DRYING OF TEA EXTRACTS WITH PGSS PROCESS

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Water extracts, obtained from different varieties of black and green teas were dried with a high pressure spray process, called PGSS (Particles from Gas Saturated Solutions).

In order to prevent polyphenol degradation, supercritical carbon dioxide is used as drying media. The solution is mixed with preheated CO_2 in static mixer, where a homogenous mixture is obtained. The mixture is depressurized to ambient pressure via nozzle into a spray tower. Fine powder is formed and the solvent (water) is removed together with CO_2. By changing process parameters, like pressure and temperature, powders with different morphologies, particle sizes, water residues and polyphenol contents can be produced.

In previous experiments with green tea degradation of samples dried at preexpansion temperatures between 133 and 145 °C was observed. The working area, which gave the most promising results was between 120 and 130 °C. In order to confirm preliminary results, and to investigate the area between 130 and 137 °C for green tea, additional experiments were carried out.

Experiments done with black and decaffeinated black tea were performed firstly to observe the degradation and secondly to observe if complex formation between polyphenols and caffeine might cause some changes in final product.

Both, black and green tea powder products show small degradation caused by high pre-expansion temperatures. Powders obtained in temperature range from 110 to 130 °C show nearly no degradation, only slight degradation was observed, when temperatures up to 138 °C were used for drying. The water residue of the powders was determined with Carl Fischer Titration and is lying in a range between 5 and 14 wt.-%. Mean particle size, determined with Malvern Mastersizer 2000, was between 0.7 – 325 µm for green tea and 1-20 µm for black tea.

Keywords: Green tea, Black tea, Decaffeinated tea, Polyphenols, PGSS, Drying

1. INTRODUCTION

In previous research extractions and preliminary drying experiments with green tea, using the PGSS process, were investigated. Due to the promising results with green tea extracts, research was expanded to drying of black tea and in addition decaffeinated black tea and some other types of green tea.

The tea used in the research work came form tea bush called Camellia Sinensis. One of the most important processes in tea manufacturing is fermentation. It is known that the conversion of tannin in tea leaves is not achieved by microorganisms but by the enzymes present in the leaves. The degree of fermentation affects the quality and the type of tea. According to the degree of fermentation, tea is classified into green tea (unfermented), oo-long (semi-fermented) and black tea (fully fermented) [1].

There have been numerous papers published concerning health benefits of green and black tea. These results demonstrate that the theaflavins, present in black tea, show at least the same antioxidant potency as catechins present in green tea, and that the conversion of catechins to theaflavins during fermentation does not alter significantly their free radical–scavenging activity [2, 3].

2. MATERIALS AND METHODS

2.1. MATERIALS

Black and green tea for these experiments was supplied by company Evonik Industries. The composition of raw materials is presented in Table 1. Reference substances were purchased from Sigma Chemical Co. All solvents for extraction and analytical purposes were purchased from Merck.

Table 1: Composition, particle size and size distribution of raw material

Parameters		Raw green tea	Raw black tea	Decaffeinated black tea
Water content	[%]	8,11	5,6 - 6,3	3,8 - 4,8
Total polyphenols	[%]	6,55	7,35	5,34
Caffeine	[%]	2,30-2,32	2,46 - 2,82	0,10 - 0,22

2.2. SAMPLE ANALYZES

Caffeine and water content of both black tea raw materials were analyzed by Evonik Industries. Total polyphenol content was determined by the Adalbert-Raps-Forschungszentrum, Freising, Germany (Technical University of Munich).

Particle size and particle size distribution of ground material and samples obtained by PGSS Drying were measured with a laser diffraction method. The morphologies of the particles were examined with a scanning electron microscope (SEM).

Moisture content of samples was measured by a Mettler Toledo DL31 Karl Fischer Titrator.

2.3. PRINCIPLES OF THE PGSS DRYING PROCESS

The maximum operating pressure of the the plant is 200 bars and the maximum operation temperature is 250°C. The solution can be heated in a vessel and is conveyed with a piston pump. The vessel is placed on a platform balance in order to determine the mass flow of the tea solution, which can be adjusted to a maximum of 5 kg/h.

Carbon dioxide is stored at vapour pressure in a high pressure tank and is 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 one-way valve into the static mixer where it contacts with the solution to be dried.

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 obtained powder is collected at the bottom of the spray tower as well as in a cyclone.

To achieve a good drying, it is important to know the solubility of the solvent in carbon dioxide under spray tower conditions. Therefore simulations with Aspen Plus, using an ideal model, were made, to see what conditions in spray tower are realistic.

3. RESULTS AND DISCUSSION

From previous results, degradation was observed at temperatures around 145 °C. What was found to be still a suitable operating preexpansion temperature was up to 130 °C. At that time, the interval between 133 and 140 °C was not investigated.

Therefore the temperature interval from 110 °C to 137 °C was investigated for green tea in these new experiments. On the one hand focus was put on degradation of the polyphenols in the temperature range between 120 and 130 °C to confirm the previous results. On the other (if you write that you must have on the one hand before) hand the interval between 130 to 137 °C was investigated, to find out, when the degradation of the polyphenols starts.

Similar conditions were used for black tea, where the preexpansion temperatures used for drying of black and decaffeinated black tea was lying in a range from 123 to 138 °C.

In all experiments the mass flow of carbon dioxide was kept constant at approximately 50 kg/h. The mass flow of extract was varied; therefore gas to solution ratio (GTS) was in the range of 30 to 42 for both black teas and from 18 to 50 for green tea. In all experiments a nozzle (1,4 mm, 90 °) from the company Schlick was used.

In Figure 1 and Table 2 the results of drying of green tea extracts, according to the descending preexpansion temperature, are presented. The standard deviation of measurements for all three teas was in the range from 0,13 to 4,16 %.

First four powders were dried at relatively high temperatures (130-137 °C). The amount of polyphenols found in this samples (Tea 3, 4, 6 and 13) was in the range from 14,66 to 13,85 wt.-%. The highest value was measured for the sample Tea 13 which was sprayed with a preexpansion temperature of 137 °C. The water residue in these samples was lying between 8,12 and 10,56 %. The overall highest amount of water was determined for the sample Tea 4 which was 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).

Table 2: Properties of dried green tea extracts

Tp [°C]	SUM polyphenols [wt.-%]	water residue [%]	max. mean particle [µm]
130 - 137	13,85 - 14,66	8,12 - 10,56	325,45
120 - 130	13,17 - 16,24	7,39 - 10,04	5,24
110	15,15	8,24	1,72

As mentioned above, results obtained in previous research showed the best working area is between 120 and 130 °C. Comparing new results, it can be seen that the highest amount of polyphenols was found in sample Tea 12 (16,24 wt.-%), where the preexpansion temperature used for drying was 120 °C. The lowest amount was found in Tea 1 (13,17 wt.-%), with a pre-expansion temperature of 130 °C. Water residues in samples range form 7,39 to 10,04 %.

The lowest temperature before expansion was used for Tea 7 (110°C). Compared to the other experiments the water residue and the polyphenol content has not change significantly.

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 will be carried out for the interval between 135 and 145 °C.

In Figure 2, results for the black and the decaffeinated black tea are presented, according to descending preexpansion temperature. As mentioned above, preexpansion temperature was changed in range from 123 to 134 °C. As it can be seen form diagram, the polyphenol contents found in the samples were in the range from 24,3 to 26,6 wt.-%. The highest amount was determined in the sample Black 4, collected form cyclone; on the other hand the same sample collected form spray tower contained a little lower amount – 25,2 wt.-%. The lowest amount was in Black 6, collected from the tower - 24,3 wt.-%. The same sample for cyclone contained 24,5 wt.-%, which is in the range of standard deviation.

Although, the preexpansion temperature was the highest in the case of Black 4, the polyphenol content was the highest. From Figure 2, it can also be seen that in general, powders collected form cyclone has slightly higher amount of polyphenols than the samples collected from the same experiment in the spray tower.

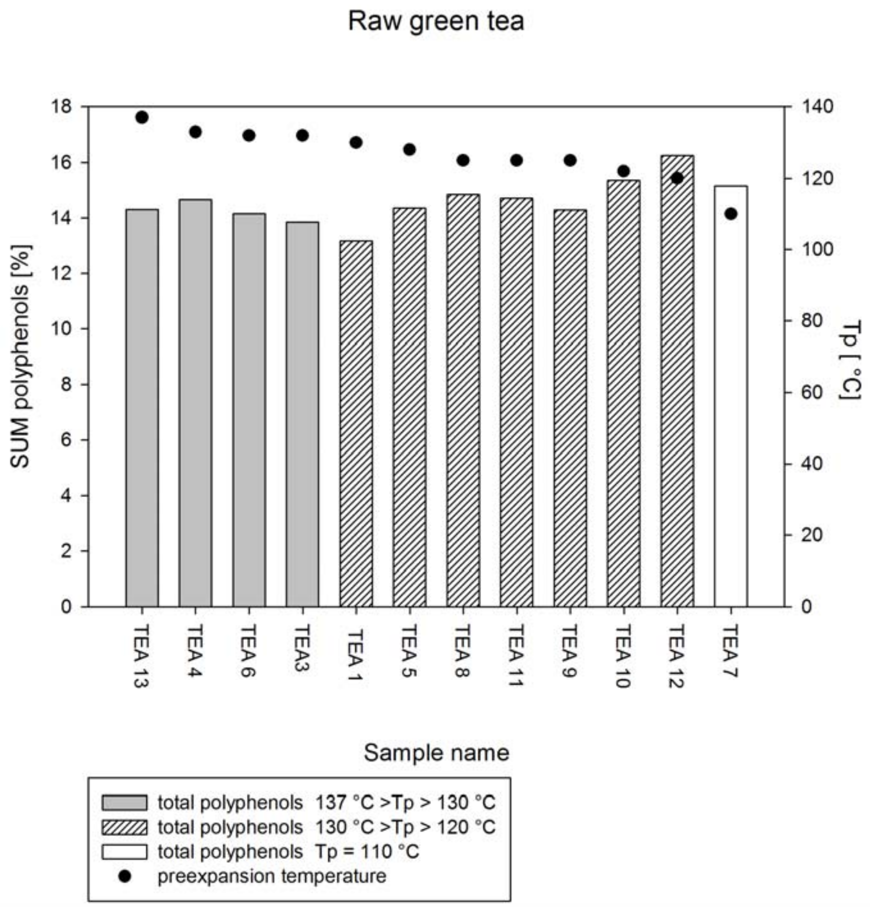


Figure 1: Influence of preexpansion temperature on polyphenol degradation in powders obtained from green tea extract

Similar results were found for decaffeinated black tea. Total polyphenols determined in the samples are descending from 26,17 wt.-% to 25,10 wt.-%. The highest amount was found in Decaf 4, collected from tower and the lowest in Decaf 1 collected from cyclone. Temperature after expansion was in both cases 128 °C. The roughest drying conditions were used for Decaf 6, where the preexpansion temperature was 138 °C, and temperature in spray tower about 78 °C. Although this conditions were used, the amount of polyphenols was 25,63 wt.-% for sample form cyclone and 25, 34 wt.-% for sample from tower. Both results lie in the deviation range of the analyzing method. For decaffeinated samples, 2, 3, 4 and 6 for, higher amount of total polyphenols were determined in the samples collected from cyclone.

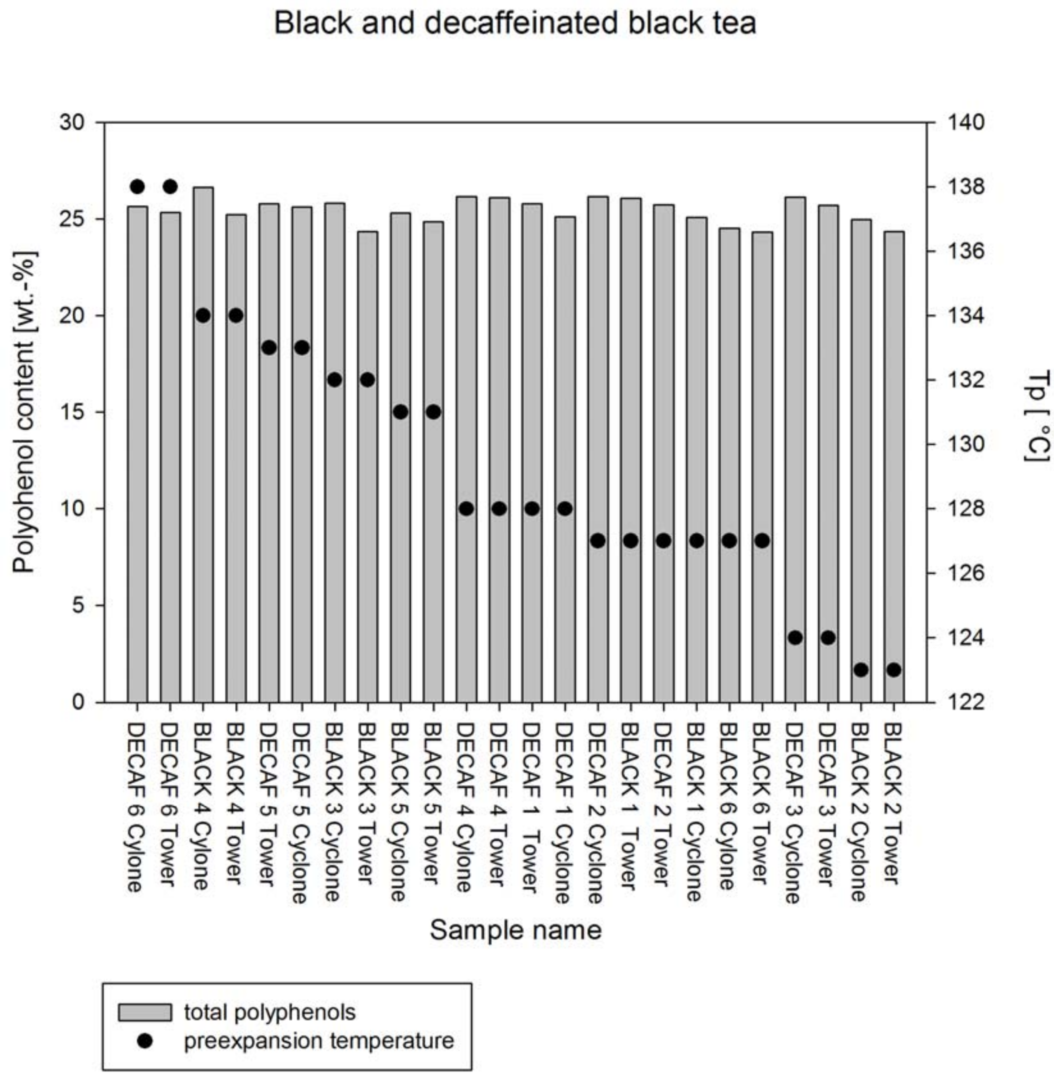
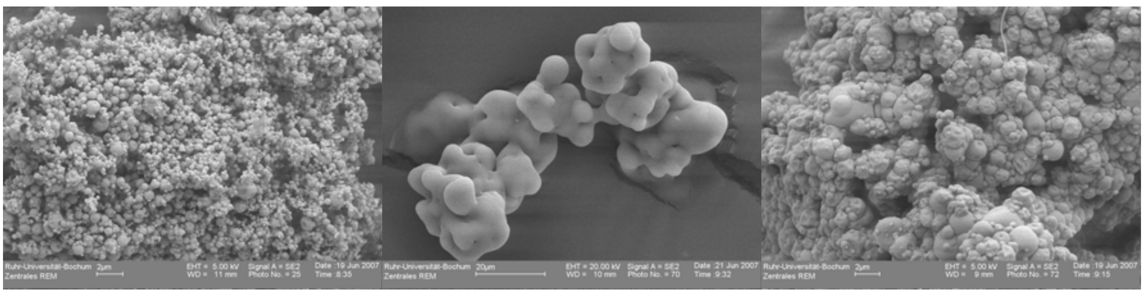


Figure 2: Influence of preexpansion temperature on polyphenol degradation in powders obtained from black tea extract

In Figure 3, particle morphology of selected samples is shows. Photos were taken with SEM microscope



a) b) c)

Figure 3: SEM photos of: a) green tea, sample Tea 12; b) black tea, sample Black 4; and c) decaffeinated black tea, sample Decaf 6; all collected form cyclone

SUMMARY

As mentioned in the text, the main focus of research was to observe the influence of relatively high temperature on degradation of active ingredients. The interval of special interest was with temperatures higher than 130 °C.

Powders produced in this experimental work showed small or no degradation, even when dried at very high temperature above 130 °C. Results confirmed preliminary research made with green tea. Furthermore, closer analysis of interval 130 – 134 °C and 138 °C showed, that powders obtained with high preexpansion temperature contain high amount of active ingredients.

The results show, that the polyphenol content in both black tea products is not influenced by the pre-expansion temperature in the temperature range from 123 to 134 (138) °C. For both teas relatively high temperatures of up to 134 °C respectively 138°C were used. Despite this high temperature the measured amount of polyphenols was with 25 wt.-% relatively high. There was difference in color of product observed for the same sample, collected from the tower and the cyclone. This is especially pronounced in case of decaffeinated black tea, where the color of samples contrasts the most, form dark yellow to almost black. Agglomeration was bigger in case of decaffeinated black tea samples, collected from cyclone. One explanation for darker color and agglomeration is higher water content of samples from the cyclone.

Concentrating on relatively narrow temperature interval (130 – 137 °C) for green tea, promising results were obtained. Taking in account standard deviation mistake of analyzes, it can be concluded, and that expanding working area up to 137 °C for green tea still gives satisfying results. Produced powders were light yellow color, with small or no agglomeration observed.

The maximum polyphenol contents which were achieved in these experiments were lying at 26,6 wt.-% for the black tea and 26,17 wt.-% for the decaffeinated tea. Therefore it can be concluded, that the polyphenol content in both teas is not influenced by the pre-expansion temperature in the range from 123 to 134 (138)°C. This becomes even more obvious if the standard deviation of the analyzing method is taken into account. The standard deviation of these experiments were in the range up to 2,82 %.

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