Valorization of unused chokeberries: encapsulation and storage stability of their phenolic extract

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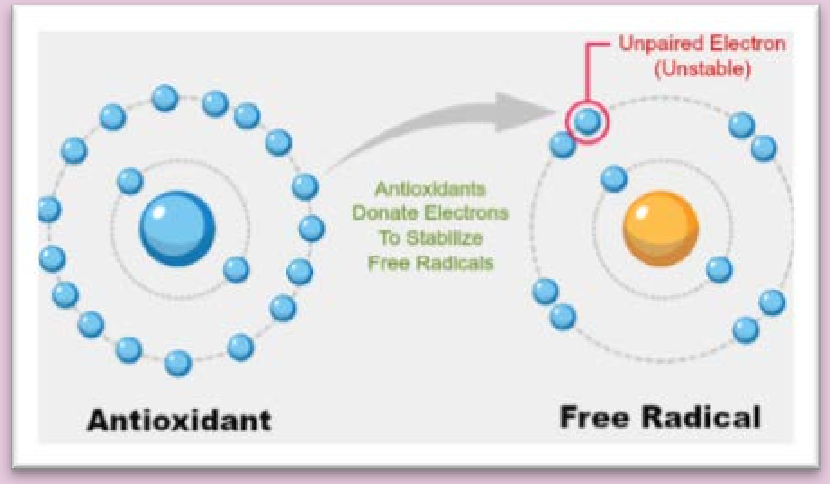
Chokeberry

- ***Aronia*** is a member of the ***Rosaceae*** family
- Two species can be distinguished:
  - ✓ ***Aronia melanocarpa*** (black chokeberry)
  - ✓ ***Aronia arbutifolia*** (red chokeberry)

- ❖ Antioxidant activity
- ❖ Anti-bacterial activity
- ❖ Anti-hypertension activity
- ❖ Anti-inflammatory activity
- ❖ Anti-atherosclerotic activity



Composition-polyphenol content of chokeberry

Component	Content
Total solids	15.60-28.80%
Total sugars	66-176 g/kg FW
Crude fibers	56 g/kg FW
Pectin	3.4–5.8 g/kg FW
Fat	0.14% FW
Protein	0.7% FW

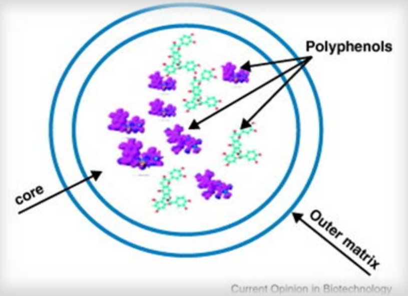
Vitamins	Content (per kg FW)
Vitamin C	137 mg
Vitamin B1	180 μg
Vitamin B2	200 μg
Vitamin B6	280 μg
Niacinamide (B_3)	3000 μg
Pantothenic acid (B_5)	2790 μg
Tocopherols	17.1 mg
Vitamin K	242 μg
Trace elements	
Na	26 mg
K	2180 mg
Ca	322 mg
Mg	162 mg
Fe	9.30 mg
Zn	1.47 mg

FW: Fresh weight
DW: Dry weight

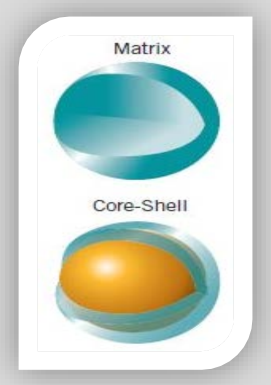
Phytochemicals	Content
Carotenoids	48.6 mg/kg FW
β-carotene	7.70-16.70 mg/kg FW
β-cryptoxanthin	4.63-12.20 mg/kg FW
Total phenolic	**7.465 mg/100 g DW**
Amygdalin	201 mg/kg FW

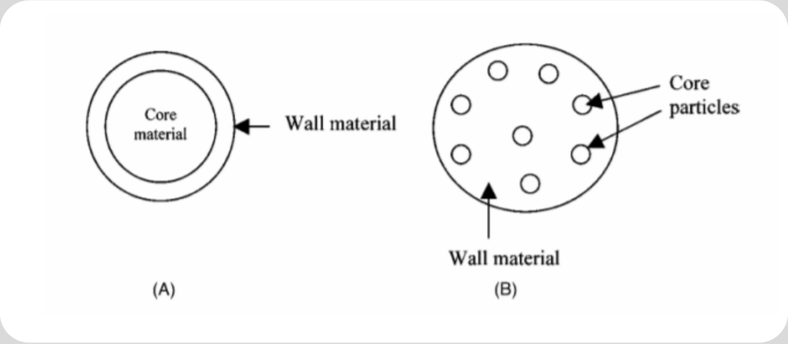
Kulling & Rawel, 2008

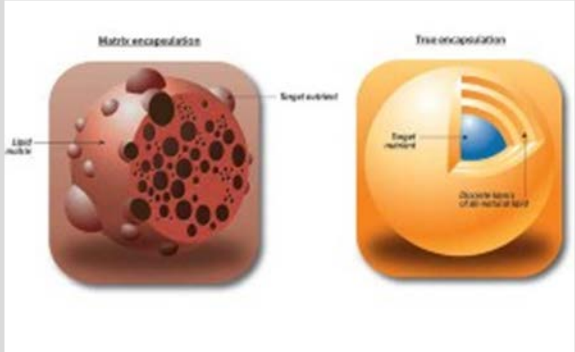
Why encapsulation of phenolic compounds



1. Masking of astringency
2. Improvement of color
3. Suitability for use as an additive in functional foods
4. Increase of their stability during storage and passage through the gastrointestinal tract

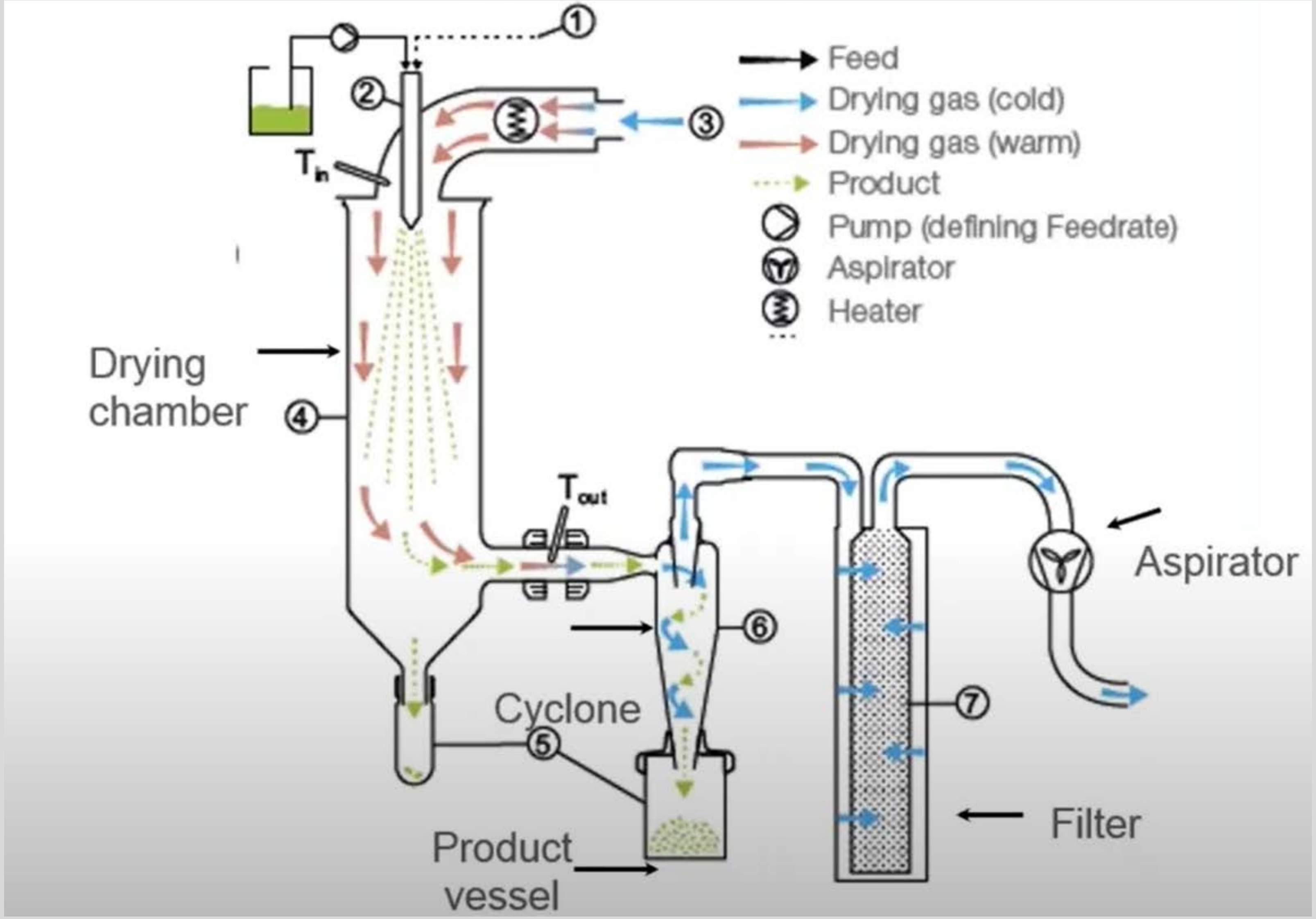




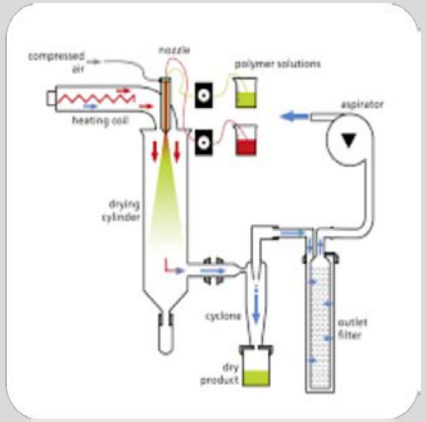


Shahidi & Han, 1993

Encapsulation with spray drying



Applications of spray drying

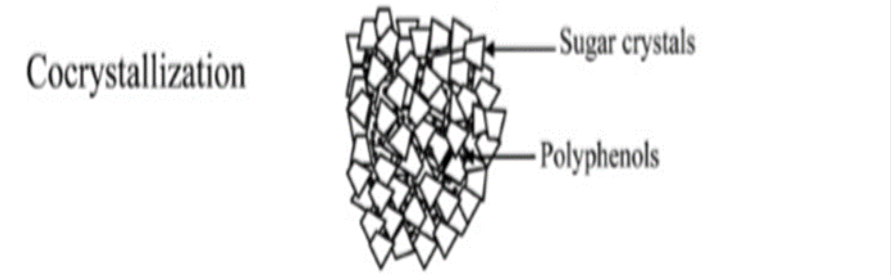


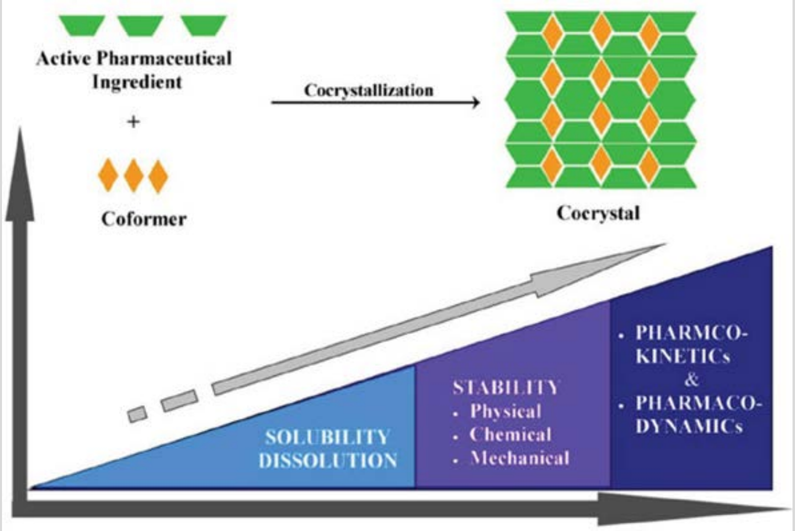
Polyphenols source	**Wall material**	**References**
Extra virgin olive oil	maltodextrin, gum arabic, or sodium caseinate	Calvo et al., 2010
Procyanidins of grape seed	maltodextrin and gum arabic	Zhang et al., 2007
Extract of olive leaves	chitozan	Kosaraju et al., 2006
Extract of soybean	maltodextrin, starch or silicon dioxide (Tixosil 333)	Georghetti et al., 2008
Extract of apples	sodium caseinate, lecithin	Kosaraju et al., 2008
Extract of oats	sodium caseinate, lactose	Rocha-Guzman et al., 2010
Pomegranate juice	maltodextrin, soy proteins isolated (SPI)	Robert et al., 2010
Bilberry juice	cyclodextrins	Wilkowska et al., 2016
Extract of black carrot	maltodextrin	Ersus & Yurdagel, 2007
Extract *Hibiscus sabdariffa* L.	citrus fibers	Chiou & Langrish, 2007

Encapsulation with co-crystallization

- It is based on the inclusion of extract between sucrose crystals that has been modified from a perfect to an irregularly agglomerated crystal
- Creation of a porous mesh and inclusion of a second active ingredient
- Applications:

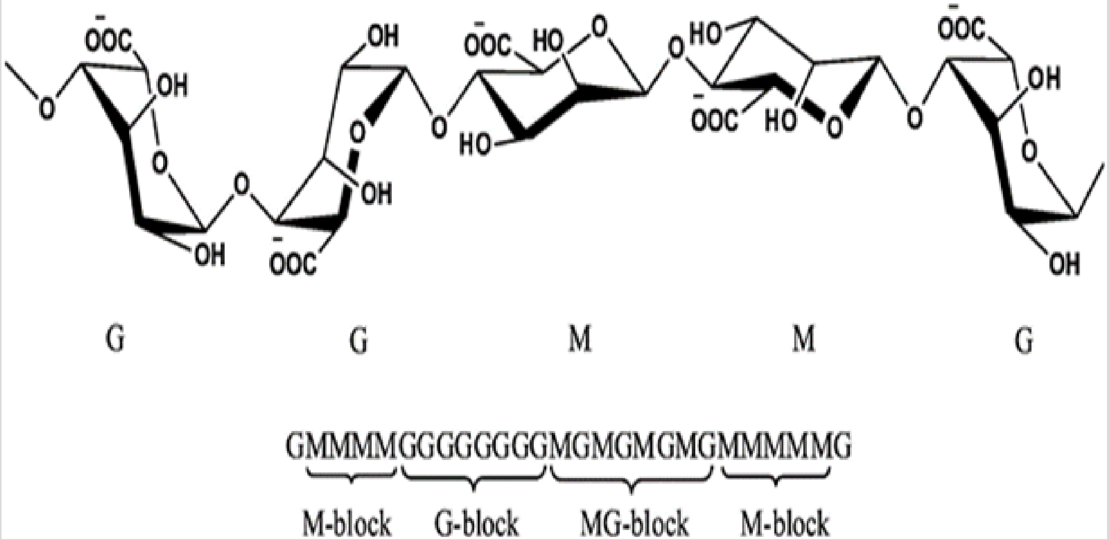
Polyphenols	Wall material	References
Extract of Yerba mate	Sucrose	Deladino et al., 2007

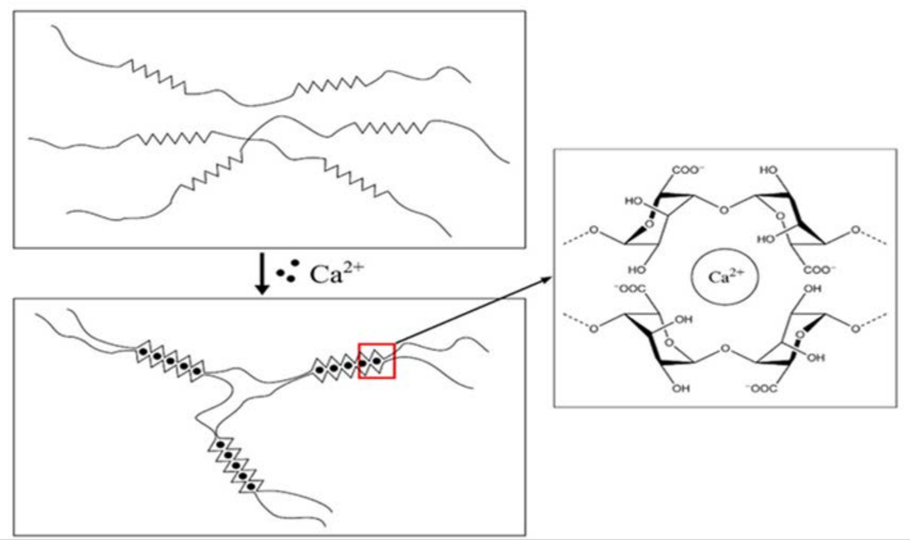




Encapsulation with extrusion

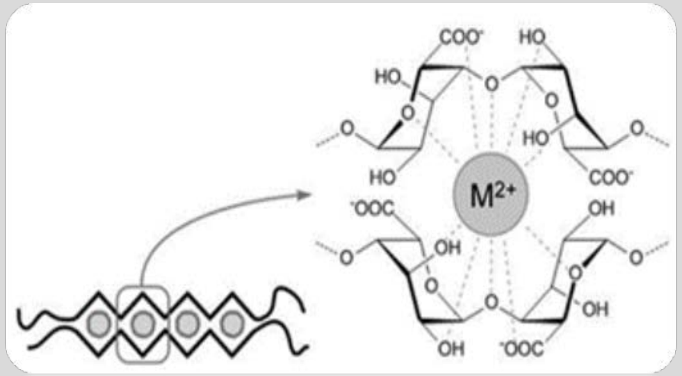
- Consists of b-D-mannuronic acid (M) and a-L-guluronic acid (G), linked by 1-4 bonds
- Based on the method of extruding an alginate in solution with Ca^{+2} cross-linking
- **Egg-box** mechanism: binding of 4 guluronic acid (G) residues to two different chains and a cation
- Ca^{+2} binds within the two opposite helical folds of guluronic acid





Applications of extrusion

Phenolic extract	Wall material	References
Extract of dandelion leaves	Alginate, alginate-whey proteins, alginate cocoa or carob powder	Bušić et al., 2018
Extract of stevia leaves	Calcium alginate	Arriola et al., 2016
Extract of chokeberry leaves	Alginate, alginate inulin	Ćujić et al., 2016
Extract of *Clitoria ternatea*	Sodium alginate	Pasukamonset et al., 2016
Extract of pomegranate peels	Calcium alginate	Zam et al., 2014



Objective

The valorization of chokeberry wastes based on:

- Encapsulation of extract by spray drying using maltodextrin, skim milk powder and whey protein concentrate as wall material
- Encapsulation of extract by co-crystallization using sucrose as wall material
- Encapsulation of extract by extrusion using calcium-alginate as wall material

❖**Optimization**:

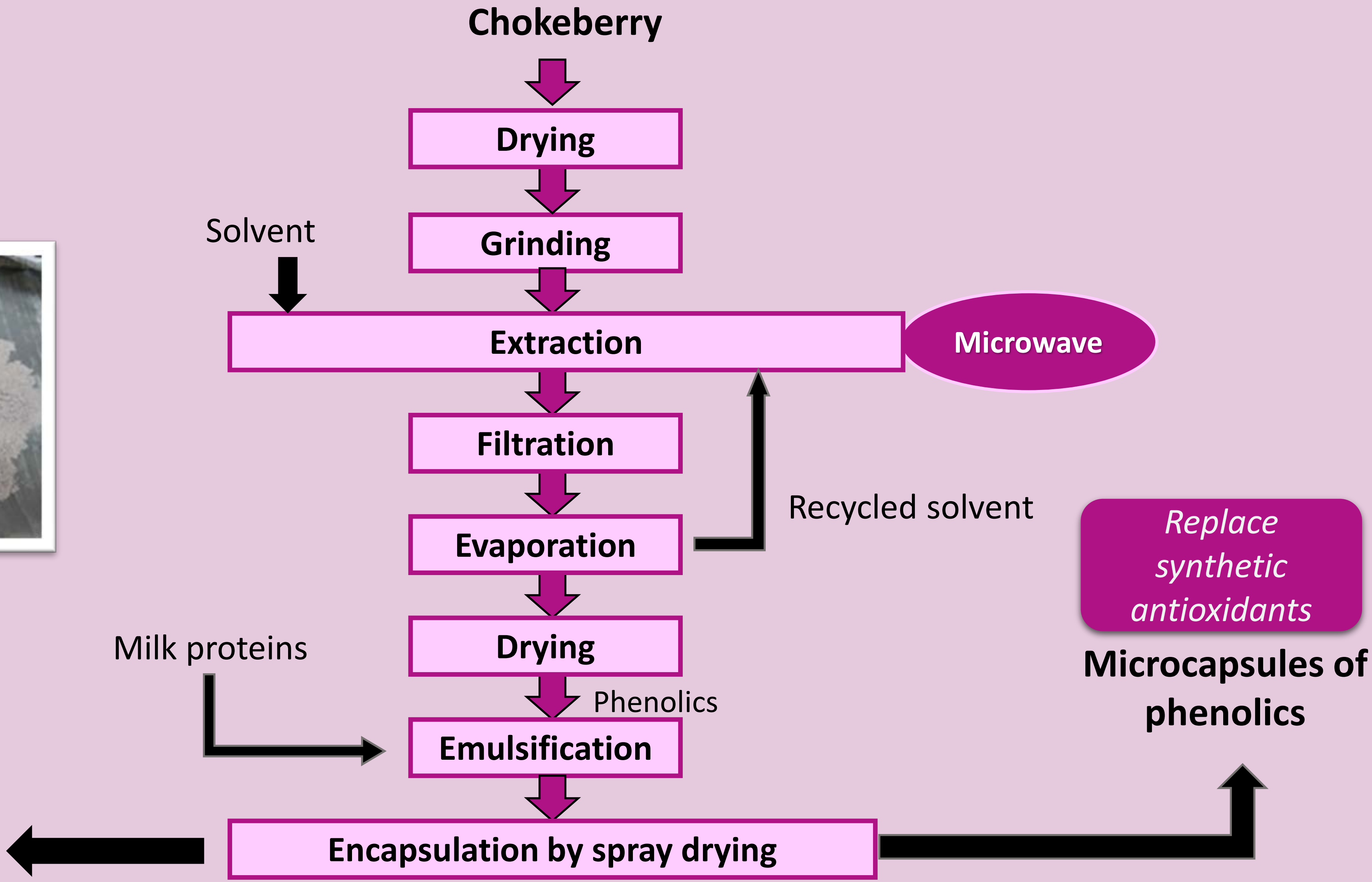
- *Encapsulation by spray drying, co-crystallization and extrusion of phenolic compounds*

❖ **Study of:**

1. *Encapsulation efficiency*
2. *Physical properties of microcapsules (moisture content, bulk density, solubility, hygroscopicity, color, size, texture, isotherms, release rate)*
3. *Storage stability of microcapsules*

Materials & Methods

Proposed process based on spray drying



Chokeberry

Drying

Grinding

Solvent

Extraction

Microwave

Filtration

Evaporation

Recycled solvent

Drying

Phenolics

Milk proteins

Emulsification

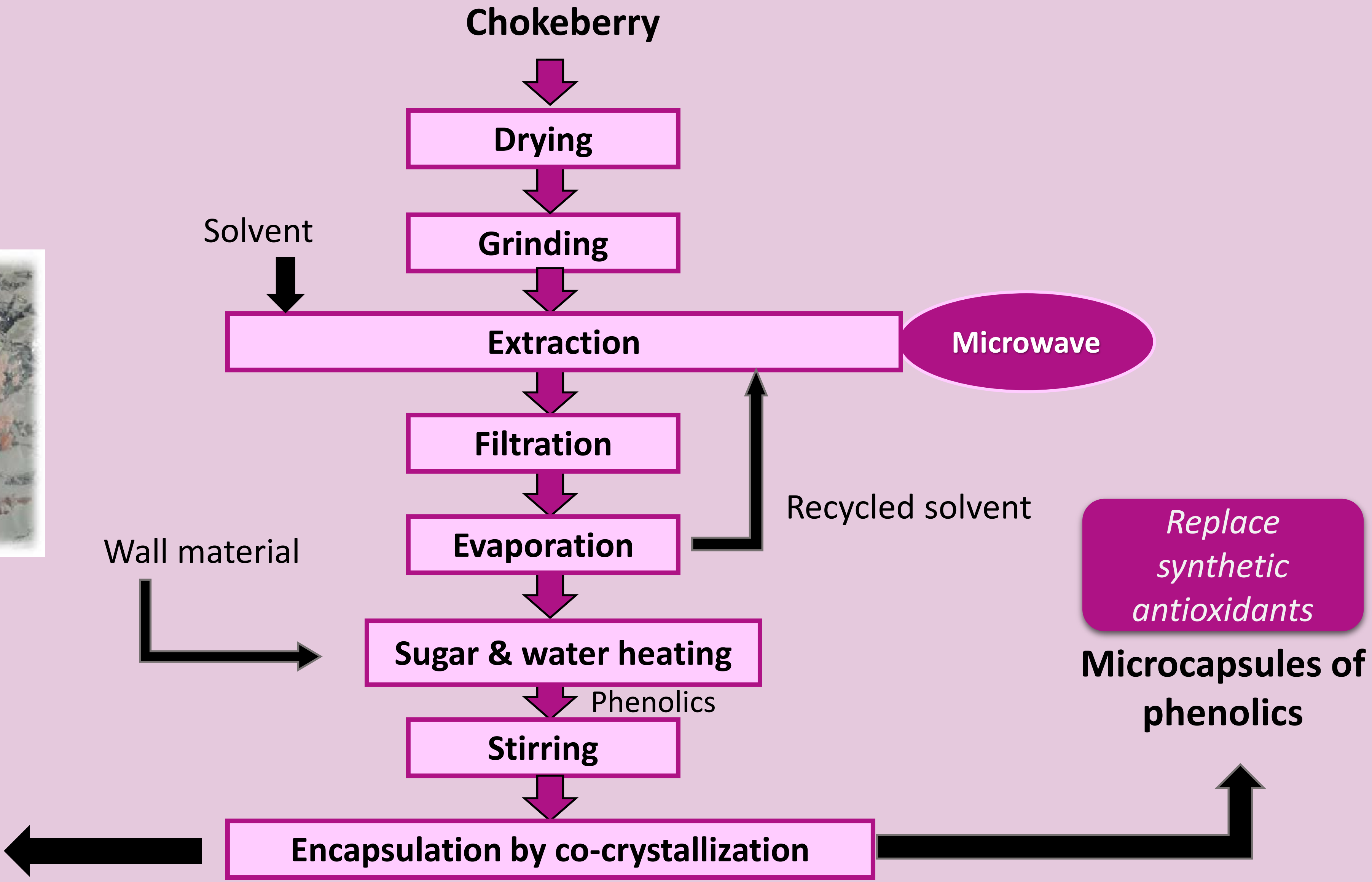
Encapsulation by spray drying

Total phenolic content: Folin Ciocalteu

Microcapsules of phenolics

Replace synthetic antioxidants

Proposed process based on co-crystallization



Chokeberry

Drying

Grinding

Solvent

Extraction

Microwave

Filtration

Evaporation

Recycled solvent

Wall material

Sugar & water heating

Phenolics

Stirring

Encapsulation by co-crystallization

Replace synthetic antioxidants

Microcapsules of phenolics

Total phenolic content: Folin Ciocalteu

Proposed process based on extrusion

Chokeberry

Drying

Grinding

Solvent

Extraction

Microwave

Filtration

Evaporation

Recycled solvent

Drying

Phenolics

Sodium alginate

Emulsification

Instillation into $CaCl_2$ & creation of beads

Total phenolic content: Folin Ciocalteu

Replace synthetic antioxidants

Microcapsules of phenolics

Experimental design for optimization of spray drying encapsulation

- Response Surface Methodology: **20 experiments x 2 wall materials**

Parameters	**Levels**				
Ratio of wall to core material (w/c)	2.3	3.7	5.6	7.3	1/9
Inlet air temperature (T_i, °C)	150	158	170	182	190
Drying air flow rate (Q_a %)	50	53	57.5	62	65

Wall material:

- Maltodextrin/SMP: 50/50
- Maltodextrin/WPC: 50/50

- *SMP: Skim milk powder*
- *WPC: Whey protein concentrate*

Experimental design for optimization of co-crystallization encapsulation

- Response Surface Methodology: **13 experiments**

Parameters	Levels				
Extract concentration (Brix^o)	35	40	52.5	65	70
Solids/sucrose (g/g)	0.1	0.19	0.4	0.61	0.7

Each experiment: 75g sucrose with 12.5g H_2O

Experimental design for optimization of extrusion encapsulation

- Response Surface Methodology: **20 experiments**

Parameters	Levels				
$CaCl_2$ concentration (% w/v)	1	1.30	1.75	2.19	2.5
Alginates concentration (% w/v)	2	2.4	3	3.59	4
Extract concentration (% v/v)	0.5	4.44	10.25	16.05	20

Efficiency of co-crystallization & extrusion

$$E_f = \left(\frac{\text{Phenolics of crystallized powder}}{\text{Total phenolics of concentrated extract}}\right) *100$$

$$E_f = \left(\frac{\text{Phenolics on beads}}{\text{Total phenolics of concentrated extract}}\right) *100$$

Efficiency and **Yield** of spray drying

$$E_f = \left(1-\frac{\text{Phenolics on microcapsule surface}}{\text{Total phenolics of microcapsule}}\right) * 100$$

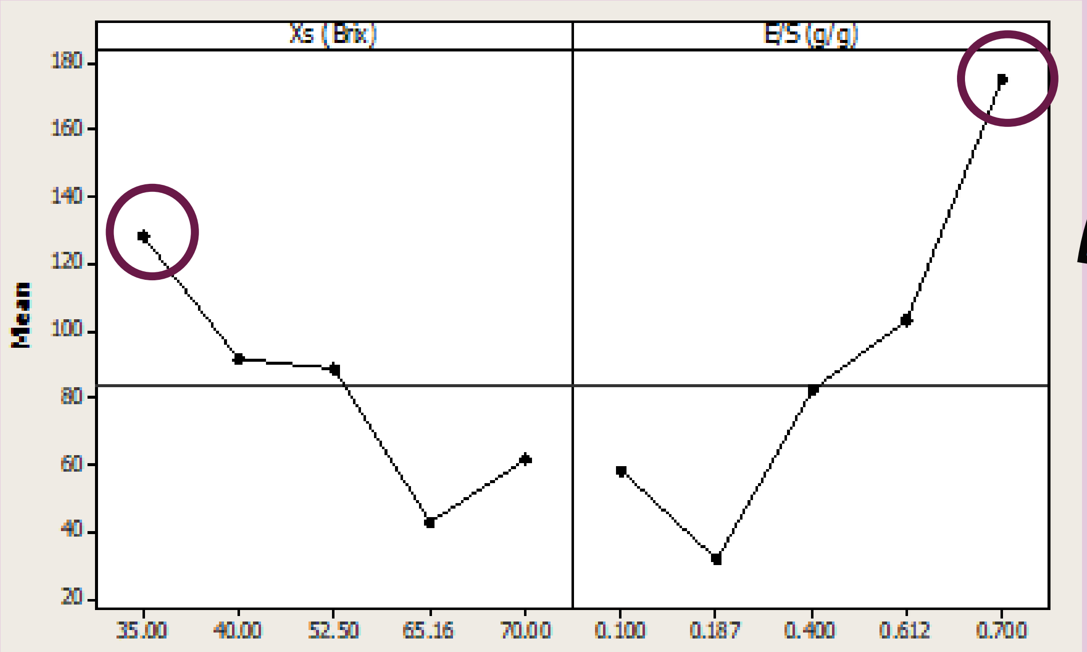
$$\Upsilon = \frac{\text{Mass of microcapsules (g)}}{\text{Total mass of initial substances (g)}} * 100$$

Characterization of encapsulated extract

1. Moisture content
2. Bulk density
3. Hygroscopicity
4. Solubility
5. Color
6. Size
7. Sorption isotherms
8. Release rate

Results

Co-crystallization
Average efficiency values



Maximum Ef:

✓ 35^0 Brix

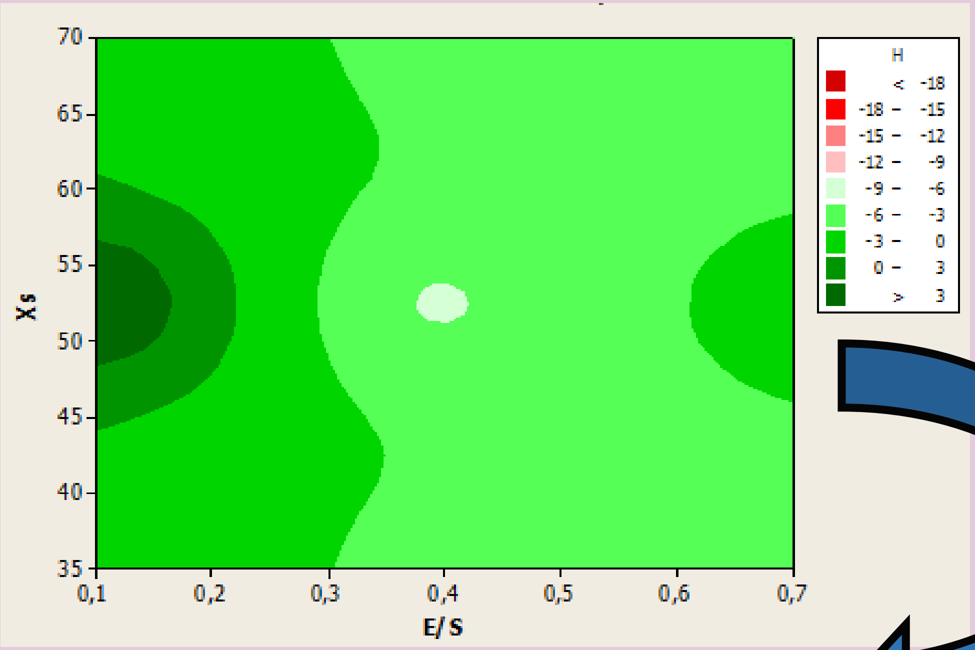
✓ ↑E/S

18.71-95.67%

E/S: Extract/Solids

Encapsulated powder properties
Contour plots:
Moisture content & Hygroscopicity

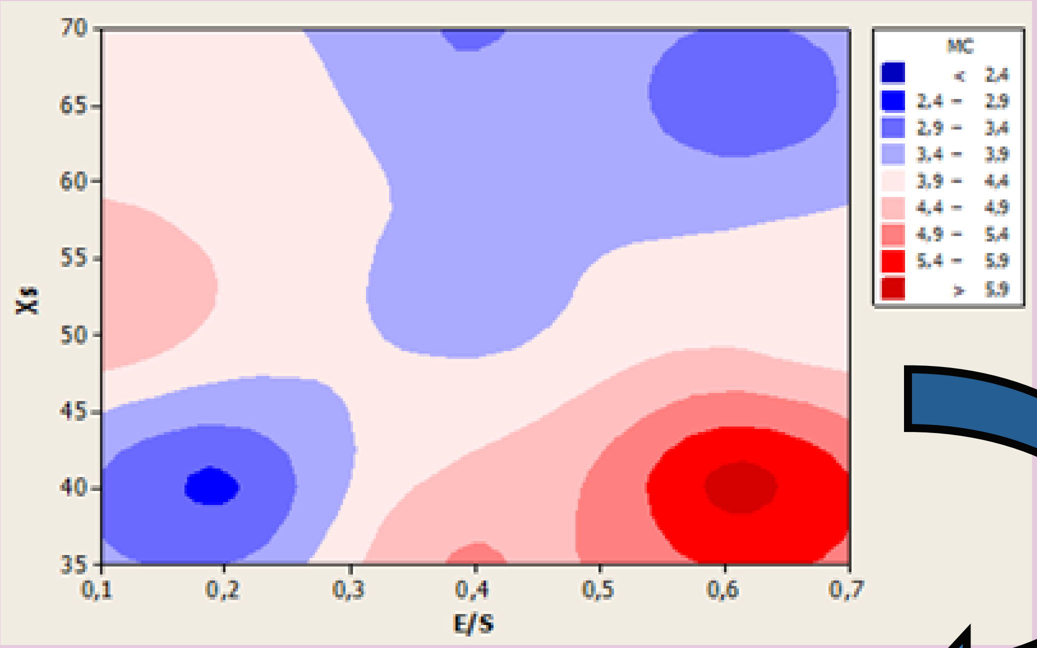
Xs: Extract concentration
E/S: Extract/Solids



Maximum hygroscopicity:

- ✓ Xs: 53^{o} Brix
- ✓ E/S: 0.1 g/g

H:
<5.00 g H_2O/g στερεών



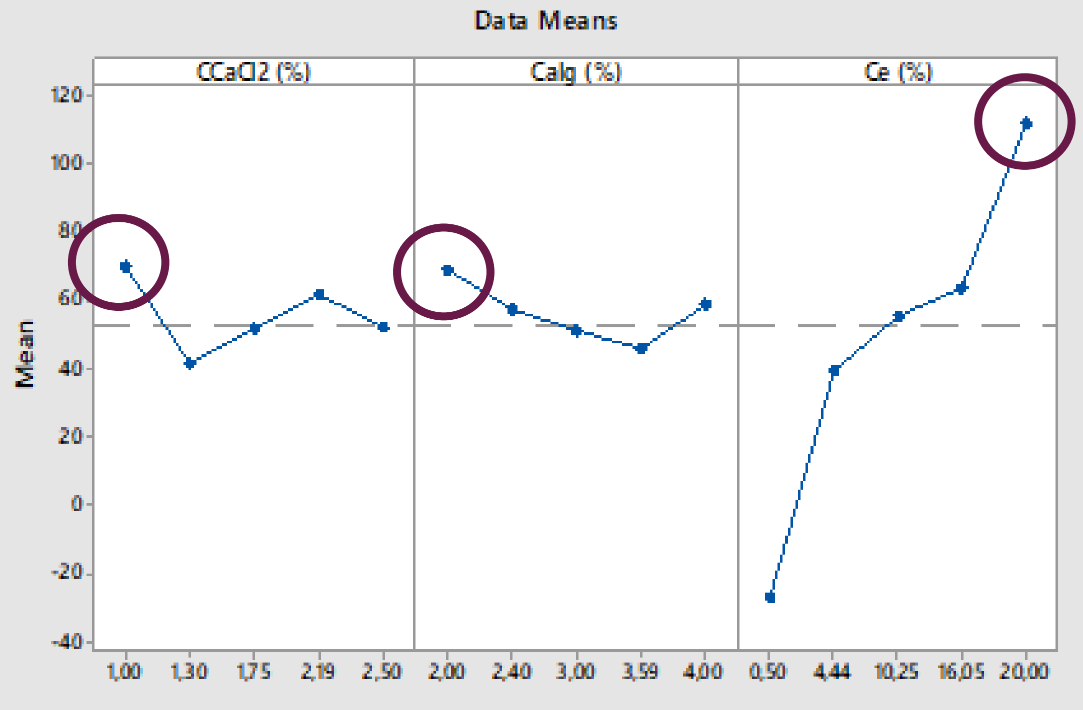
Maximum moisture content:

- ✓ Xs: 40^{o} Brix
- ✓ E/S: 0.6 g/g

MC:
2.84-6.00%

Extrusion
Average efficiency values

Ce: Extract concentration
Calg: Alginate concentration



Maximum Ef:

✓ ↓ $CCaCl_2$
✓ ↓ Calg
✓ ↑ Ce

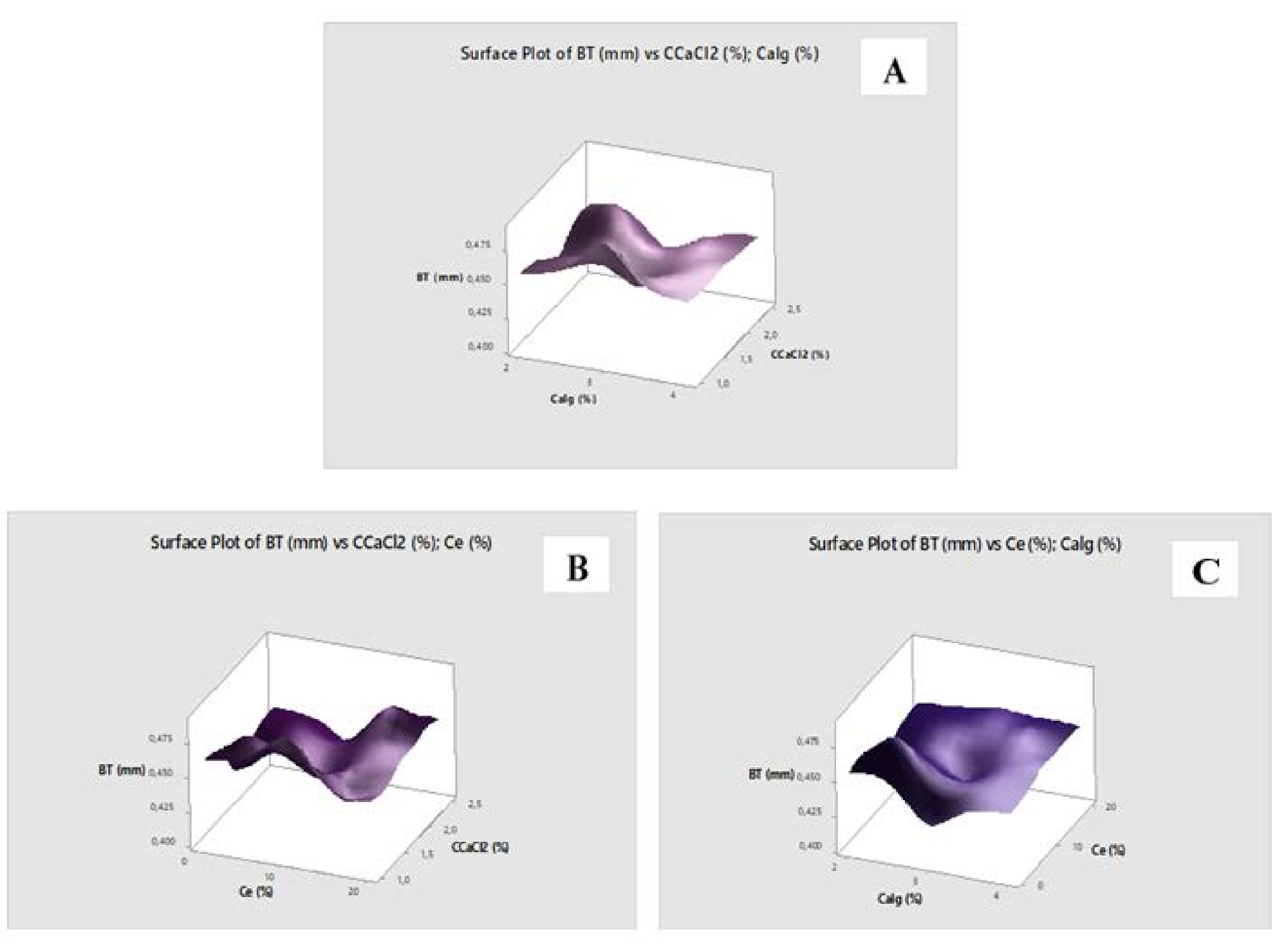
8.94-93.87%

Encapsulated beads properties

Surface plots:

Beads size

Ce: Extract concentration
Calg: Alginate concentration
BT: Beads thickness



Maximum beads size:

- ✓ ↓$CCaCl_2$
- ✓ Calg: 2.40%
- ✓ Ce: 4.44%

BT:

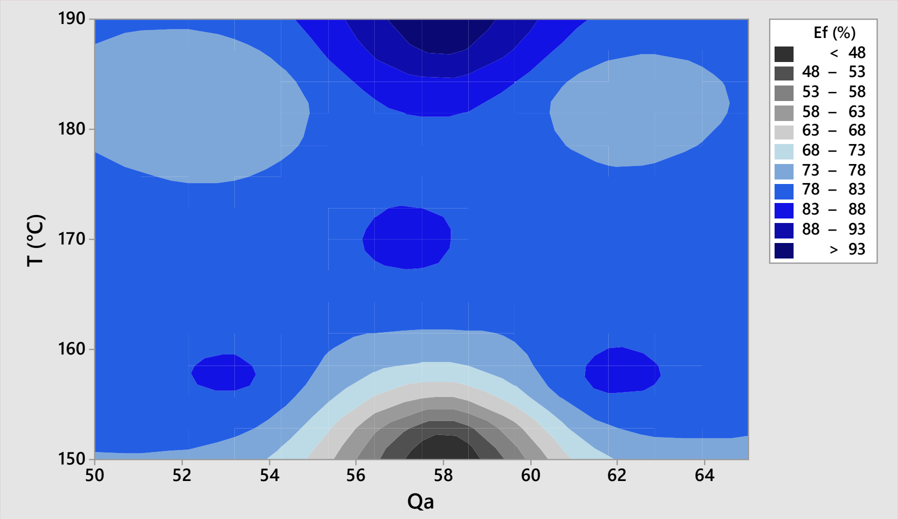
- ✓ 0.404-0.489mm

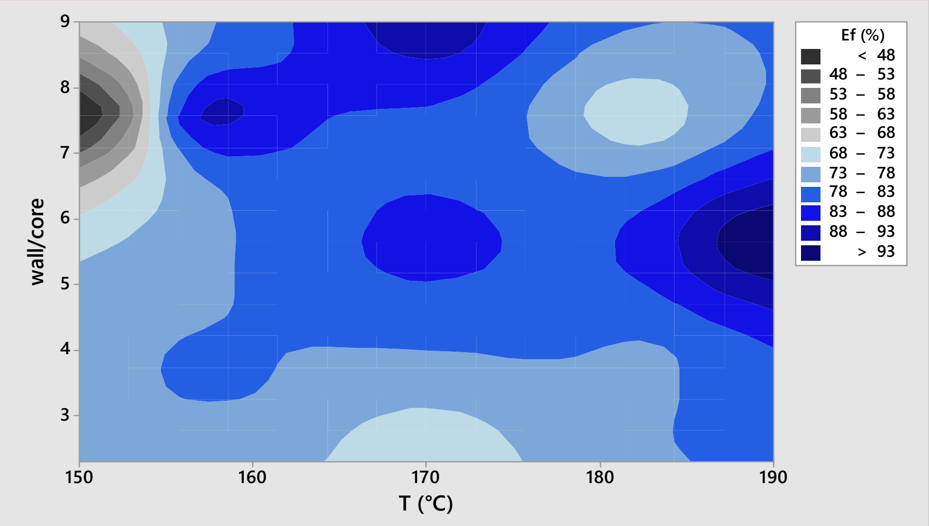
Spray drying

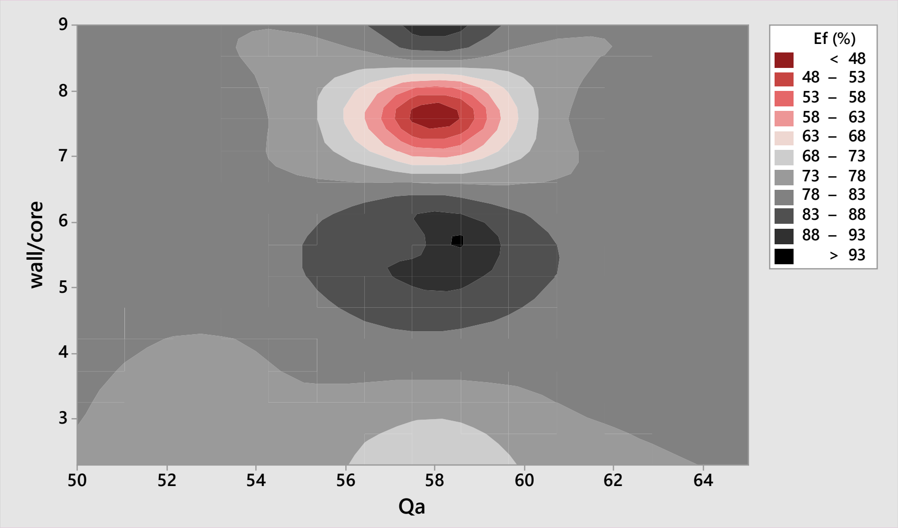
Contour plots

- ➢ wall/core-T°C
- ➢ T°C-Qa
- ➢ wall/core-Qa

MD/WPI







Maximum Ef:

✓ ↑T°C

✓ ↑Qa

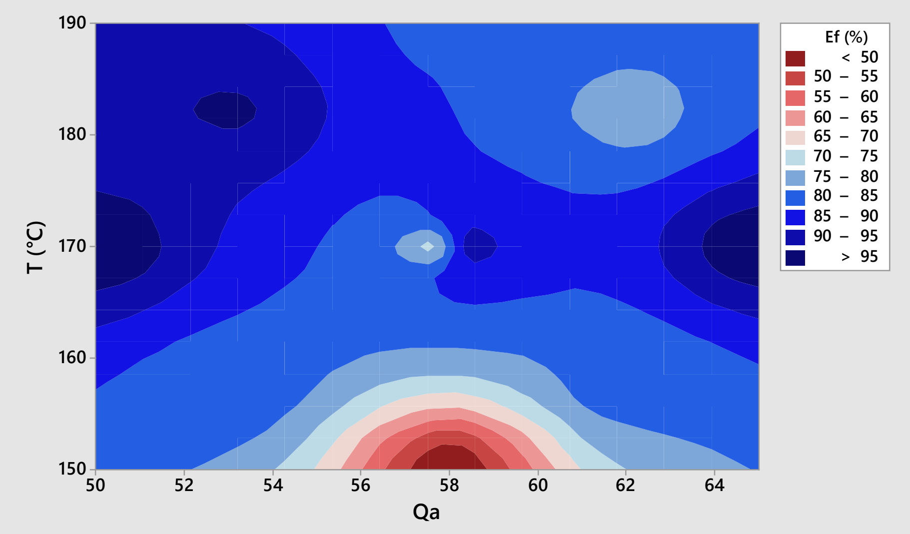
✓ ↑wall/core

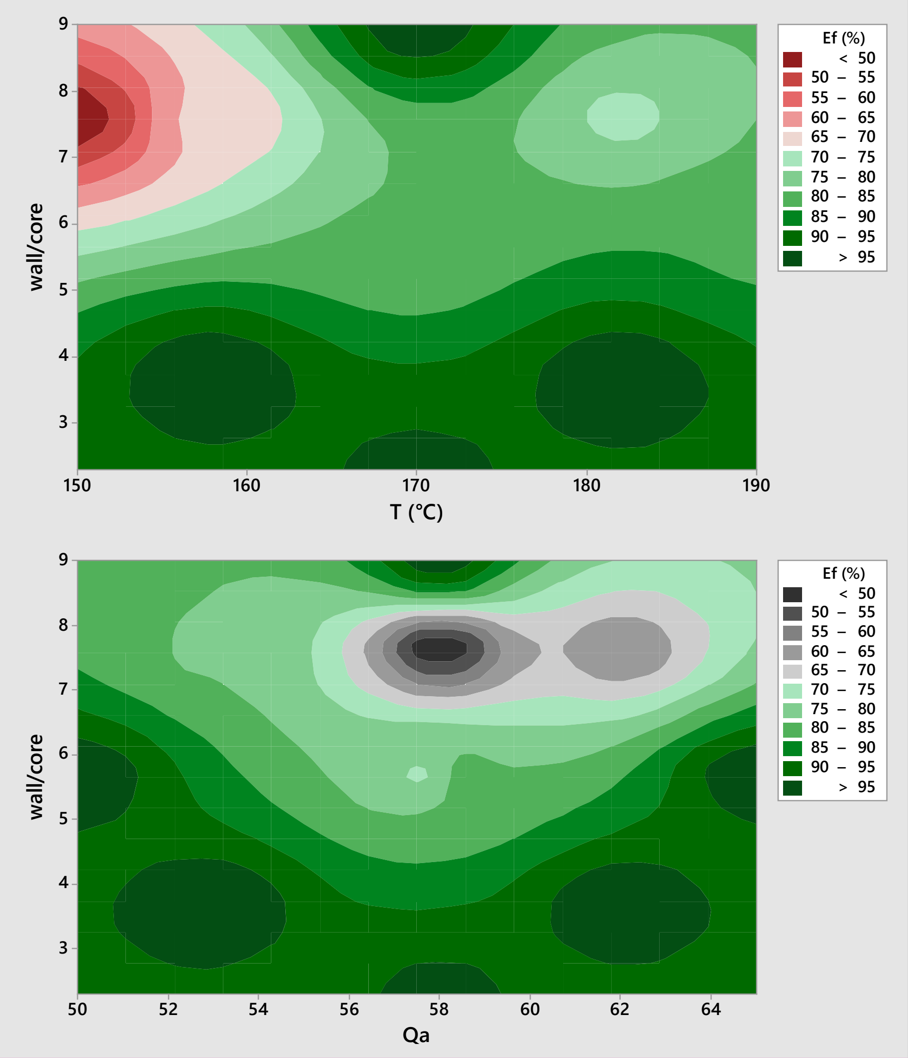
Spray drying

Contour plots

- ➢ wall/core-T^{o}C
- ➢ T^{o}C-Qa
- ➢ wall/core-Qa

MD/SMP



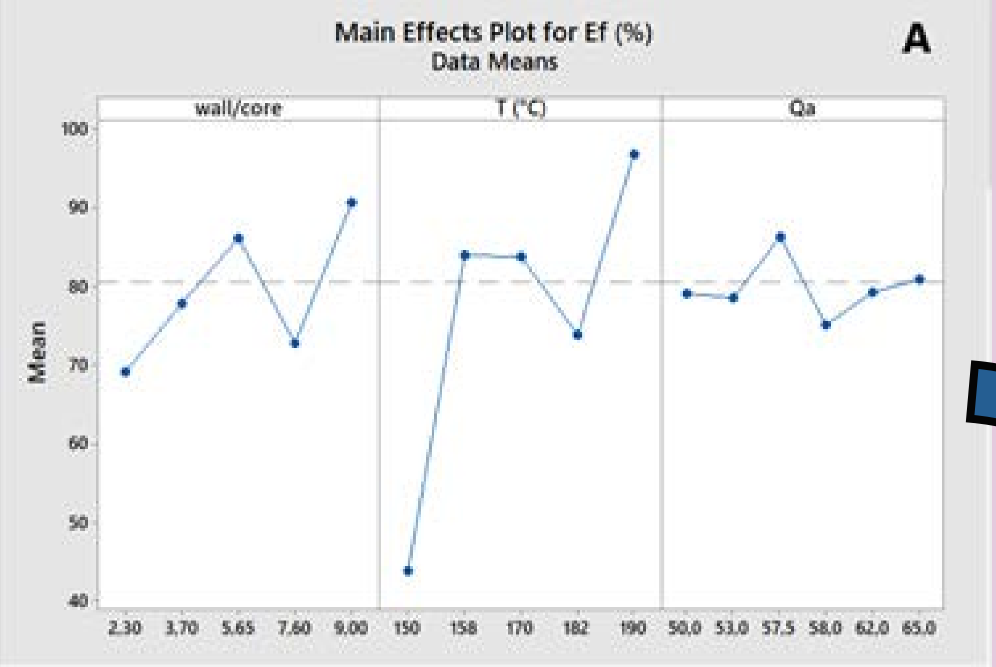


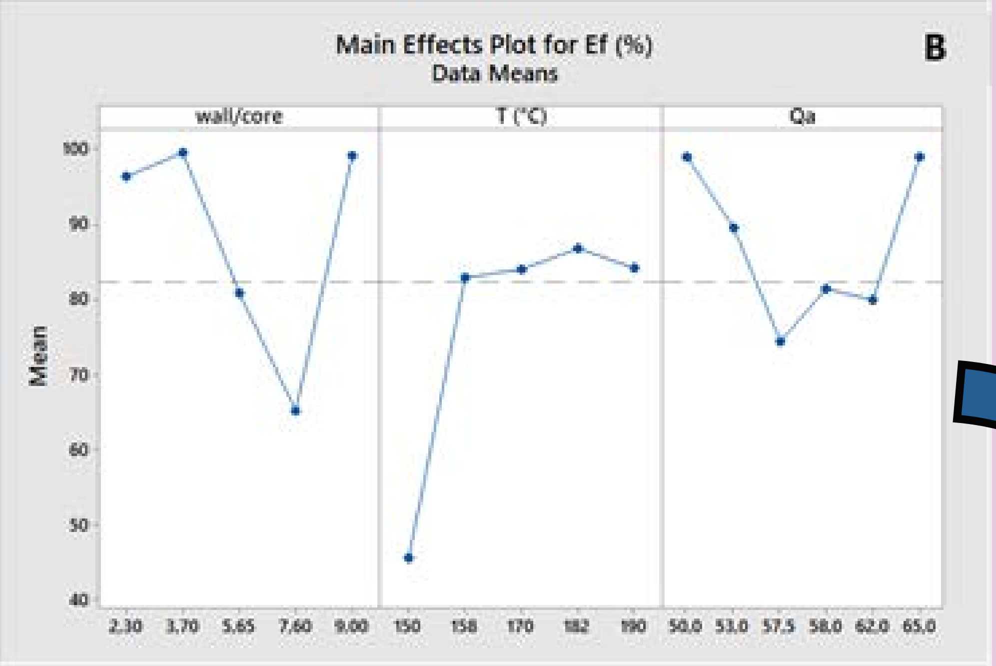
Maximum Ef:

- ✓ ↑T^{o}C
- ✓ ↑Qa
- ✓ ↑wall/core

Spray drying
Average efficiency values

- A: MD/WPI
- B: MD/SMP



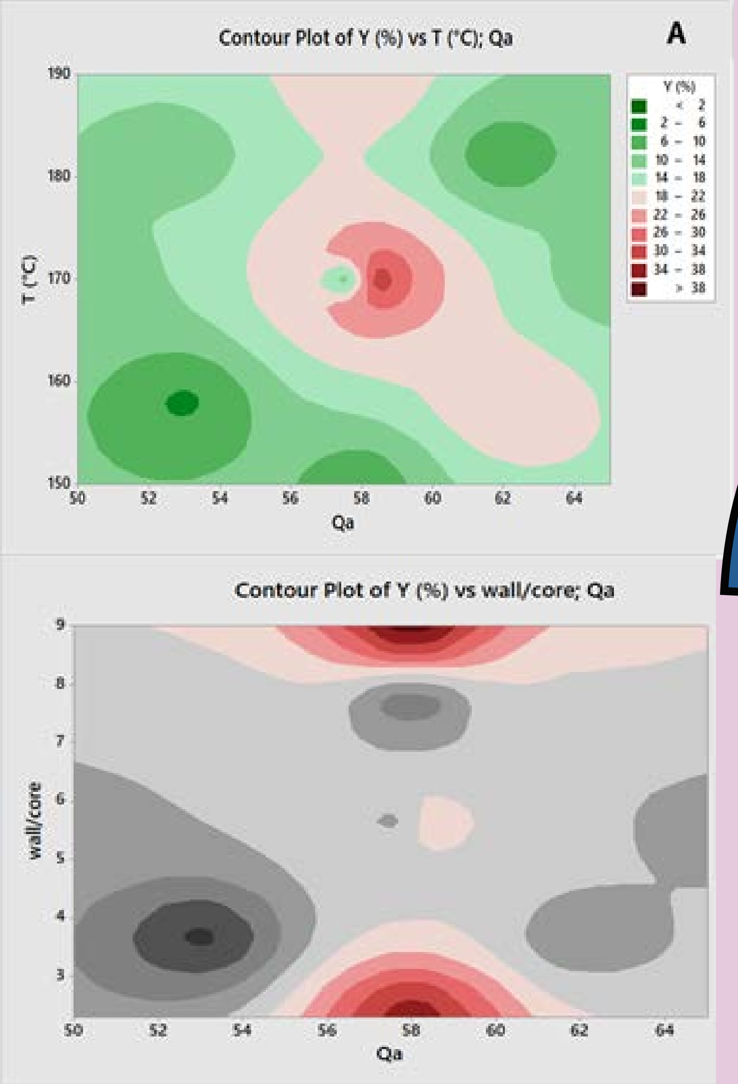


Ef:
- ✓ 43.77-96.77%

Ef:
- ✓ 44.25-99.57%

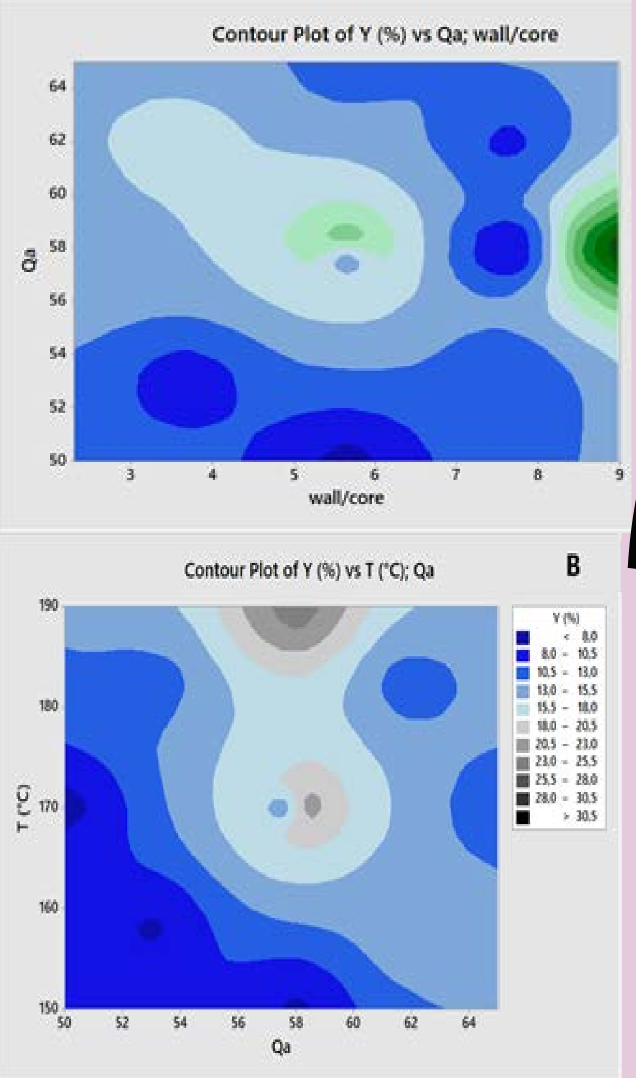
Spray drying
Average yield values

- A: MD/WPI
- B: MD/SMP



Maximum Y:

- ✓ ↑$T^{0}C$
- ✓ ↓Qa
- ✓ ↑wall/core

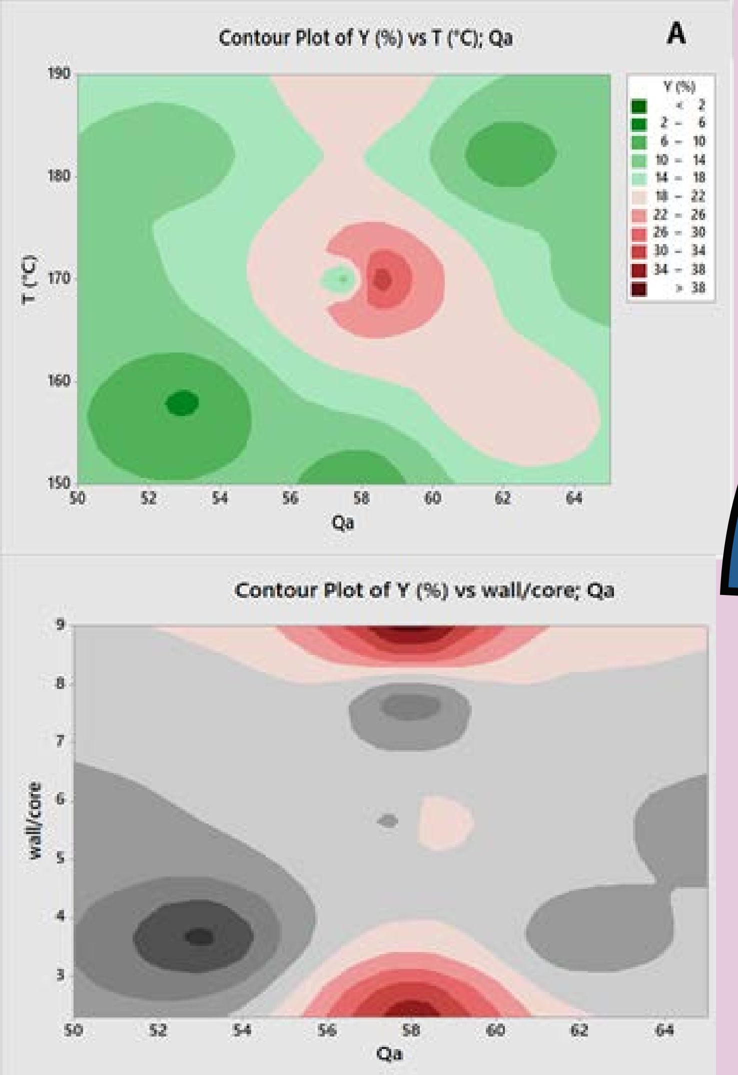


Maximum Y:

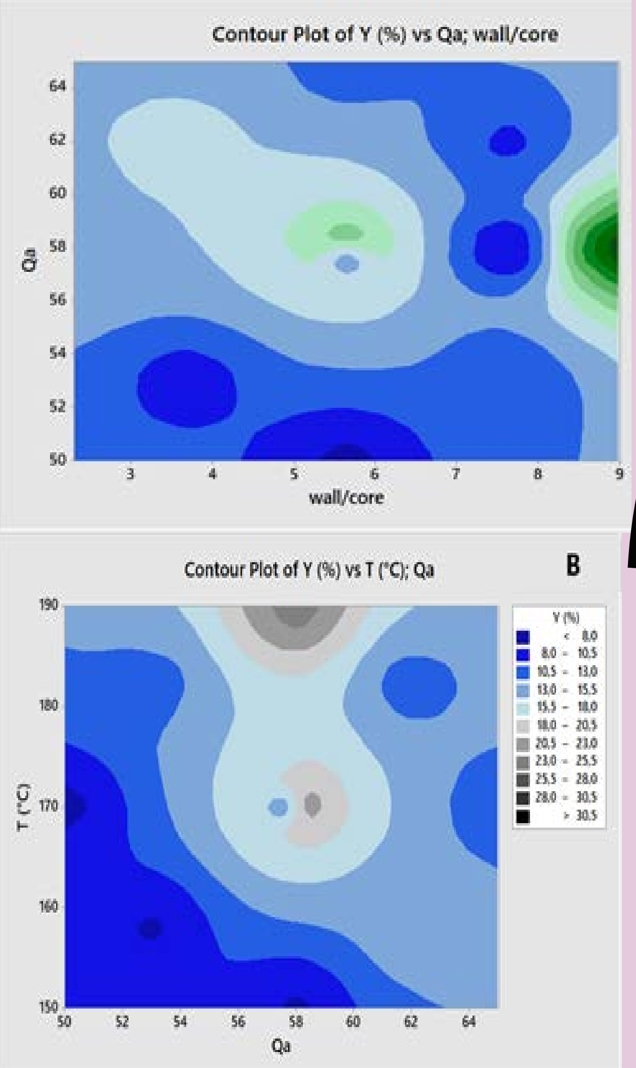
- ✓ ↑$T^{0}C$
- ✓ ↓Qa
- ✓ ↑wall/core

Spray drying
Average yield values

- ❖ **A: MD/WPI**
- ❖ **B: MD/SMP**



Y:
✓ 1.35-39.90%



Y:
✓ 8.12-31.93%

Optimization

Spray drying	
Ratio of wall to core material (w/c, g/g)	9
Inlet air temperature (T, ^{o}C)	190
Drying air flow rate (*Qa*, % ή m^3/h)	55 ή 19.25
Wall material	Maltodextrin: skimm milk
Co-crystallization	
Solid extract concentration (Xs, Brix)	35
Ratio of dry extract/sucrose (E/S, g/g)	0.7
Extrusion	
Sodium alginate solution concentration (*Calg*, % w/w)	2.0
Sodium alginate solution concentration ($CCaCl_2$, % w/v)	2.5
Extract concentration (*Ce*, % w/w)	20.0

a: Spray drying
b: Co-crystallization
c: Extrusion

Properties of encapsulated extract at optimal conditions

Parameters	Spray drying	Co-crystallization	Extrusion
Moisture content (% wet basis)	5.27 ± 0.22	5.15 ± 0.18	96.52 ± 0.41
Total phenolic content (mg GAE/g powder)	5.204 ± 0.092	0.194 ± 0.003	0.208 ± 0.04
Antioxidant capacity (DPPH, %)	74.20 ± 1.31	85.22 ± 1.91	93.14 ± 1.98
Bulk density (g/mL)	0.541 ± 0.027	0.745 ± 0.012	-
Solubility (s)	75 ± 3	136 ± 5	-
Hygroscopicity (%)	2.832 ± 0.110	0.093 ± 0.003	-
Beads size(mm)	-	-	0.482 ± 0.003
Beads texture hardness (g)	-	-	54 ± 3
Stickiness (g)	-	-	-3 ± 0.7
Color Parameters *a**	8.61 ± 0.32	9.44 ± 0.10	11.37 ± 0.16
*b**	5.40 ± 0.22	6.39 ± 0.20	2.19 ± 0.11
*L**	73.65 ± 1.59	63.58 ± 0.49	22.75 ± 0.16

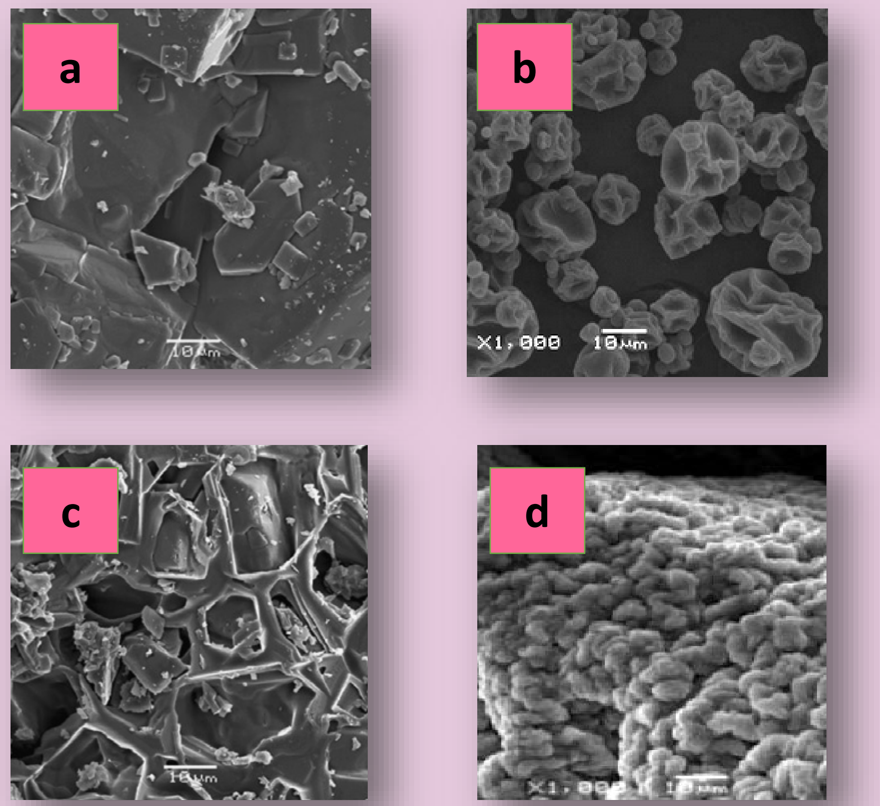
SEM:

a: Crystallized sucrose

b: Co-crystallization

c: Spray drying

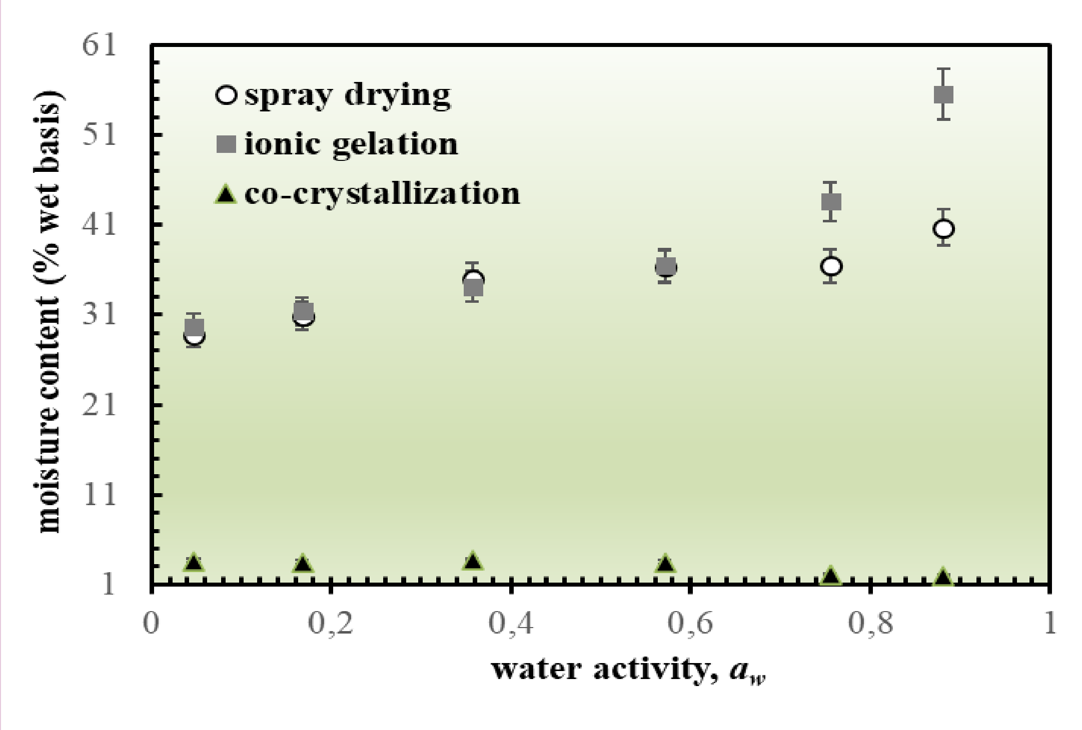
d: Extrusion

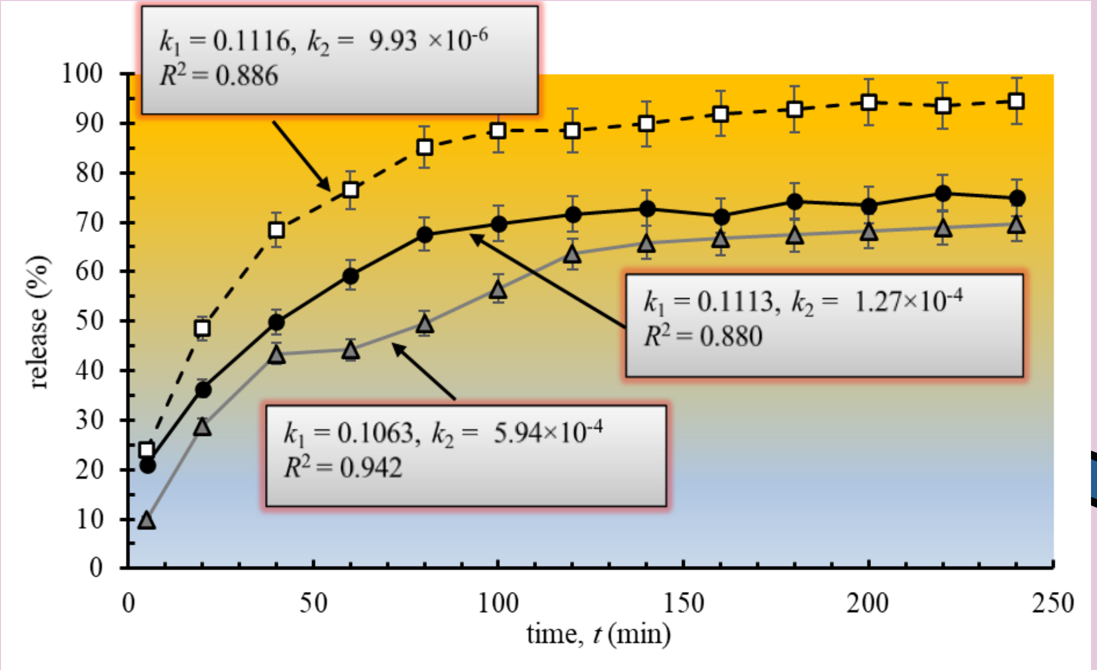


Sorption isotherms
Controlled release rate

Ficks law of diffusion:

$$\frac{M_t}{M_\infty} = k_1 t^m + k_2 t^{2m}$$



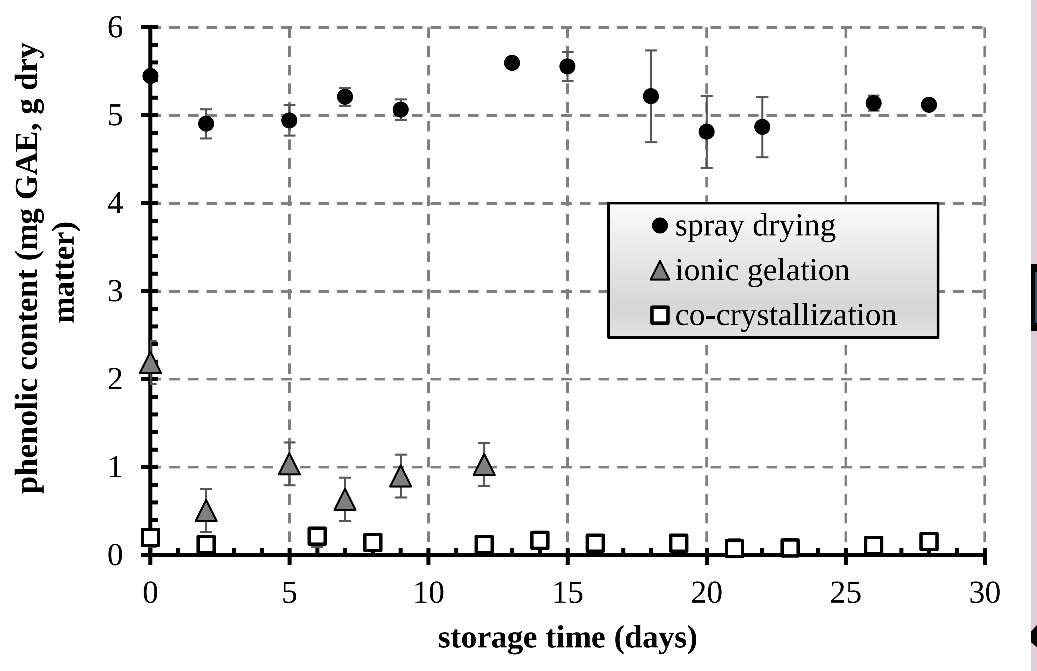


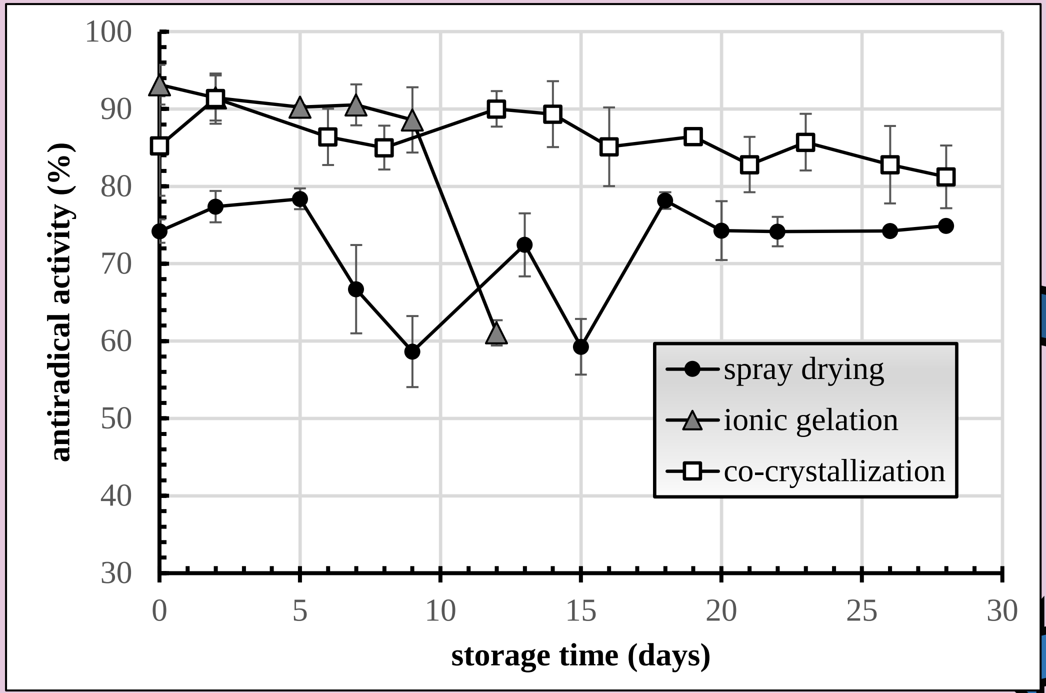
Spray drying: ↑ moisture content, ↑aw
Co-crystallization: ↓ moisture content, ↓aw
Extrusion: ↑ moisture content, ↑aw

Spray drying: 70% in 100 min
Co-crystallization: 65% in 140 min
Extrusion: 85% in 80 min

Storage stability

5^{o}C for 30 days





Spray drying: ↓6.07%
Co-crystallization: ↓24.75%
Extrusion: ↓52.97%

Spray drying: 5.204 mg GAE/g
Co-crystallization: 0.194 mg GAE/g
Extrusion: 0.208 mg GAE/g

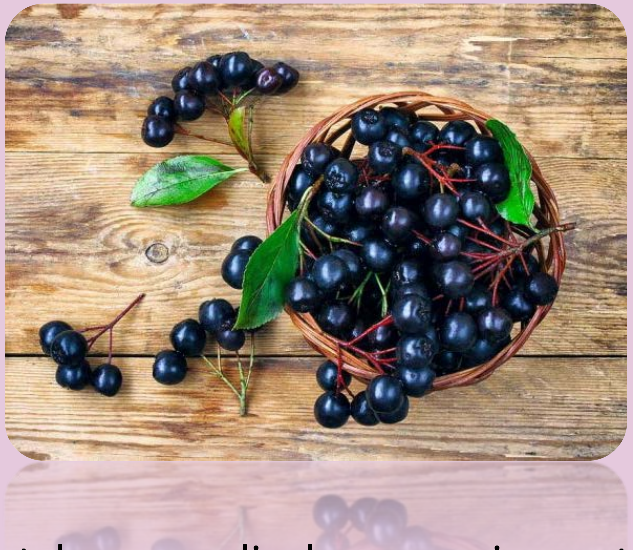
Spray drying: ↓SC (%)
Co-crystallization: ↑ SC (%)
Extrusion: ↑ SC (%)

Conclusions

Optimization of encapsulation with three methods:

Spray drying-Optimum conditions

- Ratio of wall to core material: 9/1, Inlet air temperature: 190 °C, Drying air flow rate : 55%, Maltodextrin: skim milk powder (50:50) as encapsulating agent



Co-crystallization-Optimum conditions

- Xs=35 ^{o}Brix και E/S=0.7 g/g

Extrusion-Optimum conditions

- C_{CaCl2}=2.50%, C_{alg}=2.00%, C_e=20.00%

Characterization of encapsulated extract

- The spray dried products presented better total phenolic content stability, but lower radical scavenging activity as compared to the other products.
- The drawbacks of stickiness and hygroscopicity of spray dried extract had been overcome by the co-crystallization.
- The spray dried extract and the alginate beads had higher equilibrium moisture content levels compared to those of the co-crystallized product, which was stable to relative humidities below 88%.

Thank you!