P-058 **Application of γ-cyclodextrin as oxidative stabilizer during the spray drying of fish oil**

Krawczynska W., Tarnowiecka-Kuca A., Chojnacka M., Bartkowiak A.,
The Westpomeranian University of Technology in Szczecin, ul. Kazimierz Królewicz 4,
71-547 Szczecin, Poland ; wkrawczynska@gmail.com

INTRODUCTION AND OBJECTIVES

Cyclodextrins CD are non-reducing, cyclic oligosaccharides, composed of D- glucose units linked by α-1,4 glycosidic bonds. The base cyclodextrins are α- CD (six glucose units), β- CD (seven glucose units), γ- CD (eight glucose units). The cyclodextrins due to their cyclic structure have cavity which has inside hydrophobic and outside hydrophilic character. They are able to form complexes with different hydrophobic molecules. Part of them, when make a gust-host complex, especially with hydrophobic compounds, changing the physicochemical properties, such as solubility, stability, taste and odour. For this reason they are widely applied as additives in food, cosmetic, pharmaceutical, agriculture and chemical industries. γ- CD due to appropriate size of cavity may be used as effective carrier and stabilizer for polyunsaturated fatty acids (PUFA) (Kobayashi 2007).

Fish oil is a source of long-chain polyunsaturated fatty acid of omega-3 (EPA - eicosapentaenoic and DHA - docosahexaenoic acids). Both EPA and DHA strongly contribute to beneficial health effects, where their regular intake may prevent cardiovascular diseases, certain types of cancer, inflammations and allergies as well as improve proper development and function of central nervous system. Specifically dried complexes of fish oil with cyclodextrin in the powder form is of special interest of food industry, because it can be long-term stored and applied as food additives in form of instant powder.

Spray drying is a low-cost microencapsulation technology and the most commonly applied in the food industry. It may also be useful for microencapsulation of omega-3 PUFA oils. It has been concluded in many scientific papers, that the production of fish oil microcapsules by spray drying technique is possible, however still its oxidative stability has to be improved (Kolanowski 2006)

The aim of this study was to investigate the effect of γ-CD used as complexing agent on chemical stability of fish oil during the spray drying process. Furthermore, the feasibility of two methods to determine oxidative stability of fish oil encapsulated in γ-cyclodextrins will be evaluated. Complexes of fish oil and cyclodextrins will be formed by precipitation method. After that such samples in form of water dispersion with addition of two other potential stabilizers will be spray dried.

MATERIALS AND METHODS

γ-cyclodextrin (Cyclolab, Ltd. Hungary) and Hi-Cap 100 (National Starch Food Inovation, USA) were used as main components during the spray-drying process.

Fish oil (Norway) was used as immobilized materials. Chemicals like chloroform, methanol (Chempur, Poland) were use to prepare extracts.

All γ-cyclodextrin complexes with fish oil were prepared at room temperature using classical procedure based on precipitation method. The following 1:1 and 10:1 molar ratios of γ-CD to fish oil were applied. Specific amounts of γ-CD have been dissolved in 100 ml of distilled water. After direct addition of oils, the resulting mixture has been stirred at 750 rpm for 24h at room temperature. The resulting mixtures/dispersions were mixed with 20% Hi-Cap 100 solutions and spray dried (Mini Spray Dryer B-290, Switzerland). The operating conditions of the spry dryer were as following: inlet/outlet temperature: 160/100 [˚C], feed flow: 0,12 [ml/h], volume flow: 32,5 [m^3/h]. Dried samples in form of powder were collected and applied in further tests. Stability of oxidation was determined by two methods: peroxide value (BN-74/8020-07 Branch Standard - Frozen Fish. Evaluation of lipid rancidity. Determination of the peroxide value) and ATR-FTIR (Spectrum Spotlight 300, Perkin Elmer, USA equipped with Golden Gate diamond ATR system Specac, UK).

The first method referred to determination of peroxide value. After the drying process a certain amount of dried complex was homogenized with chloroform/methanol in order to extract the oil from cyclodextrins (Bligh&Dyer extraction procedure) (Tarnowiecka A. 2006)

The second method is direct measurements based on ATR-FTIR spectroscopy with direct intensity measurement of specific bands referring to change in chemical composition of complexed fish within the dry product (Muik 2005)

All samples in powder form were stored for 2 weeks to monitor changes of both, the peroxide values and FTIR spectra.

RESULTS AND DISCUSSION

The oxidation process as function of various parameters was monitored by determination of peroxide values (Fig.1). The oxidation process proceeds slower when either oregano oil or Hi-Cap 100 was present in composition. The complexation effectiveness is strictly related to amount of γ-cyclodextrin applied in the system, where in case of this study the 1:1 ratio was to low to reach the full complexation of fish oil. .

Changes in UV-Vis Spectra (Fig. 2) also confirm that both oregano oil and Hi- Cap 100 have positive inhibition effects on oxidation processes. The samples without OO and Hi-Cap 100 have higher peroxide value and are less stable during 14 days storage.

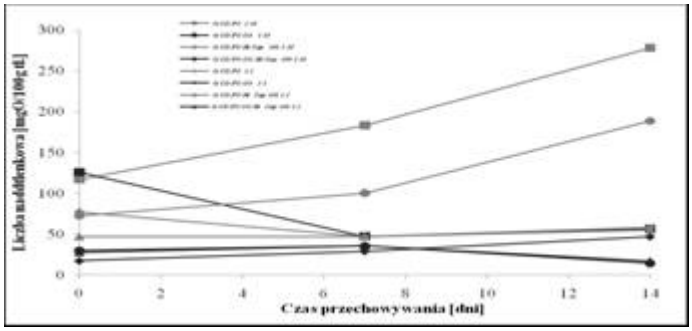

Figure 1. Oxidation change of complex fish oil (FO) with γ-cyclodextrin (G-CD), oregano oil (OO) and Hi-Cap 100.

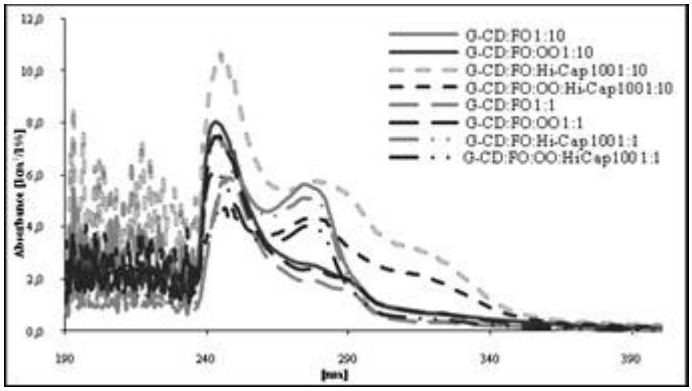

Figure 2. Change of PUFA oxidation (UV-vis spectra) in dry powder form of various complexes based on fish oil (FO), γ-cyclodextrin (G-CD), oregano oil (OO) and Hi-Cap100 determination by.

Another method which has been applied to monitor the oxidation deterioration and quality parameters of fish oil was ATR-FTIR technique (Muik 2005). By this method one can monitor changes of specific functional groups both qualitatively and quantatively. Higher temperature during spray drying process causes degradation and formation of product with various chemical compositions. The main differences were observed in peak intensities, which correspond to groups of fish oil immobilized in different matrixes. The most pronounced changes are observed for bands 1640, 1745 and 3010 cm^{-1}, which correspond to vibrations of cis double bonds [3]. There were two main regions which have been specifically monitored (Muik 2005)

- 1600-1775 cm^{-1} – increase in 1655 cm^{-1} region – corresponding to C=C stretching; formation of conjugated double bond systems;
- 2800-3050 cm^{-1} – decrease of cis-double bonds intensity in region 3007-3012 cm^{-1}.

The comparison or results shows that both. After the statements of results observed that amount (1:1 or 10:1) fish oil with/without oregano oil influences on intensity peaks derived from ester groups (C=O). Hi-Cap 100 has also impact on intensity of peaks indicating its positive effect on fish oil stabilization and protection during oxidation processes. One can pointed out that there is correlation between results of both methods (Table1) indicating that less labor-intensive ATR-FTIR technique could be applied for fast screening of fish oil oxidation processes.

Sample	Peroxide value [mqO_2/kg]	ATR-FTIR $A_{(1620-1680)}/I_{1625}$
G-CDO:FO 1:10	117,2	59
G-CD:FO:O 1:10	126,0	49
G-CD:FO:HI-CAP 100 1:10	72,7	48
G-CD:FO:OO:HI-CAP 100 1:10	30,3	44
G-CD:FO 1:1	77,3	76
G-CD:FO:OO 1:1	17,5	47
G-CD:FO:Hi Cap 100 1:1	47,2	53
G-CD:FO:OO:Hi Cap 100 1:1	27,8	50

Table 1. Results of two methods - determination of oxidation process.

CONCLUSIONS

The results obtained in this work confirm that complex of γ-cyclodextrin with fish oil has higher protection capacity in case of its higher molar ratio in respect to fish oil. Small amount of oregano extract has significant positive effect on protection against oxidation of PUFA during the spray drying process. Hi-Cap 100 protects PUFA from oxidation and has an influence on higher stability of formed systems. However, still further investigations including monitoring of oxidative stability of such powders during storage at different conditions are necessary.

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