. It can be seen, that relative humidity in the spray tower should be lower than 15 % in order to obtain free-flowing powder. A relative humidity of more than 15 % leads to agglomerates, the powder is not stable. The lowest spray tower temperature with a formation of stable powder was 63°C. Therefore, the working area to produce stable malt extract powders using PGSS drying is smaller than the mentioned in Fig. 2.

There are two possibilities to set a low relative humidity (~15 %) in the spray tower. First, a high specific gas amount can be used ($kgCO_2$/kgmalt extract) in order to work at low temperatures and to decrease the thermal stress of the product. Second, high temperatures and low specific gas amounts ($kgCO_2$/kgmalt extract) can be used. This reduces costs, but the residence time of the malt extract at these temperatures should be controlled carefully to avoid an unwanted heating treatment.

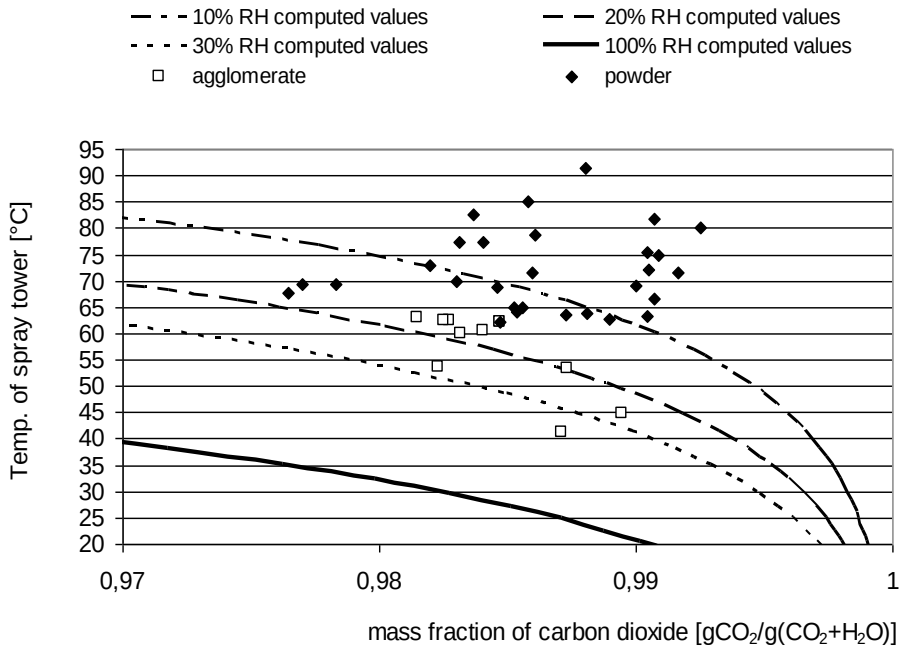

Fig. 3. PGSS experiments plotted in temperature-composition diagram for water and carbon dioxide

Thermal treatment during the PGSS drying process

As mentioned in section 1, a characteristic property of malt extract is its thermal sensitivity due to the Maillard reaction or non-enzymatic browning. The higher the intensity of the thermal treatment is, the darker is the colour of the substance afterwards. In this section, change of colour of the liquid malt and the obtained powder in dependence of the specific gas amount and use of static mixer is analysed.

For this purpose, three runs of experiments were carried out. Typically, duration of one experiment is 30 min. Vessel and pipelines (Fig. 1) of the pilot plant are heated to 50°C in order to facilitate the flow of the highly viscous malt extract ($\mu_{20°C}$=8 Pas). At this temperature, malt extract is not suffering any colour change during the pumping and experiment for more than 3 hours [11].

Experiments of run I were carried out using static mixer (8 mm diameter) with a mixing section of 100 mm length, a specific gas amount (mass flow of carbon dioxide in kgh^{-1} divided by mass flow of malt extract in kgh^{-1}) of 12±0.5, pressure before expansion of 100±2 bar and different temperatures from 125°C to 155°C. Experiments of run II were performed using the same conditions as in run I but without static mixer. The mixing elements were removed from the piping. Experiments of run III were carried out at the same conditions as in run I using an increased specific gas amount (15±0.5).

To adjust the temperature before expansion the carbon dioxide was heated at 190-215°C and the mixing section was thermally insulated. In all experiments, the spray tower temperature was in a range of 50 to 85°C.

The colour of the liquid malt extract (raw material) and of the obtained powder was determined for each experiment in order to determinate the change of colour due to the process. Fig. 4 shows the change of colour as a function of pre-expansion temperature for the three experimental runs.

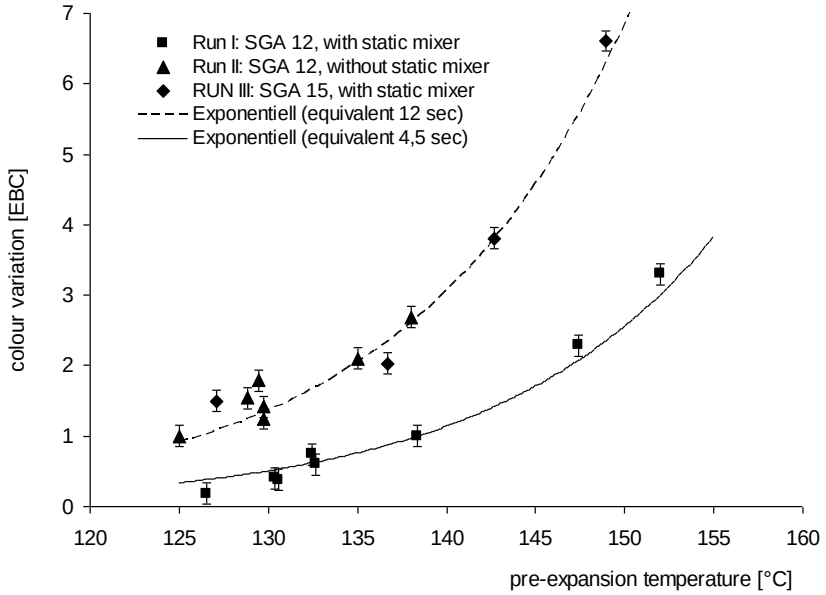

Fig. 4. Colour variation in dependence of pre-expansion temperature, specific gas amount and use of static mixers

By comparing experiments of run I and run III, it can be observed, that the residence time in the mixing section can be controlled by the specific gas amount. So it is possible to pulverize malt extract at 138°C without causing a significantly change of colour. An additional observation, which is in opposite to the expected results; is that the residence time in the mixing section can be minimized using a small specific gas amount. This Fact will be explained subsequently.

By comparing the experiments of run I and II, the influence of the static mixer can be observed. If the experiments are carried out without static mixer, the residence time in the mixing section is probably prolonged, due to the increased colour change. A probably reason for that could be a non-homogeneous mixture between malt extract and carbon dioxide. If carbon dioxide and malt extract are not mixed intensively, the viscosity of malt extract is not lowered by dissolved carbon dioxide and both phases are presumably flowing "separately".

The mechanism of mixing used by the PGSS drying is similar to the effervescent atomization, where gas is bubbling into a liquid stream before it is ejected from the atomizer [12]. Chin and Lefebvre [13] have found that an increase in SGA caused the flow regime in the mixing chamber to transition from bubbly to slug, and then finally to annular flow. The possible flow regimes in the discharge orifice are illustrated in Fig. 5.

In general the flow pattern in the discharge orifice is bubbly at low SGA and annular at high SGA (>0,4) [13]. By the PGSS experiments the SGA used to be very high in comparison to the SGA used by the effervescent atomization. For this reason, the occurrence of an annular flow pattern is very probably by the PGSS experiments, particularly when static mixers are not used. Geckler [14] and Geckler and Sojka [15] studied the near nozzle structure of sprays formed with visco-elastic liquids in effervescent atomization and observed an annular net-like structure over a wide range of SGAs. This behaviour could explain why by using higher SGA or not using static mixer, the residence time of the malt extract is longer and the thermal treatment stronger.

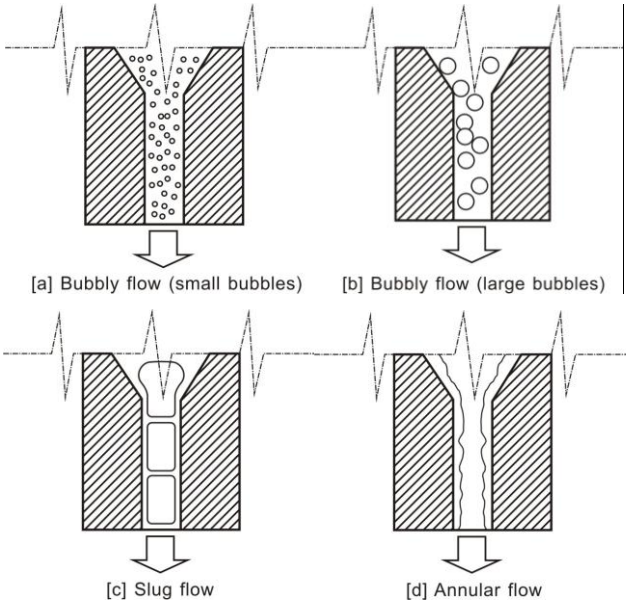

Fig. 5. Possible flow regimes in the discharge orifice [12]

Unfortunately, there is still no possibility to have a real "look" inside the mixing section due to the high pressure. Therefore, it is still unknown what percentage of the cross sectional area is occupied by malt extract and what by carbon dioxide. Nevertheless it can be assumed, that more of the cross sectional area is occupied by the highly viscous malt extract than it is suggested by the ratio of the volume flows of malt extract and carbon dioxide. Thus, carbon dioxide is probably flowing faster than malt extract and malt extract is spending more time in the mixing section. It is important to remark that at pre-expansion conditions, malt extract (assumed as a simplified binary system containing sugar and water) and carbon dioxide exist in two separate phases. This was proved by an investigation of phase equilibrium between supercritical carbon dioxide and malt extract in a temperature range of 25-160°C and a pressure range of 75-300 bars [16].

Due to the complexity of the flow behaviour of two phase flow, the exact residence time of the malt extract in the mixing section is unknown. An approximated time was calculated by comparing the change of colour during the process and the change of colour of the liquid malt at the same temperature but at ambient pressure. The influence of thermal treatment on the color of liquid malt extract (starting material) was carried out in a closed system (stainless steel tubes) under ambient pressure at different temperatures. Obtained reaction rates of colour degradation as a function of temperature were calculated using Arrhenius transformation [11]. The equivalent time for the run I is 4,5 seconds and for the runs II and III 12 seconds.

It is possible to adjust a similar residence time (and/or thermal treatment) by using static mixers and a SGA of 15 or by working without static mixers and a SGA of 12 (see also run II and III in Fig.4). However, the particles properties are different because of the nature of the mixture and water extraction.

Particles obtained by working without static mixer are porous and exhibit small bubbles. The produced powder shows a low apparent density and it absorbs moisture very fast. In Fig. 6 SEM-pictures of particles produced with (left hand side) and without static mixer (right hand side) are shown.

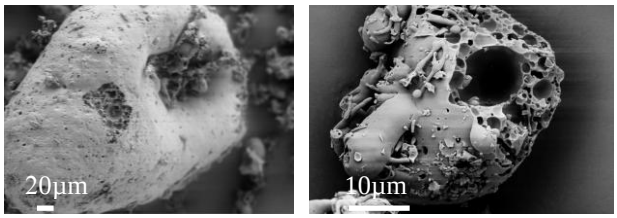

Fig. 6. SEM-pictures of malt extract particles: run I with static mixer (left) run II without static mixer (right)

Comparison of PGSS-dried malt extract powders with spray-dried and freeze dried malt extract powders

Malt extract powders were also produced by means of conventional techniques (spray drying and freeze drying) Process parameters were changed in order to obtain different types of particles with different characteristics. For the spray drying trials, concentration of solids in the malt extract solution, amount of nebulised air, air inlet temperature and ratio of malt extract mass flow to mass flow of drying air were changed. For the freeze drying trials, concentration of solids in the solution and time of drying were varied. Nevertheless, in none case the morphologies of the produced particles of the same drying process changed. Fig. 7 depicts some characteristic SEM-pictures.

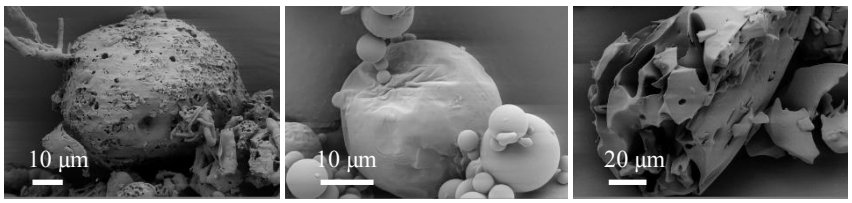

Fig. 7. SEM-pictures of PGSS malt extract (left), spray dried malt extract (middle) and freeze dried malt extract (right)

Depending on the process, different powder morphology and thus different powder properties were obtained. Table 2 summarizes the properties of the produced powder and shows the obtained maximum and minimum values for the measured properties.

Table 2. Comparison of malt extract powders produced by PGSS, spray drying and freeze-drying

Powder characteristic	PGGS		Spray dried		Freeze dried	
	max	min	max	min	max	min
Moisture [wt.-%] ± 0,05	7.4	3.1	6.12	2.0	4.3	2.5
Change of colour [EBC]	28.7	0	6.2	0	0	0
Flow index [ffc] ± 0,2	2.6	1.4	2.9	1.8	n.p.d	n.p.d
Bulk density [kg⁄m^3] ± 5	267	70	748	506	190	95
Real density [kg⁄m^3] ± 10	403	176	944	735	320	50
Particle size $d_{0,5}$ [µm] ± 2	314	11	73	10	21	13
Tendency to compaction after 1 Week [qualitative]	+++	-	+	-	+++	-
compaction after 2 weeks Force [N] ± 5	498	4	145	1	n.p.d	430
Absorption of moisture	fast		slow		very fast	

n.p.d: not possible to determine

By means of PGSS-drying process malt extract can be gently dried to a residual water content of 3 wt. %. Thermal stress and thus browning are adjustable by the residence time in the mixing section and pre-expansion temperature. The produced powders are distinguished by a high porosity, low bulk density, cohesive properties and a fast absorption of water in moist atmosphere (45% R.H. and 25°C). Particle size ($d_{50,3}$: 10 to 300 microns) and particle distribution are adjustable by process parameters. Shape and morphology of the particles vary from spherical to needle- or thread like. Powder with, as well as without strong compaction behaviour, was produced. This behaviour is strongly depending on water content and porosity of the particles.

Spray dried barley extract powders are characterized by a compact and spherical morphology, low porosity, high density, cohesive properties, and no disposition to compaction. Adsorption of moisture of the surrounding atmosphere of these powders is slower than that of freeze-dried or PGSS dried powders. Thermal stress of the particles and particle size distribution are difficult to adjust. Mono-modal and narrow particle size distributions were produced ($d_{50,3}$ around 25 microns).

Particles of high porosity and with the least density were produced by freeze-drying. The powders are very cohesive and tend to compaction. They show a very fast absorption of water, faster than the PGSS morphologies. The freeze-dried powders do not change colour. The particle size is adjustable by milling in a separate process step.

CONCLUSIONS

Malt extract can be dried successfully using the PGSS-drying process. The relative humidity in the spray tower plays an important role for powder formation. A relative humidity lower than 15% is required to obtain dry malt extract powders. The thermal treatment of the product is adjustable by means of the specific gas amount (SGA) and the use of static mixers. The morphologies of the PGGS-dried, spray dried and freeze-dried particles are different and consequently their properties also.

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