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INVESTIGATION ON THE POSSIBILITY TO ENHANCING HONEY SPRAY DRYING PROCESS AND POWDERS PROPERTIES BY ULTRAFILTRATION PRE-TREATMENT

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Linden honey ultrafiltration (15 kDa MWCO ceramic membrane) was performed as honey solution pre-treatment before spray drying. Feed and retentate solutions with the addition of maltodextrin as a carrier were spray dried. Drying yield and physical properties of powders were studied (after drying and after 12 weeks of storage). During ultrafiltration it was possible to remove some amount of sugars responsible for honey low glass transition temperature, while keeping protein compounds. Yet, it did not have a significant impact on the drying performance and improvement of powder physical properties immediately after drying and after storage. However, the possibility to remove sugars from honey solution by ultrafiltration can be an encouragement for further research.

Keywords: spray drying, honey, maltodextrin, ultrafiltration

1. INTRODUCTION

Consumers are increasingly interested in natural and easily digestible products, which are also rich in antioxidants and minerals. One such product is honey, which is characterized by unique aroma and taste, and also contains amino acids, microelements, enzymes, organic acids, polyphenols and anthocyanins. Numerous studies show that honey consumption reduces the risk of heart disease, cancer, inflammatory processes, prevents unwanted oxidation reactions and inhibits the growth and development of microorganisms (Alvarez-Suarez et al., 2010). Nevertheless, in food industry the application of honey is limited due to its high density and viscosity. Powdered honey shows much more desirable physical properties, it can be directly consumed or used as a supplement to a range of food products, dietary supplements. However, honey drying is still a difficult operation due to the high content of low molecular sugars causing low glass transition temperature of honey. Efforts were made to obtain honey powder by different drying methods: spray (Shi et al., 2013, Suhag and Nanda, 2016), vacuum (Nurhadi et al., 2012) and freeze-drying. The most perspective method seems to be spray drying, as it allows to obtain free flowing honey powder during one quick operation (Samborska et al., 2015b). However, to make it possible to transform honey solution into a powder it is necessary to modify material composition, process parameters or device design. The most popular approach is to apply the addition of drying carriers (like maltodextrin or gum Arabic), which increase material glass transition temperature to a value higher than the material temperature during drying, which is the necessary condition of successful drying. Other strategies include the application of drying aids like whey protein isolate (Shi et al., 2013), sodium caseinate (Samborska et al., 2015b), or the

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modification of honey composition with membrane processing by diafiltration (Samborska et al., 2017). Due to the membrane processing it is possible to modify the chemical composition of the raw material, and thus the influence on drying yield and the properties of the resulting powders is of interest. This work aims to investigate the relationship between honey ultrafiltration, the course of subsequent spray drying, and physical properties of powders after drying and storage.

2. MATERIALS AND METHODS

2.1. Materials

Linden honey was derived from a local beekeeper Krzemyk (Celestynów, Poland), while maltodextrin DEXTROMALT DE 15 was purchased from Hortimex (Poland).

2.2. Ultrafiltration

3XS29 membrane installation (OBR Pleszew, Poland), equipped with a ceramic 15 kDa MWCO membrane (TAMI Industries, surface 0.35 m^2, diameter 25 mm, length 585 mm) was applied. 1:1 honey solution with water was ultrafiltered for 80 min at maximum temperature of 35 °C. At time 0 and after 5, 10, 20, 30, 40, 50, 60, 70, 80 min the permeate flux J [$m^3/(s \cdot m^2)$] and extract content in permeate were measured. Feed solution (F) and obtained permeate (P) and retentate (R) were subjected to physicochemical determinations, as described in Section 2.4.1.

2.3. Spray drying

F and R obtained after UF were mixed with maltodextrin to obtain 30% of solid solutions (variants FMD and RMD), in with honey to carrier solids ratio was 50:50. In addition 30% maltodextrin solution (variant MD) was also spray dried. Spray drying was carried out in a Lab S1 dryer (Anhydro, Denmark) at the inlet air temperature 180 °C, the outlet air temperature 75 °C, the feed rate 0.9 mL/s, and the atomization disc speed 39,000 rpm. Drying was performed in duplicate. Drying yield Y was calculated as the ratio of powder solids to feed solution solids. Powders were stored for 12 weeks at room temperature in sealed BOPA/PE foil bags (thickness 55 μm) for further analysis (variants FMD12, RMD12, PMD12).

2.4. Analytical methods

2.4.1. Physicochemical characteristics of feed, permeate and retentate

Extract content determination was done by refractometer PAL-1 (ATAGO). Glucose and fructose were determined by HPLC with a refractometer detector (Agilent Technologies 1200 Series), 20 μL of each sample was injected onto 7.7 × 300 mm, 8 μm column at 85 °C with a flow rate of 0.6 mL/min. Protein content was measured by Kjeldahl method, after the determination of total nitrogen the amount of crude protein was estimated using 1 : 6.25 factor. Diastase number (DN) was determined by Schade method, based on starch standard solution hydrolysis by honey diastase during 1 h at 40 °C and quantifying the colour developed by reaction with iodine. The amount of samples F, P and R needed to prepare honey solution before determination corresponded to 10.0 g of honey (calculated based on extract content). Every determination was done in duplicate.

2.5. Selectivity analysis

Membrane selectivity regarding extract, glucose, fructose and nitrogen based compounds (NBC), after calculating the content of each component in F, P and R, was determined as retention factor R:

$$R = 1 - \left(\frac{m_P}{m_F}\right) \tag{1}$$

where m_P and m_F are the amounts of each compound in P and F (Darnon et al., 2002).

2.6. Powder analysis

Water content was determined by an oven method (105 °C/4 h). Loose and tapped bulk densities (D_L and D_T), were measured using an automatic tapper STAV 2003 (Engelsmann AG, Ludwigshafen, Germany) by determining the volume occupied by 20 g of powder (tapped density after 100 taps). Flowability and cohesiveness of powders were evaluated in terms of Hausner ratio HR:

$$HR = \frac{D_T}{D_L} \tag{2}$$

Repose angle (α) was calculated knowing the measured height of the cone created while the powder was poured from a fixed height onto a surface of a vertical metal cylinder with a diameter of 50 mm. For hygroscopicity measurement 1 g of powder (weighed with accuracy of 0.0001 g) placed in the aluminium pan was incubated in a desiccator with saturated NaCl solution (relative humidity 75%) at 25 °C. Samples were weighed after 1, 4, 24, 48, 96 and 120 h, respectively, and then water content u [g/100 g solids] and relative water content u/u_0 at the subsequent time intervals was calculated. Microphotographs of powder particles were taken using a scanning electron microscope TM3000 (HITACHI, Osaka, Japan) at a magnification of 400×. MultiScan v.18.03 software (Computer Scanning System, Warsaw, Poland) was used to determine the median diameter D_{50} – particle diameter defining exactly 50% of the distribution. All measurements were done in duplicate.

2.7. Statistical methods

All results were obtained in duplicate and statistically processed in analysis of variance, using software Statgraphics Centurion XV. Multiple range tests with least significant difference, with significance level of 0.05, were applied.

3. RESULTS AND DISCUSSION

3.1. Ultrafiltration

The whole process was run for 80 min. Permeate flow J decreased gradually during UF process what was caused by progressive membrane blocking resulting from unfavorable phenomena such as cake layer formation and concentration polarization. The extract content in permeate at the beginning of the process was 0.15% due to its dilution with water from the installation. Up to 30 min, it increased to a value close to 25%, then remained at a similar level to the end of UF. This demonstrates that the ultrafiltration membrane did not constitute a barrier to the basic components of feed solution which were low molecular weight sugars. Table 1 shows the physicochemical properties of feed solution (F), compared to permeate (P) and

Table 1. Physicochemical properties of feed solution (F), permeate (P) and retentate (R)

	F	P	R	Retention *R*
Extract [%]	31.2^{b}	22.8^{a}	24.5^{a}	0.86
Nitrogen based compounds [%]	0.175^{c}	0.064^{a}	0.104^{b}	0.91
Glucose [%]	14.1^{b}	10.4^{a}	11.7^{a}	0.86
Fructose [%]	11.4^{c}	7.9^{a}	8.7^{b}	0.87
Total sugars	25.5^{c}	18.3^{a}	20.5^{b}	

$^{a-c}$: Differences between values with the same letter in superscript in rows were statistically not significant ($p > 0.05$)

retentate (R) obtained after ultrafiltration, the differences between F and the ultrafiltration products were noted, which suggests selective separation of honey components by UF membrane. It was assumed that this separation would result in a higher drying yield and better physical properties of honey powder.

Extract retention factor *R* was 0.86 which means that 14% of extract passed to P (Table 1). *R* for NBC was 0.91, so almost the whole amount of those substances was rejected by the membrane. 9% of which passed to P could be low molecular weight free amino acids such as proline (115 Da), whose content in honey is about 0.03%. The obtained results agreed with those presented by Li et al. (2012), who proved that total protein retention is achieved using membranes with MWCO 20 and 25 kDa. 14% of glucose and 13% of fructose was transmitted to P. UF was less effective for sugar separation than that of diafiltration in the previous work (Samborska et al. 2017), in which the amount of extract, glucose and fructose was reduced in the honey solution by 22.7, 22.2 and 18.8%, respectively. Ultrafiltration membranes, although they should not theoretically constitute barriers to sugars, do not transmit them completely. Some molecules are absorbed on the surface of the membrane or are combined with other components. The time of the process and the ratio of feed solution volume to the membrane surface also have an impact. Due to the large volume of feed solution, during transfer through a membrane with a limited surface, not every sugar molecule comes into contact with it and can get into the permeate. Diastase number (DN) in F was 50, and in R it decreased to 29.4. Barhate et al. (2003) reported the approximate molecular weight of enzymes present in honey as 24 kDa for amylase, 54 kDa for α-glucosidase, and 10 kDa for glucose oxidase. Membrane used in the experiment was characterized by MWCO value of 15 kDa, so it probably rejected enzymatic proteins (retention factor *R* for NBC was 0.91). However, DN in R decreased, as a result of increased temperature (UF process was carried out at 35 °C for 80 min), and the fact that significant amount of NBC (48% – data not shown) also retained in the membrane or dynamic layer. However, the above values meet the requirements contained in the standard PN-88/A-77626. DN in P was equal 0, which demonstrated the lack of amylolytic activity/absence of diastase. Similar results were obtained by Barhate et al. (2003) after honey UF by membranes of 20, 25, 50 and 100 kDa MWCO.

3.2. Spray drying

3.2.1. Drying yield

Spray drying of MD was performed with the yield $Y = 99.4 \pm 0.0$. RMD and FMD variants had lower values of *Y*, 74.7 ± 3.6 and 72.4 ± 1.5%, respectively. Although *Y* of RMD was higher than that for FMD, the difference was not statistically significant ($p > 0.05$), while *Y* value of MD was statistically significantly higher ($p < 0.05$) than that obtained for other two variants. The drying performance of FMD and RMD was more difficult due to the presence of substances affecting lower glass transition temperature,

mainly glucose and fructose. An attempt was also made to dry UF retentate without MD addition, but no powder has been obtained. In the previous work (Samborska et al., 2017) more progressive honey sugar separation due to diafiltration led to the significant increase of drying yield from 52.5 to 64.9%. According to Adhikari et al. (2007) the criterion of successful spray drying is to achieve a total drying yield of more than 50%, so the drying processes of all variants can be considered satisfactory.

3.2.2. Powders properties

MD powder particles were apparently smaller in size and with less smooth, more wrinkled surfaces. FMD and RMD powders had the particles with spherical, regular shapes and smooth surfaces (Fig. 1).

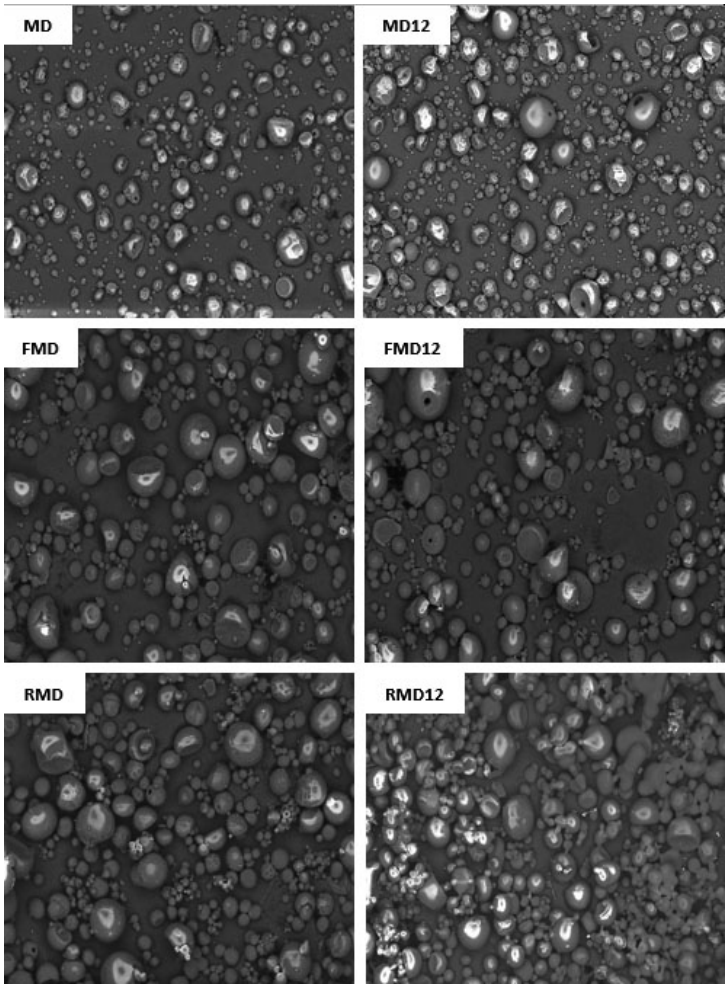

Fig. 1. SEM microphotographs of spray dried powders (mag. 400×)

The obtained powders were characterized by particles of various sizes. MD particles were smaller (mean diameter D_{50} was 16 μm) than other variants (FMD – 20 μm, RMD – 21 μm). Results were comparable to those presented by Shi et al. (2013) who spray dried honey (D_{50} values were from 16.5 to 66.8 μm depending on solution concentration). After 12 weeks of storage, the MD did not reveal any visible changes in particle morphology. Other powder particles partially stuck together to form agglomerate-like structures, which was more evident in the RMD powder, but still had smooth surfaces. After storage, the particle size of the MD and FMD powders increased (D_{50} value higher by 2 μm), while RMD powder particles decreased their size (decrease in D_{50} value by 1 μm). Despite the presence of a few particles of higher magnitude, MD particles remained smaller than those of other powders. Samborska et al. (2015a), spray dried rapeseed and buckwheat honey with the addition of Arabic gum and the mixture of Arabic gum and

sodium caseinate, demonstrated that after 12 weeks of storage the mean particle sizes of the powders were smaller. Only in case of the Arabic gum powdered particles which after storage enlarged. Samborska and Bieńkowska (2013) analyzed the morphology of honey powder particles obtained after spray drying. They proved that after 9 weeks of storage the structure of the powders has changed, the particles formed larger clusters probably as a result of progressive crystallization and the release of free water.

The water content in the powders was typical for spray-dried materials (Table 2). After 12 weeks of storage, the water content in the powders was higher than after drying due to partial water vapor permeability of packaging material. However, the differences between the values were not statistically significant due to large standard deviations. Jaya and Das (2005) studied the properties of mango powder, including the water content after storage. The initial water content of powder was 4.1%, while after 105 days of storage it increased to 8.9%. The obtained values of water content indicate that it is not advisable to apply ultrafiltration as honey pre-treatment prior to spray drying. There were no statistically significant differences between FMD and RMD variants both immediately after drying and after 12 weeks of storage.

Table 2. Physical properties of spray dried powders

	Water content [%]	Bulk loose density [g/cm^3]	Bulk tapped density [g/cm^3]	Hausner ratio	Repose angle [°]
MD	0.9 ± 0.3^a	0.43 ± 0.04^a	0.57 ± 0.06^a	1.33 ± 0.05^a	52 ± 2^a
FMD	3.8 ± 0.0^a	0.46 ± 0.03^a	0.61 ± 0.06^a	1.33 ± 0.06^a	60 ± 1^a
RMD	3.2 ± 0.5^a	0.44 ± 0.06^a	0.58 ± 0.08^a	1.32 ± 0.05^a	60 ± 2^a
MD 12	1.6 ± 0.6^a	0.45 ± 0.04^a	0.60 ± 0.04^a	1.35 ± 0.05^a	53 ± 2^a
FMD 12	4.4 ± 1.0^a	0.47 ± 0.04^a	0.64 ± 0.06^a	1.37 ± 0.17^a	62 ± 1^a
RMD 12	3.6 ± 0.8^a	0.55 ± 0.07^a	0.73 ± 0.13^a	1.34 ± 0.16^a	63 ± 2^a

$^{a-c}$: Differences between values with the same letter in superscript in rows were statistically not significant ($p > 0.05$)

The highest relative increase in water content among powders during hygroscopicity determination immediately after drying was noted for RMD powder, and the smallest for MD (Fig. 2). According to Unde et al. (2011) particle size affects hygroscopicity; in the studies on cane sugar they observed that smaller particles were more hygroscopic than the larger ones. In the current work, this relationship was not confirmed, the chemical composition of powders, including the content of sugars and proteins, was more important than the particle size. The chemical composition of powders also seems to affect the hygroscopicity – samples differed mainly in protein content. Samborska et al. (2017) examined hygroscopicity of spray dried honey powders after diafiltration pre-treatment. In their studies after 60 h the relative increase in water content in feed solution powder was about 14 (in the current work it equalled to about 6), while in the retentate powder the value was lower – about 7 (in the current work amounted about 9.5). After 120 h, it was about 15 and 8, respectively. Diafiltration proved to be a beneficial process, because the separation of sugars allowed for a reduction in the hygroscopicity of the powders. In the current work, the final values after 120 h were approximately 6.5 (FMD) and 10 (RMD) respectively, which did not indicate a beneficial effect of modification of the chemical composition of honey by ultrafiltration. In powders after 12 weeks of storage, the increase in water content during the hygroscopicity test was significantly lower than that found immediately after drying, which was caused by the higher water content and smaller driving force of water vapor adsorption.

Obtained values of bulk density were similar to those presented for honey powder (Suhag and Nanda 2016), apple juice powder (Michalska and Lech, 2018) There were no statistically significant differences

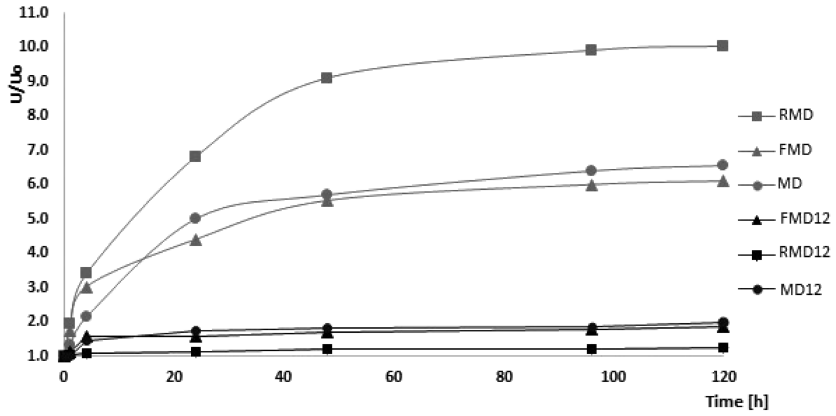

Fig. 2. Water vapor sorption kinetics of spray dried powders

in these parameters between powders. The flowability indicator for the powders was the Hausner ratio (*HR*) (Table 2). Materials with *HR* less than 1.2 are considered to be powders of good flow properties and low cohesiveness (Lumay et al. 2012). The *HR* values were from 1.32 ± 0.05 to 1.35 ± 0.05 (differences statistically not significantly), which indicated the average cohesiveness. *HR* values were higher than those presented by Samborska and Bieńkowska (2013). The angle of repose was from 52 ± 1° (MD) to 60 ± 1° (RMD). The value of the angle of repose depends on intermolecular and frictional forces, dominating in cohesive powders. Powders with poorer flowability are characterized by repose angle values above 45° (Michalska and Lech 2018), so the flowability of the obtained powders was poor or bad. After 12 weeks of storage the values were similar to those obtained immediately after drying. On the contrary, Samborska et al. (2015a) investigating the impact of storage on the properties of honey powder, showed that loose and tapped bulk density increased after storage, which was probably associated with a higher water content.

4. CONCLUSIONS

The aim of this work was to show whether the removal of some simple sugars from honey while retaining protein substances during ultrafiltration affects spray drying process and powder properties. Protein retention during ultrafiltration was higher than that for simple sugars, but the results connected with spray drying process did not indicate unambiguously the justification for application of the ultrafiltration process. Ultrafiltration did not significantly affect the improvement of drying yield. The retentate powder was more hygroscopic than others, which further adversely affected its storage. The obtained powders did not differ in terms of such properties as: loose and tapped bulk density, angle of repose or Hausner ratio. Considering the lack of impact of the pre-treatment of honey by ultrafiltration on the improvement of drying yield and physical properties of powders, this is not a recommended technique. However, the fact that it was possible to remove some of the sugars that are responsible for the low glass transition temperature of honey may encourage further research in this direction.

SYMBOLS

F	feed solution
P	permeate
R	retentate
UF	ultrafiltration

FMD feed solution mixed with maltodextrin to obtain 30% solutions
RMD retentate mixed with maltodextrin to obtain 30% solutions
MD maltodextrin solution
12 twelve weeks of storage
J permeate flux [$m^3/(s \cdot m^2)$]
R retention factor
m_P amounts of each compound (extract, glucose, fructose and nitrogen based) in permeate [g]
m_F amounts of each compound (extract, glucose, fructose and nitrogen based) in feed solution [g]
HR Hausner ratio
D_T loose bulk density [g/cm^3]
D_L tapped bulk density [g/cm^3]
Y drying yield [%]
u water content [g/100 g solids]
u/u_0 relative water content [g/g]
D_{50} particle diameter defining exactly 50% of the distribution [μm]

Greek letters

α repose angle [°]

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