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STUDY OF THE OXIDATION OF AN OMEGA-3 CONCENTRATE AFTER FORMULATION AS OIL IN WATER EMULSIONS

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Introduction

Fish oil,Natural source
EPA (C20:5n-3) and DHA
(C22:6n-3)

Importance in human health
Reduction risk of cardiovascular diseases and cancer, improve brain development, prevention inflammatory related pathologies

Essential fatty acids
n-3 PUFA entirely
derived from diet

Omega-3 polyunsaturated fatty acids (n-3 PUFA)

Incorporation of fish oil to food products
Strategies

Food habits: meat, fast food, snack food…
Rich in saturated fatty acids
Low proportion PUFA

Development of products enriched with n-3 PUFA
Nutritional suplements
Fuctional foods

Nutritionists: necessity of consuming fish and green vegetables to prevent many diseases

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Introduction

Disadvantages (n-3 PUFA)

Highly susceptible to lipid oxidation, in presence of oxygen and temperature

Negative impact on shelf life, nutritional value and flavor of foods

Low water solubility

Avoid or delay oxidation

Improve dispersability in water systems

Required Formulation n-3 PUFA

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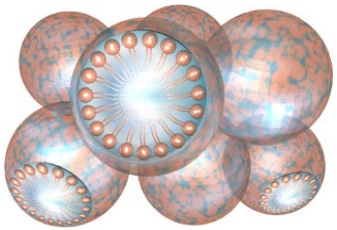
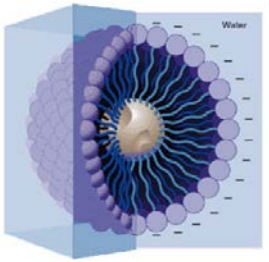
Objectives

Development of an optimum formulation of an omega-3 concentrate as oil in water emulsion

Carrier material: OSA-starch





- ✓ Study of the oxidative stability of the emulsion over time
- ✓ Study of the effect of antioxidants addition to the developed formulation on the oxidative stability over time

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Omega-3 concentrate

Commercial Omega-3 polyunsaturated fatty acids (**n-3 PUFA**) concentrate

Total content of DHA: 73%

Total n-3 PUFA: 92%

72 % triglycerides

11% diglicerides

2% monoglycerides

15% ethyl esters

Oxidation state

Peroxide value	Anisidine value
3.79 ± 0.017 meq O2/kg oil	11.94 ± 0.065

Suitable for human consumption

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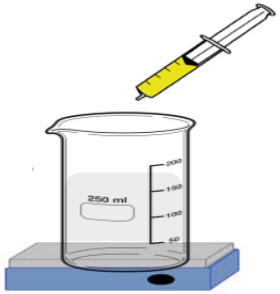
Experimental Section

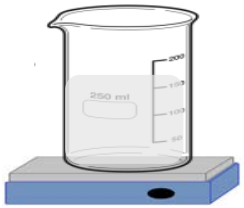
Preparation OSA-starch dissolution

Addition of oil phase (ω-3 concentrate)

Pre-mixing Pre-emulsion

Emulsification by Ultrasounds





Study the effect of amplitude, ultrasounds time and oil content on the droplet size

Experimental Design
Response Surface Methodology
(RSM)

Optimal emulsion

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Optimal conditions by RSM

Effect of different variables on droplet size (Y)

Oil content (X_1): 3-9 % w/w (total solids: 30% w/w)

Ultrasounds emulsification time (X_2) : 60-300 s

Amplitude (X_3): 50-100%

Central Composite Design

17 experimental settings

3 replicates in central point

Second order polynomial equation: prediction response values of droplet size as a fuction of X_1, X_2 and X_3.

Analysis of variance with 95% confidence level

Optimal conditions

R^2= 96,1715%

Oil content: 6 % w/w
Ultrasounds time: 180 s
Amplitude: 100%

Predicted Value: 116 nm
Experimental value: 121 nm

Droplet size ↓ when amplitude ↑ (at X_2= 180s)
Droplet size ↓ when ultrasounds time ↑

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Optimal conditions by RSM

Effect of different variables on droplet size (Y)

Oil content (X_1)	**Ultrasounds emulsification time (X_2)**	**Amplitude (X_3)**
3-9 % w/w (total solids: 30%)	60-300 s	50-100%

Central Composite Design

17 experimental settings

3 replicates in central point

Second order polynomial equation: prediction response values of droplet size as a function of X_1, X_2 and X_3.

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{23}X_2X_3$$

Analysis of variance with 95% confidence level

All coefficients statistically significant

Exception: a_{11}, a_{33} and a_{13}

Effect of variables on droplet size

Droplet size ↓ when amplitude ↑

Droplet size ↓ when ultrasounds time ↑

Droplet size ↓ when oil content ↓

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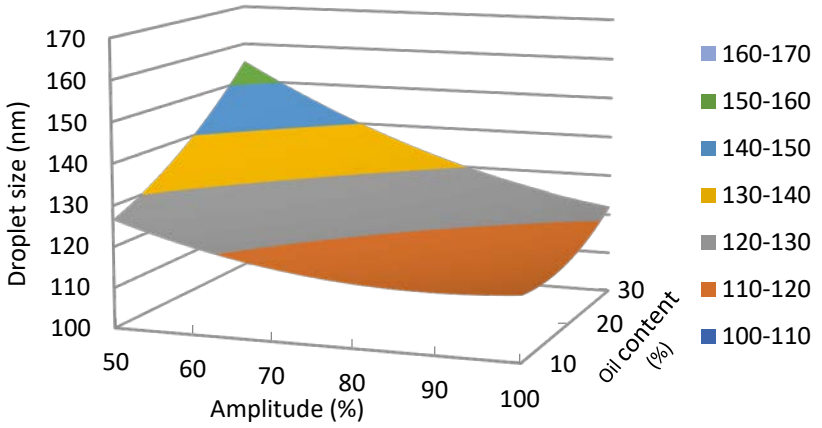
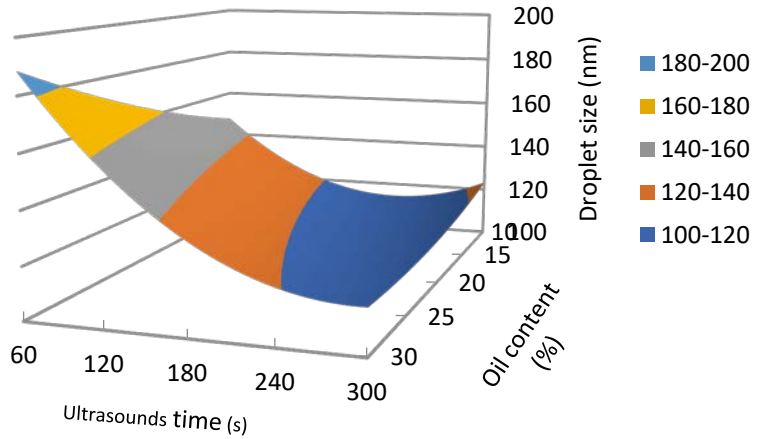
Optimal conditions by RSM

Time: 180 s



Amplitude: 75%



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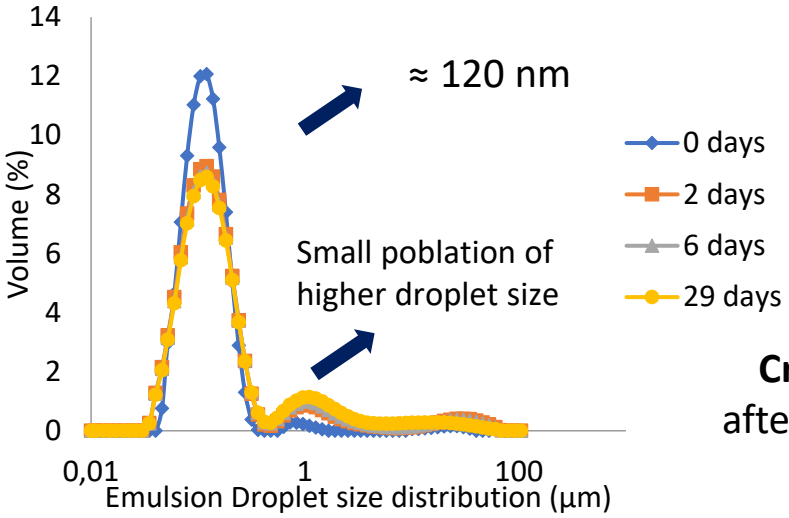
Optimal emulsion stability during storage



Creaming: from 6 days after emulsion preparation

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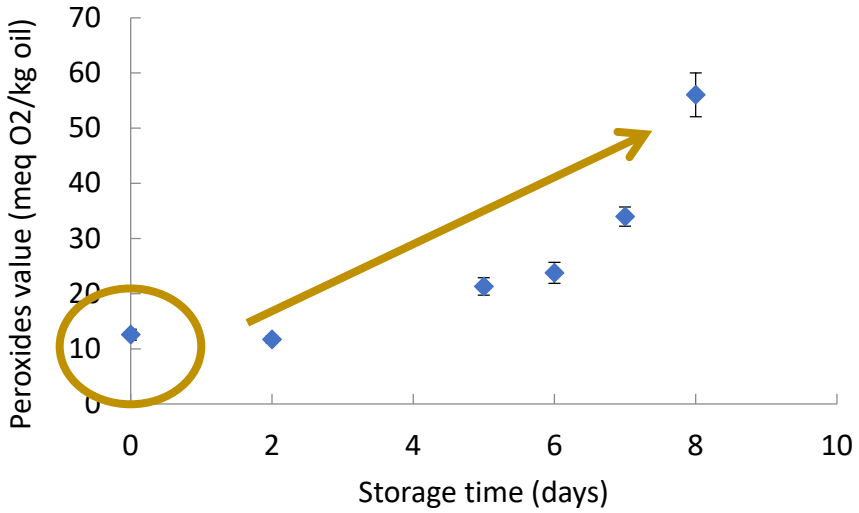
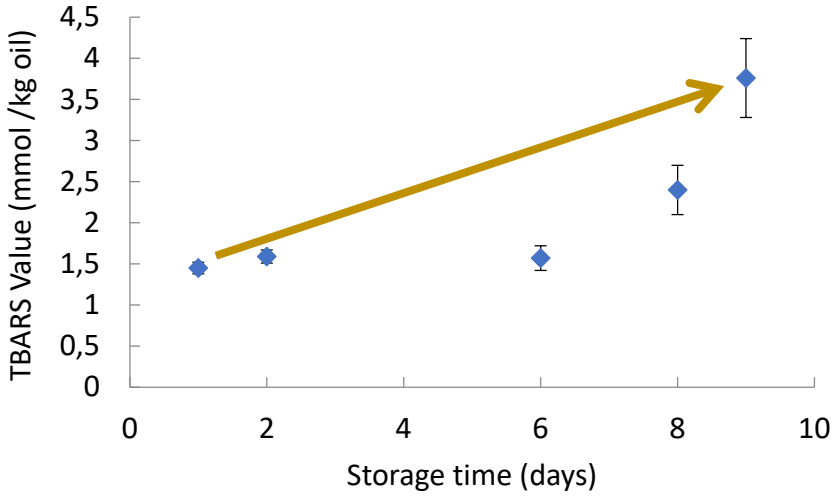
Oxidative stability of emulsion

Preliminary study

- Opening the oil container and handling without N_2 atmosphere
- Emulsion storage at ambient temperature and darkness





- At t = 0 days, PV ↑↑
- High values of PV and TBARS over time

Required to open and handle the oil container with N_2

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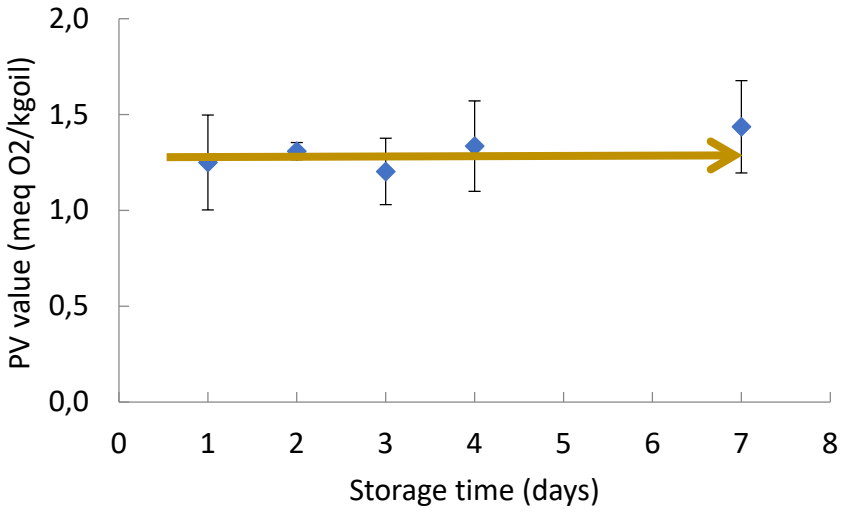
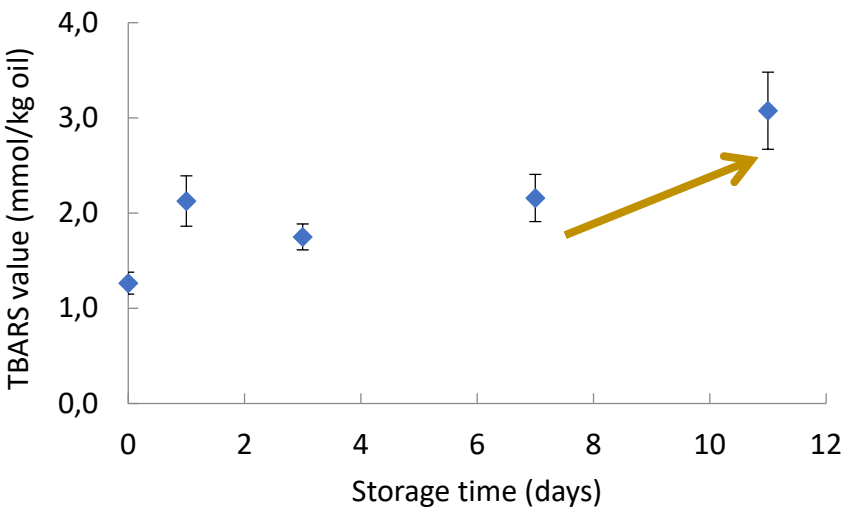
Oxidative stability of emulsion

- Open and handle the oil container with N_2 atmosphere
- Emulsion storage at ambient temperature and darkness





- Constant PV over time (PV= 1-1.5 meq O_2/kg oil)
- TBARS values increase considerably from 7th day of storage
- PV at t=0 days > PV oil (3.8 meq O_2/kg oil)

Formulation protects against oxidation of omega-3 concentrate

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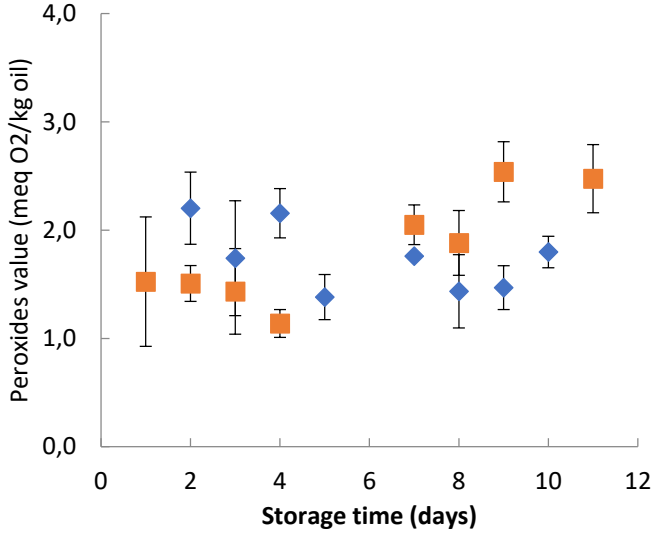
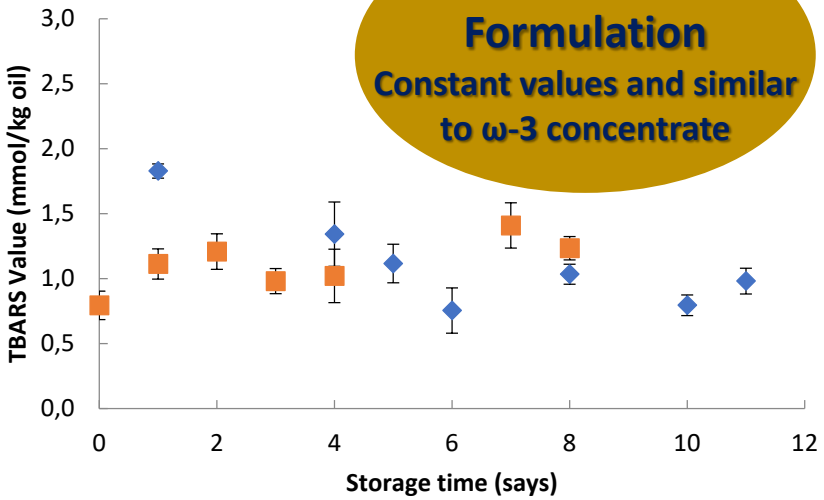
Oxidative stability of emulsion

Emulsion with addition of Ascorbic Acid (20 mM)





Suitable Formulation
Constant values and similar to ω-3 concentrate

Storage with N_2 and T=4ºC

Storage at ambient temperature and darkness

- Slighly lower PV and TBARS values when emulsion was stored with N_2 and at 4ºC.
- Almost constant values of PV with addition of AA as reported in literature (Uluata et al. 2015).
- TBARS values were constant over time, similar to ω-3 concentrate TBARS value (0.825 ± 0.033 mmol/kg)
  - **The formulation of ω-3 concentrate as oil in water emulsions adding AA, was suitable to delay the lipid oxidation**

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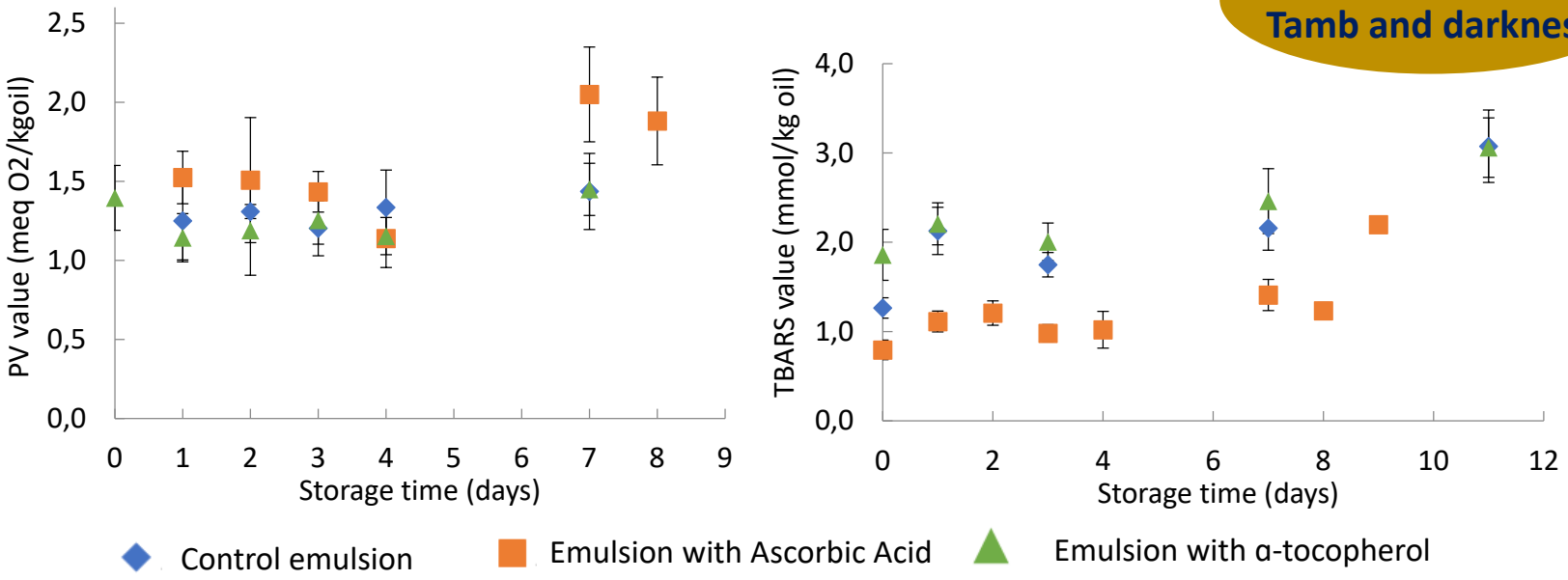
Oxidative stability of emulsion

Comparative: Emulsion with addition of Ascorbic Acid (20 mM), α-tocopherol (1.75 mg/g oil) and control emulsion

Emulsion storage
Tamb and darkness



- Similar values of PV comparing with the control emulsion. The addition of antioxidants to the emulsion did not affect to the primary oxidation
- Control and α-TOC emulsions → similar TBARS values.
  - Adding α-TOC to emulsions did not delay the secondary oxidation
- Adding AA to emulsions delays the secondary oxidation

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Conclusions

- Development of a suitable formulation of an omega-3 concentrate as oil in water emulsions by ultrasounds
  - Optimum emulsion (120 nm): 6% oil content, 180s of ultrasounds emulsification time and 100% amplitude
- Oxidative stability of emulsion
  - Preliminary study → **Required to open and handle the oil container under N_2 atmosphere**
  - Under N_2 atmosphere, PV decreased comparing with the preliminary study (PV= 1-1.5 meq O_2/kg oil)
    → **Formulation protects against oxidation of ω-3 concentrate**
  - Effect of adding different antioxidants
    - Addition of Ascorbic Acid: contant values of PV and TBARS (and similar to the ω-3 concentrate)
      → **Suitable to delay the lipid oxidation**
    - Addition of α-tocopherol: similar values of PV and TBARS compared with control emulsion

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THANK YOU FOR YOUR ATTENTION

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