Comparing PGSS and GAS Process for Drying of Green Tea Extracts

Darja Meterc*[1], Maria José Cocero[2], Eckhard Weidner[1]

[1] Ruhr University Bochum, Chair for process technology, Universitätsstraße. 150, 44801 Bochum, Germany,
Tel : +49 234 32 22507, Fax : +49 234 32 14277, Email : meterc@vtp.ruhr-uni-bochum.de
[2] University of Valladolid, Departamento de Ingeniería Química y T.M.A., Valladolid, Spain

Micronisation processes, such as PGSS (particles from gas saturated solution) and GAS (gas antisolvent process); are commonly used in the pharmaceutical and/or food industry for obtaining powders with the desired particle size and particle size distribution.
The focus of the present study is to compare these two high pressure processes, for the drying of green tea extracts. Green tea was chosen because of its high amount of antioxidants (polyphenols) and therefore its health benefits.
It has been proven that the green tea powders with high amount of antioxidants can be obtained with both processes. In this work the influence of different operating conditions on the quality of the final product is discussed.
To evaluate particle size and morphology, measurements with a Malvern Mastersizer were performed and SEM photos were taken (Figure 1). Water content was determined by Karl Fischer; polyphenols and caffeine were analyzed with HPLC**.**
Obtained results show high process efficiency (what does this mean in that case – high amount of polyphenols, 52% for the PGSS drying and 42% for the GAS process, regarding to polyphenol content in the product.

Key words: Green tea, Polyphenols, PGSS, GAS

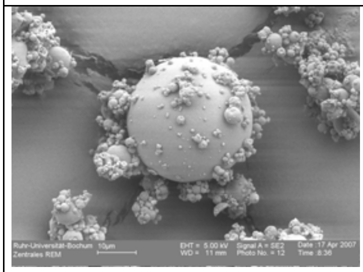
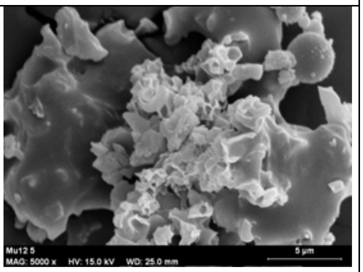
PGSS	GAS
T= 48 °C, P = 118 bar	T= 47 °C, P = 140 bar
	

Figure 1: SEM photos of samples dried with PGSS and GAS process.

INTRODUCTION

Polyphenols are one of the most important components present in the green tea, presenting 5-30 wt.-% of the tea plant, with the highest concentration in the leaves. Among polyphenols, catechins prevail and are of special interest. Currently the tea plant is known to contain seven major catechins, which are proven to be powerful antioxidants and possible substitutes for commonly used ones, such as vitamin E [1].

Since there is more and more discovered about antioxidative properties of polyphenols, the interest for their possible application continues to grow.

In order to separate catechins from the plant source, usually extraction processes with different solvents are used, followed by different drying techniques, such as spray drying, evaporation and freeze drying in order to obtain highly concentrated powder.

As an alternative, high pressure processes can be used for drying of natural substances, usually using CO_2 at moderate temperature as drying media. Due to the low temperatures and the oxygen free atmospheres in these processes, the degradation of valuable sensitive substances can be prevented.

There have been several micronisation techniques proposed for the particle formation using supercritical fluids [2,3]. Depending on the principals used, they can be divided into three main groups. In the first process (RESS), the particles are formed as a result of a rapid expansion of a supercritical fluid [4,5]. In the second process, so called PGSS, particles are formed from a solution, which was saturated with a supercritical fluid [6]. In the third group particles are formed using antisolvent power of a sub- or near critical fluid used in the process. Here different modifications of the process are in use. The most common are GAS (gas antisolvent), SAS (supercritical antisolvent), SEDS (solution-enhanced dispersion), and PCA (precipitation with a compressed antisolvent) [7].

In this research work, two high pressure processes (PGSS and GAS) were used in order to obtain dry powders and determine the quality of the product.

MATERIALS AND METHODS

Two different samples of dry and ground raw green tea were provided from Evonik industries from Germany. The initial composition is listed in Table 1.

The reference substances like caffeine and major catechins, were purchased from Sigma Aldrich.

Table 1: Water content, total polyphenols and caffeine content in raw material

Parameters		Raw PGSS green tea	Raw GAS green tea
Water content	[%]	8,11	1,63
Total polyphenols	[%]	6,55	9,45
Caffeine	[%]	2,30-2,32	2,59 - 2,82

The initial step of the work was an extraction step. Here two solvents were used, deionised water and ethanol in order to extract polyphenols from the raw tea (water for PGSS and ethanol for the GAS). Extraction was performed for 15 min at the boiling temperature of absolute ethanol and at 80 °C for water. The conditions for the extraction process were selected on a basis of preliminary research in order to optimise the extraction process. The filtered extract was used in PGSS or GAS process. Polyphenol content in the sample extracted with water was 17,94 wt.-% and in the sample extracted with ethanol 17, 85 wt.-%.

Work was carried out at two universities; therefore different apparatus were used for analytical purposes. After drying with antisolvent process, water content was determined by

Mettler Toledo DL35 Karl-Fischer Titrator. For the samples produced with PGSS, 633 Karl Fischer Apparatus, with 725 Dosing Unit and 703 Titrator from Metrohm was used.

Catechins and caffeine were determined with high performance liquid chromatography (HPLC) - diode array detector (DAD).

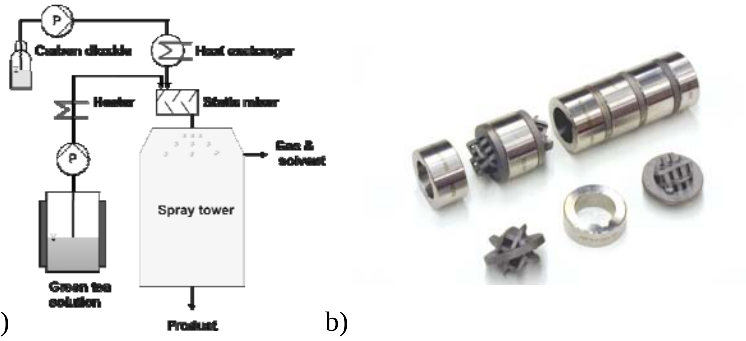
For the HPLC analysis, 0.2 g of the extract (dry product) is put into a 25 ml flask. As a solvent, a mixture of 30% bidistilled water and 70% of acetonitril is used and filled to the mark on the flask. The mixture is placed for 10 minutes into the ultrasound bath and/or stirred for 10 minutes. Before the measurement of the sample by means of HPLC, the solution is filtered over a diaphragm filter.

The evaluation of active ingredients of the samples is carried out over corresponding calibration curves of standards. In addition, the morphologies of the particles were examined with a scanning electron microscope (SEM).

Principles of the PGSS Drying process

In Figure 2, the flow sheet of the PGSS Drying pilot plant is shown. The maximum operating pressure of the plant is 200 bar and the maximum operation temperature is 250°C. The solution (extract) is put into the vessel, which is placed on a platform balance in order to determine the mass flow of the green tea solution.

Carbon dioxide is stored at vapor pressure in a high pressure tank and taken as liquid from the tank with a diaphragm pump. The carbon dioxide mass flow is measured with a coriolis flow meter and can be varied between 10 and 60 kg/h. Subsequently the gas is heated in a tube coil heat exchanger. Carbon dioxide is led through an oneway valve into the static mixer where it contacts with the solution to be dried.



a) b)

Figure 2: a) Flow sheet of the pilot plant and b) static mixer

Due to the construction of the mixing elements (Figure 2b) the solution and the supercritical carbon dioxide are mixed under high pressure and elevated temperatures. During the mixing supercritical carbon dioxide is partly dissolved in the green tea solution and the mixture is sprayed by a single path nozzle into a spray tower.

Driven by the expansion of the gas, fine droplets are formed, and the heated gas evaporates the solvent, which is exhausted together with CO_2 by a blower. The solid contents of the extracts precipitate. The obtained powder is collected at the bottom of the spray tower.

Principle of Supercritical antisolvent process-SAS

A schematic diagram of the pilot plant used for the SAS precipitation is shown in Figure 3. Two diaphragm pumps Dosapro, (Spain) are used to feed the Sc-CO_2 and the organic solution to the precipitation vessel. The precipitator is an AISI 316 stainless steel vessel of 1.5 l of volume and isolated with a heating jacket. This precipitator is equipped with a concentric tube nozzle for the injection of the solution and CO_2, and with a porous metallic frit for the collection of particles at its outlet. Two backpressure regulator valves placed in parallel for safety reasons control the pressure in the precipitator. An additional vessel is used to achieve the separation of solvent and CO_2 after pressure release.

A typical experiment starts by pumping pure CO_2 into the precipitator. When the desired operating conditions (temperature, pressure and flow rate) are achieved and remain stable, the solution is fed to the precipitator. When enough powder is obtained, the liquid pump is stopped and only pure CO_2 is fed. The flow of CO_2 is maintained during a period, long enough for the complete removal of solvent from the precipitator. After the decompression, a sample of the particles retained in the frit is collected. All the samples are stored under nitrogen atmosphere, protected from light and at temperatures below 5 °C, to avoid the decomposition of the product [8].

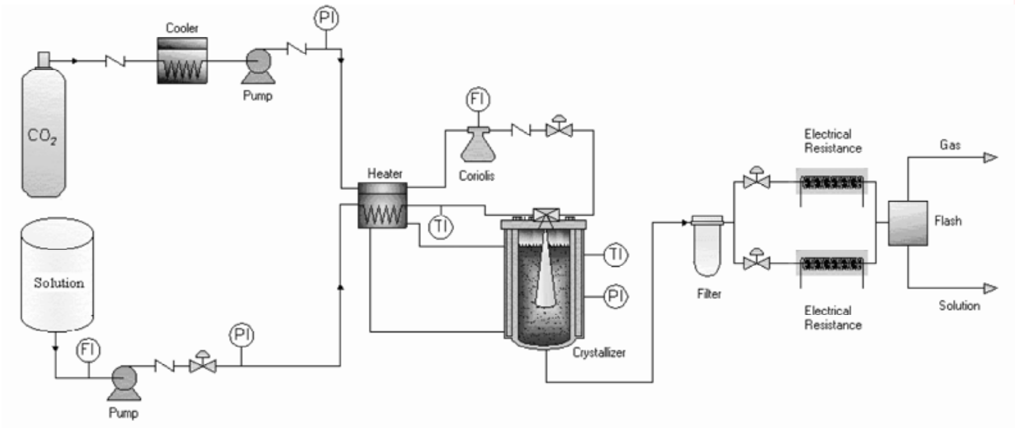


Figure 3: Schematic presentation of SAS plant

RESULTS

In Table **2** the results of drying of green tea extracts with the PGSS process, according to the descending preexpansion temperature, are presented. The standard deviation of measurements for all the samples was in the range from 0,13 to 4,16 % (resulting from non homogenous powders). First four samples were dried at relatively high temperatures (130-137 °C). The amount of polyphenols found in this samples was in the range from 14,66 to 13,85 wt.-%. The highest value was measured for the sample sprayed with a preexpansion temperature of 137 °C (14,66 wt.-%). The water residue in these samples was between 8,12 and 10,56 %. The overall highest amount of water was determined for the sample sprayed at 133 °C. The high water content leads to an agglomeration of the powder and resultant the highest mean particle sizes were measured for this sample (325 µm).

The next set of samples in Table 2 was dried at temperature in the range of 120 to 130°C. The highest amount of polyphenols (16,24 wt.-%) was found in sample, where the preexpansion temperature used for drying was 120 °C. The lowest amount (13,17 wt.-%), was found in sample, with a pre-expansion temperature of 130 °C. Water residues in samples ranged from 7,39 to 10,04 %.

Temperature of spray tower, where product was collected varied form 33 to 65 °C. Samples sprayed at the same conditions (pressure, temperature, mass flow) with the exception of spray tower temperature were analysed for polyphenol content and water residue. There has been no significant effect on the amount of active ingredients found in the product. On the other hand higher temperature resulted in the lowed water residue.

Table 2: Properties of dried green tea extracts with PGSS process

Tpre-expansion [°C]	SUM polyphenols [wt.-%]	Water residue [wt %]	CAF [wt.-%]
130 - 137	13,85 - 14,66	8,12 - 10,56	6,40
120 - 130	13,17 - 16,24	7,39 - 10,04	6,10
110	15,15	8,24	6,53

The lowest preexpansion temperature used was 110°C. Compared to the other experiments the water residue and the polyphenol content have not significantly changed.

This research confirmed preliminary investigations made with green tea; preexpansion temperatures up to 130 °C do not have significant effect on polyphenol degradation of the samples. When increasing preexpansion temperature up to 137 °C, minor degradation of samples occurred. To be able to determine the “critical point” for our process, further investigation have been carried out for the interval between 135 and 145 °C, where almost complete degradation has occurred [9].

Experiments with antisolvent process were performed at four different pressures, 80, 100, 120 and 140 bar and temperatures in the range from 20 to 50 °C. Since there has been no influence of the pressure noticed, only the results at 80 bar are presented in this paper.

In Table 3 the results of the spray experiments at 80 bar are listed according to the ascending temperature regions. The first set of experiments was sprayed at temperature 22-24 °C. In this temperature interval, liquid CO_2 was used for drying the extract. The highest amount of polyphenols determined in the samples was 21,91 wt.-%, in addition, the highest water residue in this product was measured with 6,8 wt.-%.. In the next step, temperature was carefully selected to come to near critical region (29-31 °C). The amount of polyphenols (app. 21 wt.-%), found in this powders is comparable to the amount found in the products which were dried with liquid CO_2. The water content in this samples was in maximum 6,1 wt.-%. When using supercritical CO_2, up to 49 °C, the amount of polyphenols in the powder is increased to 27 wt.-%, and the same time water residue was decreased to 3,8 wt.-%.

Table 3: Amount of active ingredients in the product dried with GAS process

Tower [°C]	SUM polyphenols [wt.-%]	Water residue [wt %]	CAF [wt.-%]
22-24 °C	21,91	6,0-6,8	2,35
29-31 °C	20,69	5,3-6,1	1,91
37-40 °C	26,34	3,3-5,2	2,31
43-44 °C	24,80	2,3-4,4	1,97
47-49 °C	27,13	3,8-4,4	1,97

CONCLUSION

There have been several experiments preformed in order to show the influence of temperature, solvent, mixing time and the drying process on the quality of the products.

Comparing different conditions applied for PGSS drying process it was observed, that high pre-expansion (Tp) temperatures (145 °C) cause degradation of polyphenols (1.05 wt.-%). Concentrating on a narrow interval (130 – 137 °C), where relatively high temperatures are used for green tea, promising results were obtained. Taking in account standard deviation of the analysis, it can be concluded, that expanding working area up to 137 °C for green tea still gives satisfying results. Produced powders showed light yellow colour, with small or no agglomeration observed. The variations of the spray tower temperature, ranging from 33 °C to 65 °C, have no significant effect on the amount of total polyphenols, but higher temperature results in lower water residue in the sample. The PGSS Drying showed promising results for drying of green tea extracts, because of low drying temperatures and oxygen free atmosphere.

Products, dried with GAS process contained up to 27 wt.-% of active ingredients, when Sc-CO_2 is used as a drying media. Under these conditions also the lowest water residue was determined. There has been no significant influence of temperature and pressure at this mass flow noticed on the particle size or particle morphology. Since it was possible to obtain dry powder at all conditions, using lower temperatures, slightly above critical temperature, is recommended due to temperature sensitivity and to reduce the energy consumption.

Both GAS and PGSS process gave satisfying and comparable results (taking into an account different raw material used) for drying of green tea extracts.. Since both processes use CO_2 as drying media in order to avoid degradation during process, and can be operated at moderate temperature, selection of a process can base on the solvent used for extraction. The experiments demonstrated that the high pressure processes enabled to produce powders with different water and polyphenol content, by changing process parameters.

ACKNOWLEDGMENTS

This work has been financed by the project “Green/Clean Processing of Bioactive Materials (SUB CLEAN PROBIOMAT)”; contract Nr. MEST-CT-2004-007767, in the Sixth EU Framework Programme (FP6).

The authors would like to thank Adalbert-Raps-Forschungszentrum, Freising, Germany (Technical University of Munich) for analyzing the samples and their kind help and Evonik Industries for supplying the green tea.

REFERENCES

[1] Y. Hara, Green tea, Health Benefits and Applications (CRC (February 15, **2001**)), ISBN: 0824704703

[2] Jung, J., Perrut, M., Particle Design Using Supercritical Fluids: Literature and Patent Survey, Journal of Supercritical Fluids, Vol.20, **2001, p.** 179

[3] Weidner, E., Knez, Z., Particles formation and particle design using supercritical fluids, Current Opinion in Solid State and Materials Science Vol.7, **2003**, p.353-361

[4] Matson, D., Petersen, R., Shmith, R., Formation of Silica Powders from the Rapid Expansion of Supercritical Solutions, Adv. Ceram. Mater., Vol.1, **1986**, p. 242-246.

[5] Matson, D., Fulton, J. Petersen, R., Shmith, R., Rapid Expansion of Supercritical Fluid Solutions: Solute Formation of Powders, Thin Films, and Fibers, Ind. Eng. Chem. Res., Vol. 26, **1987**, p. 2298-2306

[6] Weidner, E., Knez, Z., Novak, Z., PGSS (Particles from Gas Saturated Solutions) - a New Process for Powder Generation, Proceedings of the 3rh International Symposium on Supercritical Fluids, G. Brunner and M. Perrut (Eds.), Tome 3, Strasbourg, **1994**, p. 229-234

[7] Knez, Ž, Weidner, Precipitation of Solids with Dense Gases, Alberto Bertucco and Gerhard Vetter (Eds.) High Pressure Process Technology: Fundamentals and Applications, Elsevier Science, Amsterdam, **2001**, p.587-611

[8] F. Miguel, A. Martın, T. Gamse, M.J. Cocero, Supercritical anti solvent precipitation of lycopene. Effect of the operating parameters, J. Supercrit. Fluids Vol.36, **2006**, p.225–235

[9] D. Meterc, M. Petermann, E. Weidner, Drying of aqueous green tea extracts using a supercritical fluid spray process J. Supercritical Fluids, Vol. 45, Issue 2, 2008, p. 253-259