MŰEGYETEM 1782

Ph.D. Thesis

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APPLICATION OF FRUCTO-OLIGOSACCHARIDES IN OSMOTIC DEHYDRATION BY DIFFUSION AND DEGRADATION KINETIC APPROACH

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1. Introduction, aims

The guiding principles of the modern nutrition encourage the food producers and food scientists of the 21st century to develop new, health-protective functional food products, which maintain the human health, can be applied in up-to-date diets and are attractive for the consumers.

With full knowledge of the domestic nutrition habits, it is important, that the fruit and fiber consumption of the Hungarian population is very small. The fiber enriched foods – like fruit products enriched by fructo-oligosaccharides are of overriding importance in the field of functional food development. Fructo-oligosaccharides have several nutritional benefits; prebiotic activity could be the considerable of them.

Osmotic dehydration fits well into the technology of dried fruit products, which eliminate the seasonal nature of fruit consumption beside their evident values. Osmotic dehydration is a water removal process. Due to the transport phenomena – especially solid gain in the tissues - occurring during this technological unit operation functional components could be introduce into plant matrix.

Fructo-oligosaccharides are not yet known as osmotic medium based on the available scientific literature. Due to their nutritional benefits, they could be functional food components. **The enrichment of fruit matrix with fructo-oligosaccharides by diffusion came forward as a real industrial problem, which has to be solved therefore, I set to my study the aim to investigate the technological applicability of fructo-oligosaccharides as osmotic agent.**

The aims of the study:

- Comparative investigation of the diffusion coefficient of fructo-oligosaccharides (Raftilose® P95, ORAFTI) and sucrose, scrutinizing the unique diffusion coefficient of each oligomer component, describing the transport phenomena.

- Investigation of the effect of treatments carried out before osmotic dehydration (blanching, microwave-treatment) on the texture, cell-membrane permeability, changes of the solid content, additionally on the transport phenomena occurring during osmotic dehydration in apple model (*Malus domesticus* cv. Idared).
- Characterization of the osmotic dehydration combined with vacuum-treatment, investigation its effect on the dehydration quality and fruit texture.
- Determination the rate of hydrolytic degradation occurring during technological unit operations. Kinetic study of the degradation based on laboratory simulation.

2. Experimental and calculation methods

- Determination of carbohydrate composition by HPLC (Merck & Hitachi system, L-6200 pump; Waters 6250 differential refractometer; D 2500 Integrator; Spherisorb SQ NH (SUPELCO) column, acetonitrile-water eluent.
- Measurement of tissue permeability (Labvig conductometer with 100 cell).
- Determination of the texture properties (Lloyd LR-5K texture analyser + Nexygen software; SMS TA.XT. Plus texture analyser + Texture Exponent 32 software.
- Dry matter and water content determination by gravimetric method; determination of soluble solid content (Carl Zeiss refractometer); volume measurement by granula exclusion, determination of density and porosity (picnometer 21/996).
- Sensory evaluation by scoring.
- Characterization of the water loss (1) and the solid gain (2); determination of the diffusion coefficient (3):

$$WL = \frac{m_b \cdot (MC_b / 100) - m_{OD} \cdot (MC_{OD} / 100)}{m_b \cdot (TSC_b / 100)} \quad (1)$$

$$SG = \frac{m_{OD} \cdot (TSC_{OD} / 100) - m_b \cdot (TSC_b / 100)}{m_b \cdot (TSC_b / 100)} \quad (2)$$

$$D_{eff} = \frac{m}{Fo} \cdot \frac{a^2}{3} \quad (3)$$

(1)-(2): WL: water loss, g/g; SG: solid gain, g/g; m: mass, g; MC: moisture content, w/w%; TSC: total solid content, w/w% (b: after blanching; OD: after osmotic dehydration)
(3): D_{eff}: effective diffusion coefficient, m^2/s;

m: slope of the function: $\ln\left(\frac{c - c_\infty}{c_0 - c_\infty}\right)$ - f(t), Fo: Fourier number

- Kinetic description of fructo-oligosaccharide degradation by numeric solving of (4)-(10) differential equations (Maple™ 9 - Maplesoft™).

$$\frac{dc_7}{dt} = -k_7^6 * c_7 - k_7^5 * c_7 - k_7^4 * c_7 \qquad (4)$$

$$\frac{dc_6}{dt} = -k_6^5 * c_6 - k_6^4 * c_6 - k_6^3 * c_6 + k_7^6 * c_7 \qquad (5)$$

$$\frac{dc_5}{dt} = -k_5^4 * c_5 - k_5^3 * c_5 + k_7^5 * c_7 + k_6^5 * c_6 \qquad (6)$$

$$\frac{dc_4}{dt} = -k_4^3 * c_4 - k_4^2 * c_4 + k_7^4 * c_7 + k_6^4 * c_6 + k_5^4 * c_5 \qquad (7)$$

$$\frac{dc_3}{dt} = -k_3^2 * c_3 + k_7^4 * c_7 + 2 * k_6^3 * c_6 + k_5^3 * c_5 + k_4^3 * c_4 \qquad (8)$$

$$\frac{dc_2}{dt} = -k_2^1 * c_2 + k_7^5 * c_7 + k_6^4 * c_6 + k_5^3 * c_5 + k_4^2 * c_4 + k_3^2 * c_3 \qquad (9)$$

$$\frac{dc_1}{dt} = k_7^5 * c_7 + k_6^4 * c_6 + k_5^3 * c_5 + k_4^2 * c_4 + k_3^2 * c_3 + k_2^1 * c_2 \qquad (10)$$

(4)-(10): c_i: i concentration of oligomer having degree of polymerization: i;
k_i^j : rate constant of the degradation of oligomer having degree of polymerization i to oligomer having degree of polymerization j

- Statistical evaluation was carried out by Excel (Microsoft) and Statistica 7.1 softwares (StatSoft).

3. New scientific outcomes

I. I have proved that the input of fructo-oligosaccharides into apple tissue by diffusion has acceptable rate from technological aspect. Based on this fact there is possibility to develop functional (e.g. prebiotic) fructo-oligosaccharide enriched fruit products by applying osmotic dehydration. /Matusek et al. (2005) Élelm Ipar LIX(1), 18-20.; Czukor et al. (2005) Konzervújság, 4, 92-96.; Matusek et al. (2008) Innov Food Sci Emerg Technol, in press/

There is not any difference between the physical properties of the samples - treated by the two different osmotic media - after blanching. However, after osmotic dehydration significant alteration was observed in their texture. The elasticity coefficient increases, the hardness of the fruit does not alter during osmotic dehydration in sucrose solution, meanwhile both of the two physical parameters decline by 30-50%.

II. I have established that the diffusion rate of fructo-oligosaccharides and sucrose are in the same order. The diffusion of fructo-oligosaccharides is more hindered than that of sucrose; it is a significant difference in the dehydration capacity of them. The dehydration capacity of fructo-oligosaccharides is less at room temperature, but it increases by the temperature, and it is better than for sucrose at 40-50°C. /Matusek & Merész (2002) Per Pol, 46(1-2), 83-92.; Matusek et al. (2005) Hung J Ind Chem, 33(1-2), 43-48.; Matusek et al. (2004) Élelm Ipar LVIII(4), 103-108.; Matusek et al. (2008) Innov Food Sci Emerg Technol, in press/

The sucrose gain is just twofold higher than the fructo-oligosaccharide gain however, the value of water loss is only by 30-40% greater. In case of osmotic dehydration by sucrose tissues have higher concentration of sugar regarding to the higher amount of soluble solid flowing into them whereas in case of fructo-oligosaccharide solution, the water loss causes same refraction in the tissues. The refraction of the tissues – being the resultant of the two transport phenomena – does not alter significantly in case of the two osmotic media.

III. I have found that the unique diffusion coefficient of oligomer components do not alter significantly from each other. The effective diffusion coefficient of dimer is 0, since steady state exists related to it. /Matusek et al. (2008) Eur Food Res Technol, in press/

The amount of monomer molecules decrease by the time of osmotic dehydration, since the concentration of them in the untreated fruit is higher, than in the oligomer mixture containing only a little amount of monomer. Hence, it diffuses from the fruit tissues into the solution. The amount of dimer molecules (mostly sucrose) is constant in the investigated range of the treatment. The amount of oligomers having higher degree of polymerization (DP3-DP6) increases logarithmically in the function of diffusion time. The values of effective diffusion coefficients are 2,3-2,5×10-9 m2/s.

Based on the assay of transport phenomena neither the sucrose nor the fructo-oligosaccharide gain are not affected by the temperature and time of blanching. On the contrary, water loss is influenced by these technological parameters. Water loss increases by the increase in the temperature and time of blanching. The changes are stronger in case of sucrose.

Heat treatment causes significantly lower hardness comparing to the untreated sample. The increase of heat treatment temperature from 60°C to 70°C decline the value of hardness significantly, while further increase by 10°C does not change the hardness significantly. The elasticity coefficient decrease significantly under the treatments comparing to the untreated sample, but the other blanching parameters do not alter its amount significantly in the studied range. Blanching causes decrease in the mass of the apple samples due to the damage of tissue structure, this is stronger in case of oligofructose solution. Fructo-oligosaccharides soften more the structure of the fruit. It is an important alteration between the two blanching agent, that after the pre-treatment by oligofructose followed by osmotic dehydration the mass loss is by 3-5% higher (18-20% compared to 14-17%).

In case of microwave treatment, the decrease of hardness is more notable than in case of conventional blanching. The microwave – treatment time and temperature have significant effect on the elasticity coefficient and hardness.

The tissue permeability increases monotonous by the increase of blanching temperature. The increase of temperature to 60°C the effective diffusion coefficient increases (2,2×10-9 m2/s), the alteration on higher temperature is not significant. The tissue permeability increase monotonous and significant also affected by microwave treatment. The value of diffusion coefficient increases significant by the temperature.

IV. I have showed that the vacuum-treatment does not alter the diffusion rate during osmotic dehydration operation. I have established that the technological advantage of the combined vacuum-blanching pretreatment is the increase of tissue permeability, but its drawback is the damage of the texture properties. /Matusek et al. (2008) Eur Food Res Technol, in press/

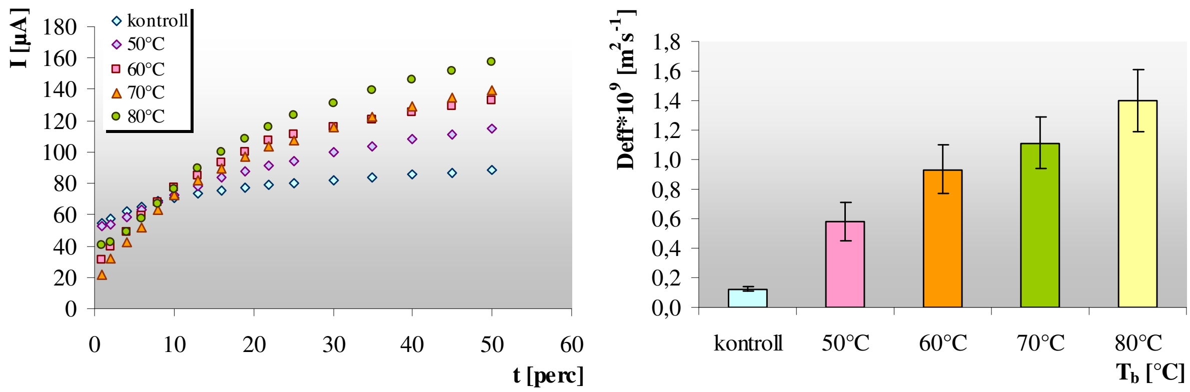

Fig. 1. Change of tissue permeability, ion-diffusion coefficient in the function of vacuum-blanching temperature

During osmotic dehydration which follows either conventional blanching or vacuum pretreatment similar diffusion coefficient was observed: 1.8-2.2×110^{-9} *m*^{2}*/s. In the course of combined pretreatment the tissue permeability increases by the increase of temperature (Fig. 1). The diffusion coefficient increases monotonous by the increase of temperature, and was higher also in case of treatment at 50°C. Between 50-80°C it increased from 0.6×10*$^{-9}$ *to 1.4×10*$^{-9}$ *m*^{2}*/s. However,* *the damage of texture properties emerges in the decrease to one third of elasticity coefficient, hardness and mass loss.*

V. I have proved that the degradation of fructo-oligosaccharides is a proton-catalytic process and under technologically real conditions (pH=2.7-3.3) a change by 0.3 unit in pH causes four fold alteration in the degradation rate. I have found that in buffered solution the activation energy is 70-120 kJ/mol dependent on pH. /Matusek et al. (2008) Acta Aliment, accepted; Matusek et al. (2008) submit. Eur Food Res Technol/

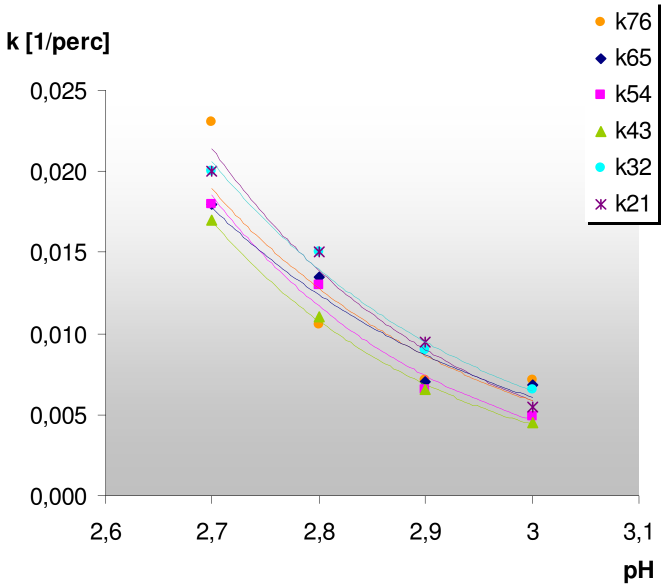

Fig. 2. Degradation coefficient in the function of pH at 80°C, in buffered solution

The degradation of oligomers can take place under the conditions of processing technologies (Fig. 2), if pH is under 3.5 and the temperature exceeds the 60°C. By lower pH than 3.0 the apple matrix, namely the component of the apple accelerate the degradation process (Fig. 3). Several theories can be drafted on the matrix effect of apple. First, the rate of degradation is catalyzed by the H^+ concentration, moreover the acid component of apple can also accelerate, catalyze the processes.

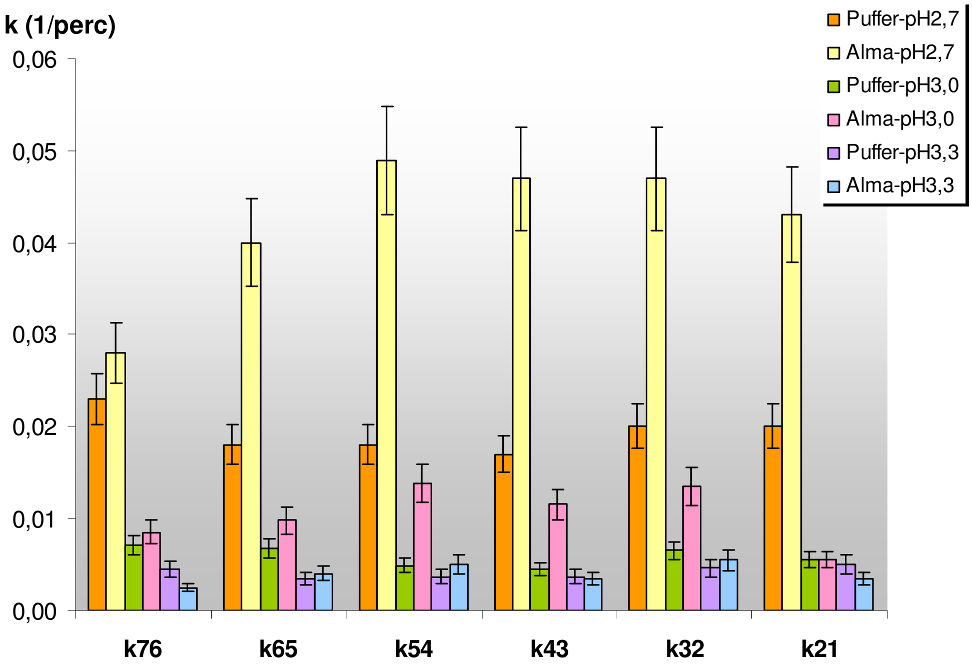

Fig. 3. Degradation coefficients in the function of number of oligomer units at different pH (2.7-3.0-3.3) in buffered solution and apple pulp

VI. I have showed that the rate of degradation depends on the degree of polymerization. According to the activation energy, the degradation rate of oligomers having higher degree of polymerization (DP6-7) is significantly greater. /Matusek et al. (2008) Acta Aliment, accepted; Matusek et al. (2008) submit. Eur Food Res Technol/

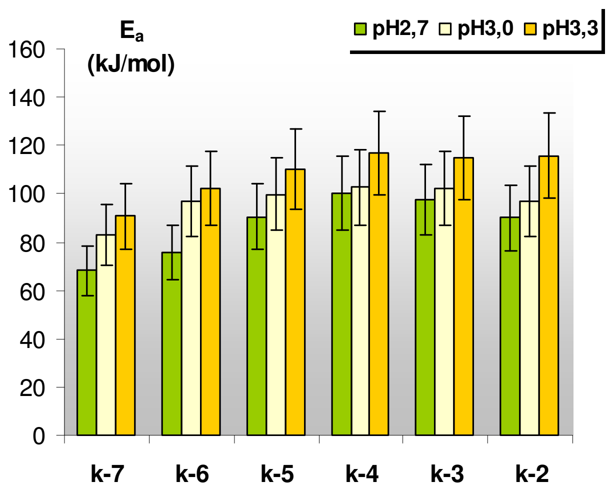

Fig. 4. The activation energy calculated by the summarized degradation coefficient in buffered solution (k-7, k-6, k-5, k-4, k-3, k-2: sign of the number of oligomer units)

VII. I have proved that among the possible degradation paths the rate of reaction that causes end-chain degradation is higher than the rate of inside-chain hydrolysis. /Matusek et al. (2008) Acta Aliment, accepted; Matusek et al. (2008) submit. Eur Food Res Technol/

Table 1. Degradation coefficients according to degradation paths (80°C, pH=2.7; buffered solution)

Degradation coefficient (1/min)					
End-chain degr.		Inside-chain degradation			
k_{76}	0,023	k_{75}	0,004	k_{74}	0,003
k_{65}	0,018	k_{64}	0,005	k_{63}	0,003
k_{54}	0,018	k_{53}	0,005		
k_{43}	0,017	k_{42}	0,005		
k_{32}	0,020				
k_{21}	0,020				

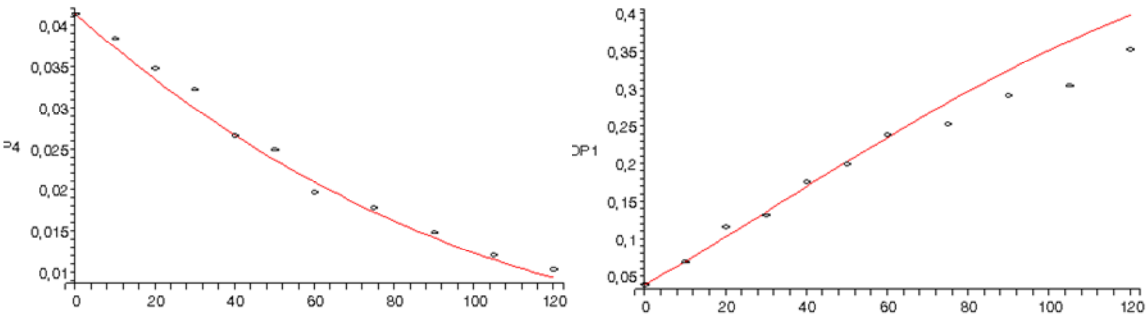

Fig. 5. Comparison of the calculated and measured oligomer and monomer concentration (Degradation of tetramer and formation of monomer (80°C, pH=2.7; buffered solution)

4. APPLICATION

The input of fructo-oligosaccharides into apple tissue by diffusion has acceptable unit operation rate. Based on this fact it is possible to develop functional (e.g. prebiotic) fruit products, which are enriched by fructo-oligosaccharides by applying osmotic dehydration.

The results of technological and kinetic experiments summarized in the Ph.D. thesis can be utilized in the development of foods enriched by fructo-oligosaccharides. The adapted methods help the technological planning and are suitable for the investigation of the products. Several types of production technologies can contain the step of osmotic dehydration, as the method to enrich tissues in functional components, so exact technological recommendation could be suggested only in view of the end product. However, some general guide-lines could be stated:

- In the processing technology of fruits applying fructo-oligosaccharides under the natural pH (3.0) the operation temperature should not exceed the 60°C, avoiding the degradation of fructo-oligosaccharides.
- For an apple based product having high value and good organoleptic properties, blanching of the raw material in isotonic solution and osmotic dehydration at low temperature (<60°C) could be suggested.
- The osmotic dehydration combined by vacuum-treatment could be used by such a special product group, semi-final products, when the damage in the texture properties is not important because of the further technological processing resulting a more complex food matrix, where the osmotically dehydrated material is only a component of the end product.

5. PUBLICATIONS RELATED TO Ph.D. THESIS

Papers in English

1. Matusek, A., Merész, P. (2002). Modelling of sugar transfer during osmotic dehydration of carrots. *Periodica Polytechnica Ser. Chem. Eng*., 46(1-2), 83-92.

2. Matusek, A., Czukor, B., Merész, P., Örsi F. (2005). Mathematical modelling in osmotic dehydration. *Hungarian Journal of Industrial Chemistry,* Special Issue on Recent Advances in Computer Aided Process Engineering, 33(1-2*)*, 43-48.

3. Matusek A., Czukor, B., Merész P. Comparison of diffusion of fructo-oligosaccharide components during vacuum impregnation and osmotic dehydration, *European Food Research and Technology*, In press, Available online: 2007. augusztus 24. IF: 1,084

4. Matusek, A., Czukor, B., Merész, P. Comparison of sucrose and fructo-oligosaccharides as osmotic agents in apple. *Innovative Food Science and Emerging Technologies,* In press, Available online: 2007. november 4. IF: „*publishing in 2008*."

5. Matusek, A., Merész, P., Le T. K. D., Örsi F. (2008) Fructo-oligosaccharide degradation in apple pulp matrix, *Acta Alimentaria*, In press IF: 0,253

6. Matusek, A., Merész, P., Le T. K. D., Örsi F. (2008) Effect of temperature and pH on the degradation of fructo-oligosaccharides, Submitted to *European Food Research and Technology* IF: 1,084

Papers in Hungarian:

7. Matusek, A., Czukor, B. (2005). Frukto-oligoszacharidok felhasználási lehetőségei gyümölcskészítményekben. *Élelmezési Ipar*, LIX. (1), 18-20.

8. Czukor, B., Matusek, A., Léder Ferencné., Schusterné Gajzágó, I., Vásárhelyiné Perédi, K. (2005). Az egészségmegőrzést szolgáló minőségnövelő anyagok alkalmazása élelmiszerek előállításánál. *Konzervújság,* 4., 92-96.

9. Matusek, A., Czukor, B., Merész, P., Örsi F. (2004). Szacharóz és frukto-oligoszacharidok diffuzivitásának összehasonlító vizsgálata almán. *Élelmezési Ipar*, LVIII. (4), 103-108.

10. Matusek, A., Czukor, B., Merész, P. (2003). Az ozmotikus dehidratáció élelmiszeripari alkalmazásának szempontjai és modern megoldásai. *Élelmezési Ipar*, LVII. (5), 136-140.

Proceeding in Hungarian:

11. Matusek, A., Czukor, B. (2005). Az ozmotikus dehidratálás művelete a gyümölcsfeldolgozás folyamatában. *Műszaki Kémiai Napok '05*, Veszprém, 2005. április 26-28., Konferencia Kiadvány, 74-77.

Summary in Hungarian

12. Czukor, B., Matusek, A., Léder Ferencné., Schusterné Gajzágó, I., Vásárhelyiné Perédi, K. (2005). Minőség növelést célzó anyagok alkalmazása élelmiszerek előállításánál. *Konzervújság*, 2., 36.

Poster presentations in English:

13. Matusek, A., Czukor, B., Merész, P. Fructo-oligosaccharides in the functional food development. ***The First International Congress on Food Safety*** (SAFE Congress), Budapest, 11-14. June, 2006.

14. Matusek, A., Czukor, B., Merész, P., Örsi, F., Kupeczik, M. Comparative investigation of the osmotic behaviour of sucrose and fructo-oligosaccharides in apple. ***6th International Conference on Food Science***, Szeged, 20-21. May, 2004.

15. Matusek, A., Czukor, B., Merész, P., Örsi, F. Osmotic enrichment of apple by fructo-oligosaccharides. ***2nd Central European Food Congress*** (2nd CEFood Congress), Budapest, 24-26. April, 2004.

Poster presentations in Hungarian:

16. Matusek, A., Léder Ferencné, Czukor, B. Kedvező érzékszervi tulajdonságú prebiotikus frukto-oligoszacharidokkal dúsított élelmiszerek. ***Magyar Táplálkozástudományi Társaság XXXI. Vándorgyűlése***, Keszthely, 5-7. October 2006.

17. Czukor, B., Matusek, A., Merész, P., Örsi, F. Diszacharid és oligoszacharid ozmózisos hajlamának összehasonlító vizsgálata almában. ***„Lippay János – Ormos Imre – Vas Károly" Tudományos Ülésszak***, Budapest, 6-7. November 2003.

Lecture in English:

18. Matusek, A., Czukor, B., Merész, P., Örsi, F. Mathematical modelling in osmotic dehydration. ***10th International Workshop on Chemical Engineering Mathematics,*** Budapest, 18-20. August 2005.

Lectures in Hungarian:

19. Matusek, A., Czukor, B., Merész, P., Albók, N. Vákuum-kezeléssel kombinált ozmotikus dehidratálás vizsgálata almán. ***„Lippay János – Ormos Imre – Vas Károly" Tudományos Ülésszak,*** Budapest, 19-20. October 2005.

20. Matusek, A., Czukor, B. Prebiotikus szénhidrátok felhasználása gyümölcskészítményekben. ***74. Országos Mezőgazdasági és Élelmiszeripari Kiállítás (OMÉK), Fiatal Kutatók Fóruma***, Budapest, 1 September 2005.

21. Czukor, B., Matusek, A., Léder Ferencné., Schusterné Gajzágó, I., Vásárhelyiné Perédi, K. (2005). Minőség növelést célzó anyagok alkalmazása élelmiszerek előállításánál. ***XXXVII. Nagykőrösi Konzervipari Napok Tudományos Tanácskozás***, Nagykőrös, 9-10. May 2005.

22. Matusek, A., Czukor, B. (2005). Az ozmotikus dehidratálás művelete a gyümölcsfeldolgozás folyamatában. ***Műszaki Kémiai Napok '05***, Veszprém, 2005. április 26-28., Konferencia Kiadvány, 74-77.

23. Matusek, A., Czukor, B., Örsi, F. Az ozmotikus dehidratálás vizsgálata almán. ***II. Doktoráns Konferencia***, BME, 24. November 2004.

24. Matusek, A., Czukor, B. Gyümölcskészítmények előállítási technológiájának kidolgozása frukto-oligoszacharidokkal. ***A Magyar Táplálkozástudományi Társaság XXIX. Vándorgyűlése***, Hajdúszoboszló, 28-30 October 2004.