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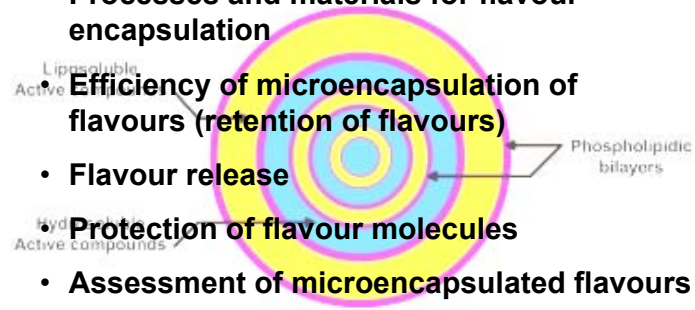
Capsule performance in the microencapsulation of flavour molecules

P.R. Venskutonis, R. Baranauskienė
Department of Food Technology,
Kaunas University of Technology

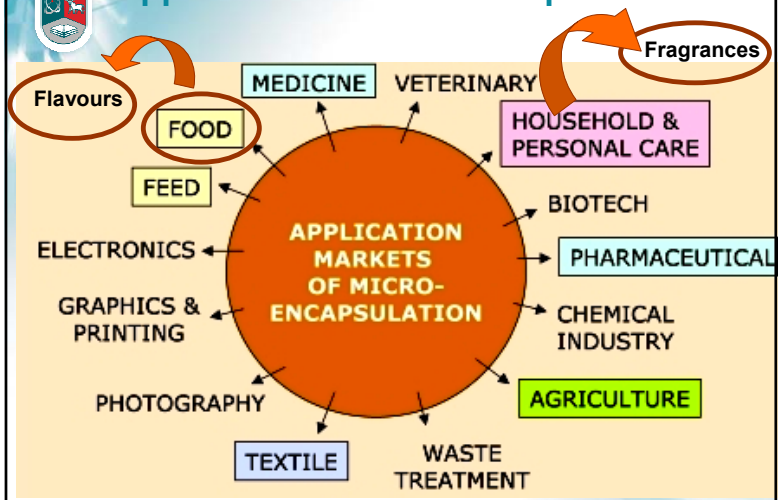
COST865 Spring 2009 Meeting, Luxembourg, April 24-25

Content

- Introduction
- Processes and materials for flavour encapsulation
- Efficiency of microencapsulation of flavours (retention of flavours)
- Flavour release
- Protection of flavour molecules
- Assessment of microencapsulated flavours



Applications of microencapsulation



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http://www.gate2tech.com/article.php3?id_article=14

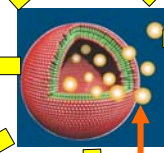
What do we need from the capsule in flavour microencapsulation?

To retain volatile aroma compounds in a food product during storage

To guard against either light-induced reactions or oxidation

To protect the constituents from undesirable interactions with the food

To provide to liquid flavourings free-flowing powder properties



To minimise flavour/flavour interactions

To effect the controlled release of flavour and other volatile bioactive compounds

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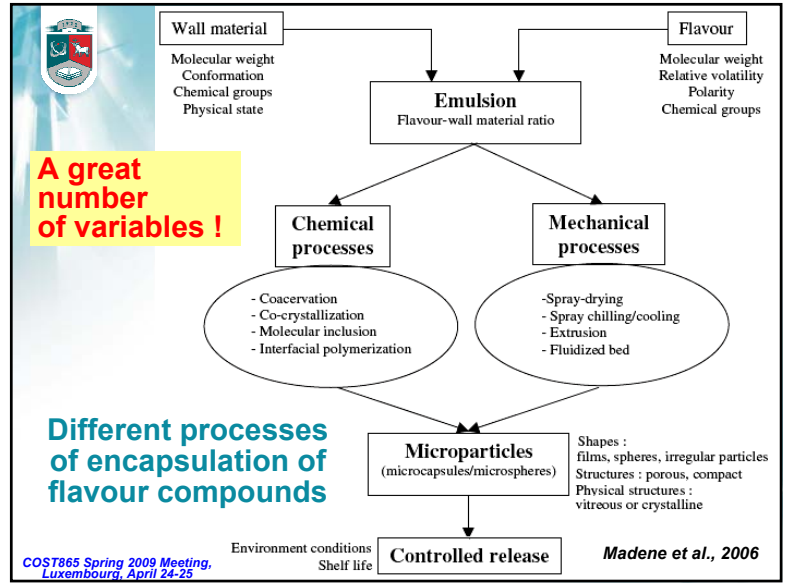
Encapsulation of food and flavours: global research activities

Key words	No. of records
Microencapsulation and food	223
Microencapsulation and oil	496
Microencapsulation and fatty acid*	78
Microencapsulation and vitamin*	43
Microencapsulation and antioxidant*	41
Microencapsulation and oleoresin*	17
Microencapsulation and volatile	43
Microencapsulation and flavour	25
Microencapsulation and essential oil	30
Microencapsulation and aroma	22

SCI-EXPANDED: 1990-2009



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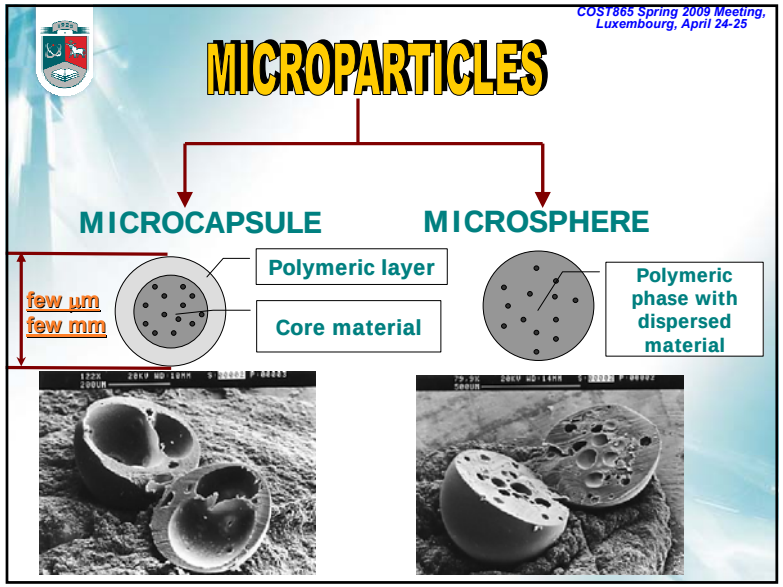
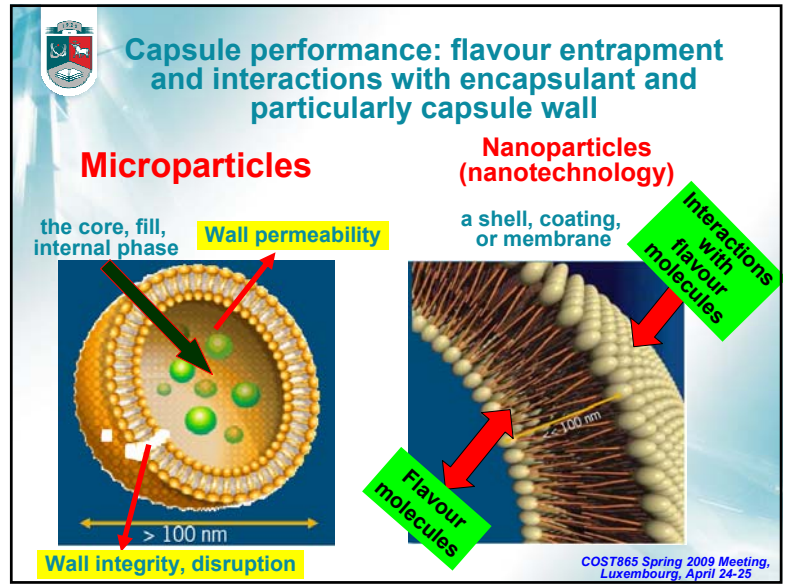


Capsule performance: flavour entrapment and interactions with encapsulant and particularly capsule wall



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Characteristics of the wall material used for encapsulating flavours

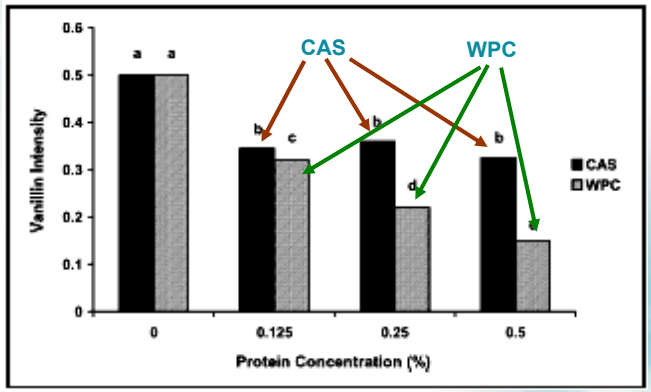
Wall material	*Interest*
Maltodextrin (DE < 20)	Film forming
Corn syrup solid (DE > 20)	Film forming, reductability
Modified starch	Very good emulsifier
Gum arabic	Emulsifier, film forming
Modified cellulose	Film forming
Gelatin	Emulsifier, film forming
Cyclodextrin	Encapsulant emulsifier
Lecithin	Emulsifier
Whey protein	Good emulsifier
Hydrogenated fat	Barrier to oxygen and water

Wall materials: binding data for the interactions between 2-nonanone and milk proteins (25 ◦C)

	n	*K* [M^{-1}]	Reference
WPC	61	1920000	Jasinski and Kilara (1985)
	0.2	53000000	Liu and others (2005b)
WPI	1	2059	Zhu (2003)
Sodium caseinate	0.3	1858	Zhu (2003)
β-Lg	1	2439	O'Neill and Kinsella (1987)
	0.2	6250 (≤ 40 ppm)	Charles and others (1996)
	0.5	1667 (≥ 45 ppm)	
	14	122	Jasinski and Kilara (1985)
α-La	33	11	Jasinski and Kilara (1985)
BSA	5–6	1800	Damodaran and Kinsella (1980b)
	15	14100	Jasinski and Kilara (1985)
	7	933	Jung and others (2002)

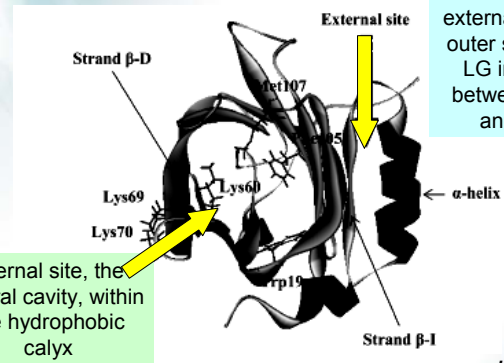
***n*, number of binding sites per monomer**
***K*, intrinsic binding constant**

Vanillin flavor intensity relative to the reference in the presence of sodium caseinate (CAS) and whey protein concentrate (WPC)



Hansen and Heinis (1991)

Capsule performance depends on molecular weight, conformation, chemical groups and physical state of the wall materials



external site on the outer surface of β-LG in a groove between strands and R helix

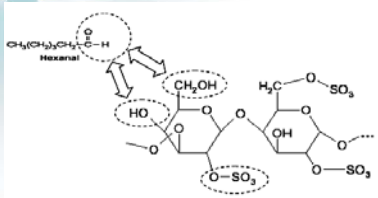
internal site, the central cavity, within the hydrophobic calyx

Uhrinova et al., 2000

The secondary structure of β-LG is arranged as at least two hydrophobic binding sites are present

Protection of active aroma compound against moisture and oxygen by encapsulation in biopolymeric emulsion-based edible films

Possible interactions between hexanal and the chains of carrageenan (CH_2OH, OH, and sulfate)



Types of film-forming solutions

	ι-carrageenans + glycerol	aroma compound (*n*-hexanal)	fat (GBS)
woa:wof	**		
wa:wof	**	**	
woa:wf	**		**
wa:wf	**	**	**

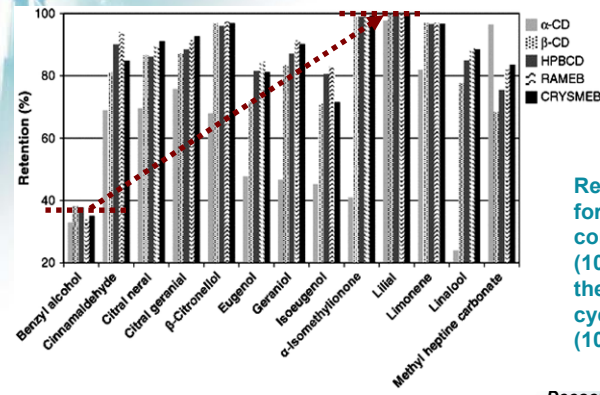
woa, without aroma compound;
wof, without fat;
wa, with aroma compound;
wf, with fat;
**, tested.

A calorimetry analysis showed that the aroma compound interacts more with the fat, which proves fat's capacity to encapsulate and to protect aroma compounds.

Moreover, the carrageenan matrix brings efficient protection against the oxygen transfer because the permeability remains unaffected in the presence of the aroma compound.

Hambleton et al., 2008

Capsule performance depends on molecular weight, relative volatility, polarity and chemical groups of the flavour compounds

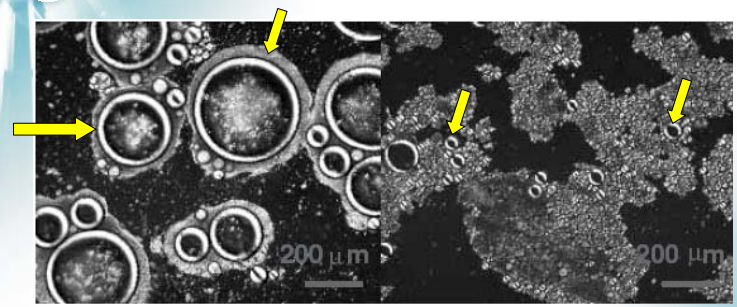


Retention (%) for the aroma compounds (100 ppm) with the different cyclodextrins (10 mM)

Decock et al. 2008

Hydroxypropyl-β-cyclodextrin (HPBCD),
Randomly methylated-β-cyclodextrin (RAMEB)
Low methylated-β-cyclodextrin (CRYSMEB)

Encapsulated orange flavour with WP/GA coacervates, 5% oil, Cp=1%, pH=4.0, Pr:Ps=2:1;



Large droplets prepared with magnetic stirrer

Large droplets individually surrounded by a thin coacervate layer

Small droplets prepared with a blender

Small droplets encapsulated in a matrix of coacervate

Weinbreck et al., 2004

Hydroxypropyl cellulose (HPC) - a "smart," temperature responsive membrane for flavour encapsulation and delivery

The diffusion properties of HPC barrier membranes can be manipulated by controlling crosslink density, crosslink temperature, and hydrophobicity.

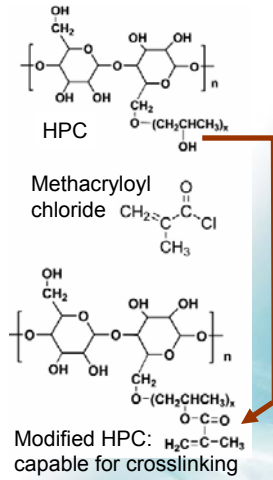
The room T diffusion properties are similar to baseline alginate membranes. With proper choice of synthetic protocol, however, HPC membranes show substantially reduced high-T diffusivity compared to alginate.

Although factors other than morphology could impact transport properties, it was possible to reduce high-T diffusivity by manipulation of the morphology.

Using processing conditions to control molecular structure makes it possible to reach desired transport properties.

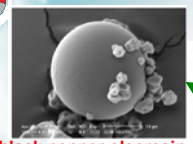
HPC, therefore, is a credible encapsulant candidate with improved high-T retention of flavours.

Heitfeld & Schaefer, 2008



Spray-drying is widely used in flavour microencapsulation

in gum arabic



black pepper oleoresin

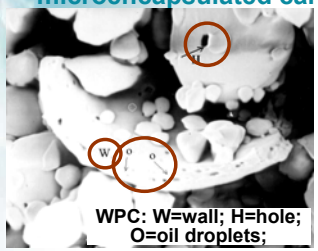
in MS HiCap-100

Advantages and disadvantages of the using of spray-drying

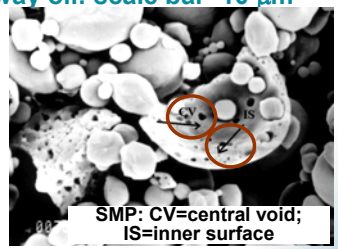
Advantages
- Low operating cost
- High quality of capsules in good yield
- Rapid solubility of the capsules
- Small size
- High stability capsules

Disadvantages
- Produce no uniform microcapsules
- Limitation in the choice of wall material (low viscosity at relatively high concentrations)
- Produce very fine powder which needs further processing
- Not good for heat-sensitive material

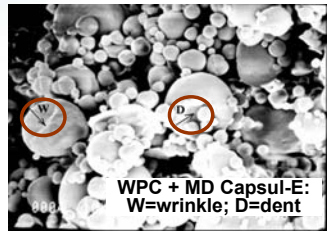
Micrographs showing the inner structure of microencapsulated caraway oil: scale bar=10 μm



WPC: W=wall; H=hole; O=oil droplets;



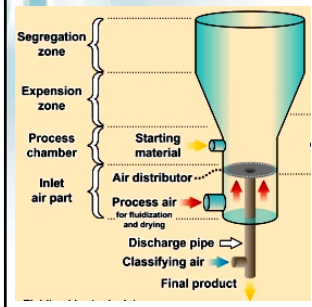
SMP: CV=central void; IS=inner surface

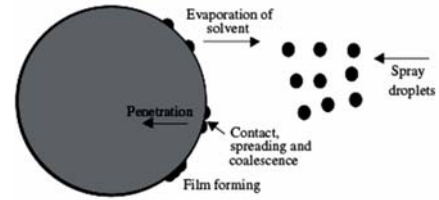


WPC + MD Capsul-E: W=wrinkle; D=dent

SMP+MD Encaps 855 W=wrinkle

Fluidized bed ("hot melt") method - re-crystallization of molten lipids around the nucleus leading to the protection of either liquid or solid phase material from its environment

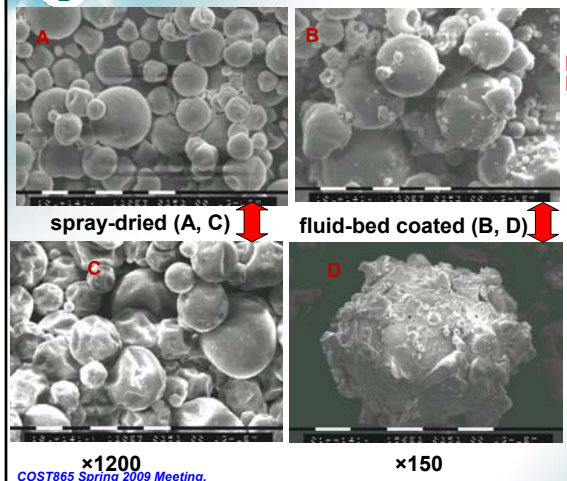




Schematic approach of film formation with the fluid bed coating device

Richard & Benoit, 2000

Microstructure and particle size distribution Micrographs of and thyme oil microcapsules



Mean diameter $D_{3,2}$ 12.4 → 29.3 µm

SMP ×1200, scale bar 10µm

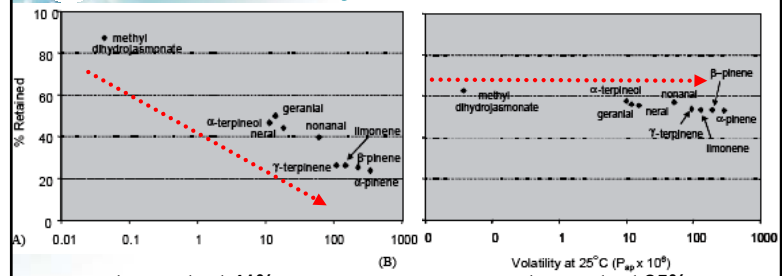
spray-dried (A, C) ↕ fluid-bed coated (B, D)

Mean diameter $D_{3,2}$ 13.3 → 75.2 µm

Hi-Cap 100 scale bar 10µm

×1200 ×150

Flavour retention during fluid bed coating of flavour emulsions (lemon oil on maltodextrin) on sugar crystals at 35–40C



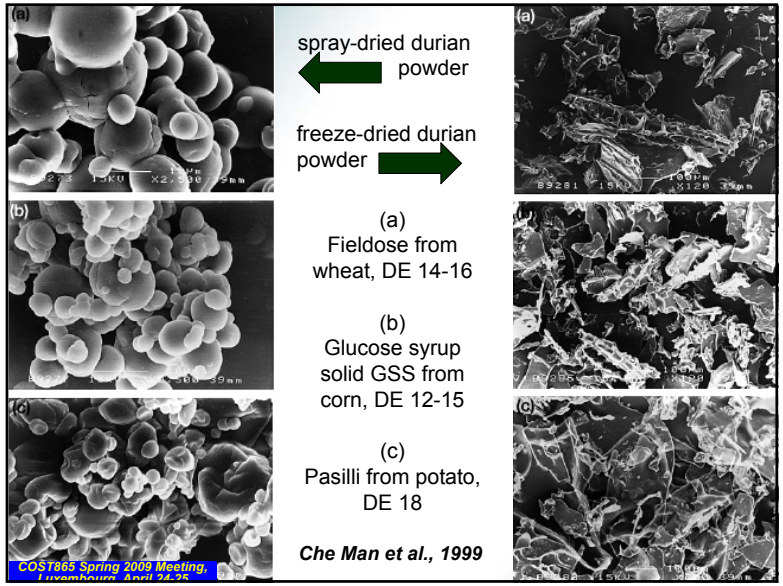
water content 41%
carrier - maltodextrin

water content 25%
carrier - maltodextrin-sugar 2:3

thermodynamically controlled: clear relationship between retention and volatility

kinetically controlled: negligible effect of the volatility

during drying the sugar–maltodextrin syrup of B is completely stagnant whereas in A there is still some convective diffusion possible



spray-dried durian powder ←

freeze-dried durian powder →

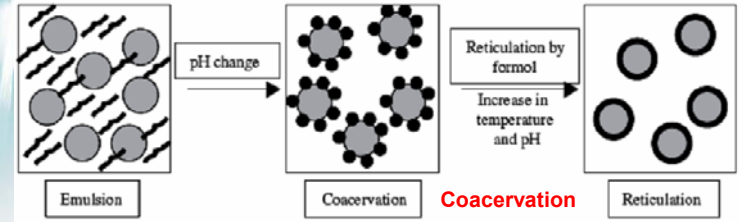
(a) Fieldose from wheat, DE 14-16

(b) Glucose syrup solid GSS from corn, DE 12-15

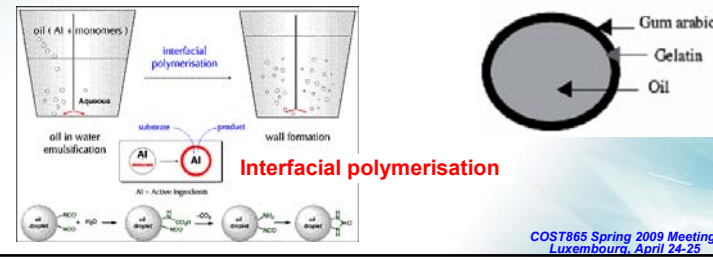
(c) Pasilli from potato, DE 18

Che Man et al., 1999

Other methods of flavour encapsulation



Coacervation

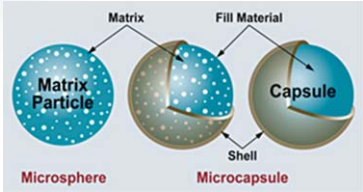


Interfacial polymerisation

Characteristics of encapsulation processes

	Encapsulation method	Particle size	Max. load (%)	References
Chemical techniques	Simple coacervation	20–200	<60	Richard & Benoît, 2000
	Complex coacervation	5–200	70–90	Richard & Benoît, 2000
	Molecular inclusion	5–50	5–10	Uhlemann *et al.*, 2002
Mechanical techniques	Spray-drying	1–50	<40	Richard & Benoît, 2000
	Spray chilling	20–200	10–20	Uhlemann *et al.*, 2002
	Extrusion	200–2000	6–20	Uhlemann *et al.*, 2002
	Fluidised bed	>100	60–90	Richard & Benoît, 2000

Madene et al. 2006



Particle size and morphology can be tailored to achieve the desired product performance

Adopted from SWRI microencapsulation.swri.org

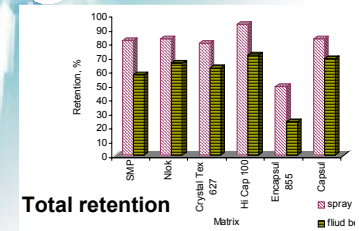
The capsules should retain core flavour and entrap it inside the wall

Encapsulating agent	Total oil, %	Surface oil, %	Efficiency, %	Moisture, %
Whey protein concentrate	80.7	1.9	78.8	3.5
WPC+MD N-lok (9:1)	87.8	2.0	85.9	2.9
WPC+MD Encaps 855 (9:1)	85.5	2.5	83.0	3.7
WPC+MD Capsul–E (9:1)	84.1	2.4	81.7	2.7
Skimmed milk powder	76.1	2.0	74.1	3.3
SMP+ MD N-lok (9:1)	71.0	1.4	69.6	2.2
SMP+ MD Capsul–E (9:1)	70.9	1.0	69.8	2.5
SMP+ MD Encaps 855 (9:1)	69.2	1.2	68.1	3.0

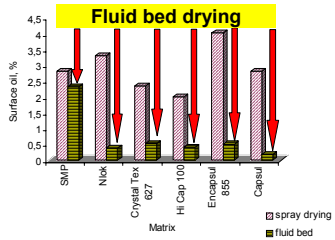
Characteristics of caraway oil encapsulation with different matrices

Bylaité et al., 2001

Encapsulation characteristics of thyme essential oil

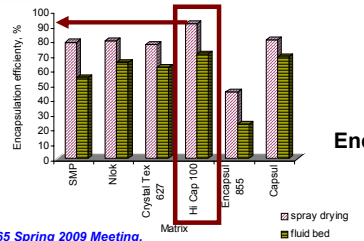


Total retention



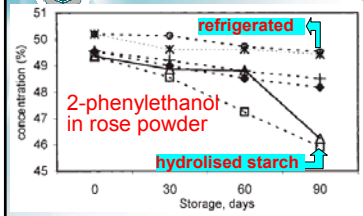
Surface oil

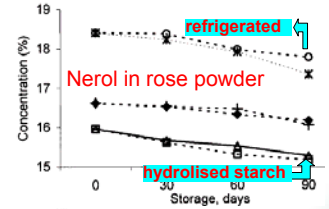
Strong interactions with SMP proteins ?

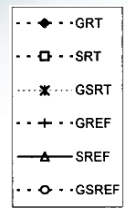


Encapsulation efficiency

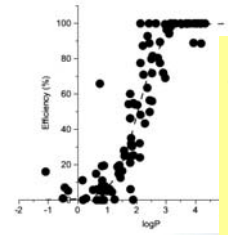
The capsules should protect volatile flavours against their losses during storage: study with rose oil







G = gum
S = hydrolysed starch
GS = gum + starch
RT = room temperature (27 °C);
REF = refrigerated temperature (4 °C)

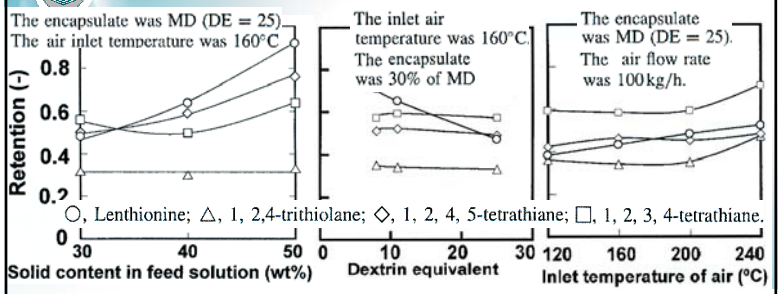


Experimental efficiency of encapsulation for 98 flavour compounds varying in logP properties from 1.09 to 6.39 (plain circles) Fit using Eq. with s = 1.32 (dashed line)

$$E_F = 100\frac{[F]_V V_V}{Q} = \frac{100}{\frac{1}{V_V} + \frac{V_W}{K_{VW} V_V}} = \frac{100}{\frac{1}{V_V} + \frac{V_W}{10^{logP} V_V}}$$

Verma et al., 2005

Effects of various factors on retention of shiitake flavours in spray-dried powder *Shiga et al, 2004*

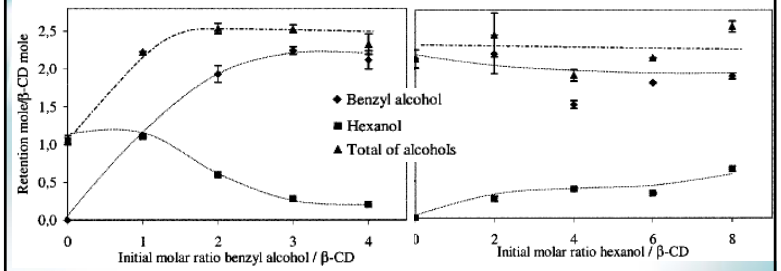


α-CD10%/MD20% powder made the retention of all flavours increase markedly as compared with α-CD10% or MD30% powder

Effects of Type of CD on Flavor Retention during Spray Drying

Composition of carrier solid	Retention (—)			
	lenthionine	1,2,4,-trithiolane	1,2,4,5-tetrathiane	1,2,3,4-tetrathiane
α-CD10%	0.49	0.46	0.25	0.25
β-CD10%	0.14	0.44	0.46	0.33
γ-CD10%	0.27	0.18	0.23	0.31
MD30%	0.51	0.25	0.38	0.28
α-CD10%/MD20%	0.98	0.67	0.87	0.82

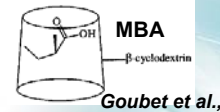
Retention of alcohols after freeze-drying of β-cyclodextrins initially saturated with:



With 2mol hexanol/mol of β-CD, in which increasing amounts of benzyl alcohol have been added

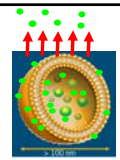
4 mol of benzyl alcohol/mol of β-CD, in which increasing amounts of hexanol have been added

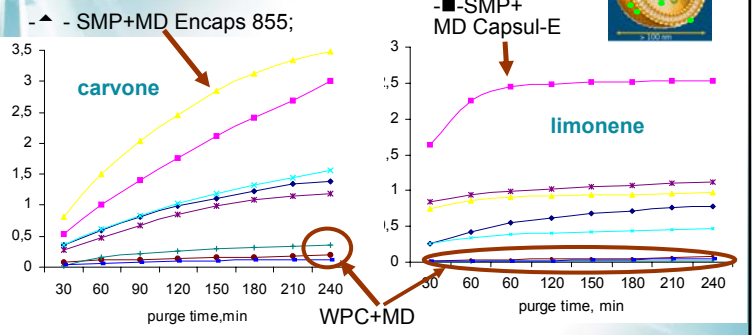
volatile compounds compete for the same binding sites on β-cyclodextrin



Goubet et al., 2009

Limonene and carvone, released from microencapsulated caraway oil products (DHS)





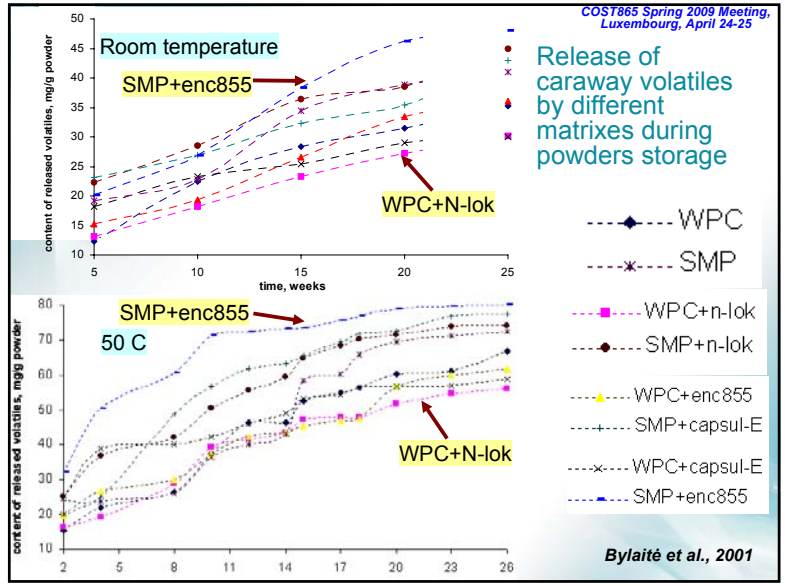
-♦-SMP; -■-SMP+MD Capsul-E;
-▲- SMP+MD Encaps 855;
-x-SMP+MD N-lok;

--*-WPC; -•-WPC+MD Capsul-E;
-+-WPC+MD Encaps 855;
--WPC+MD N-lok

Bylaité et al., 2001

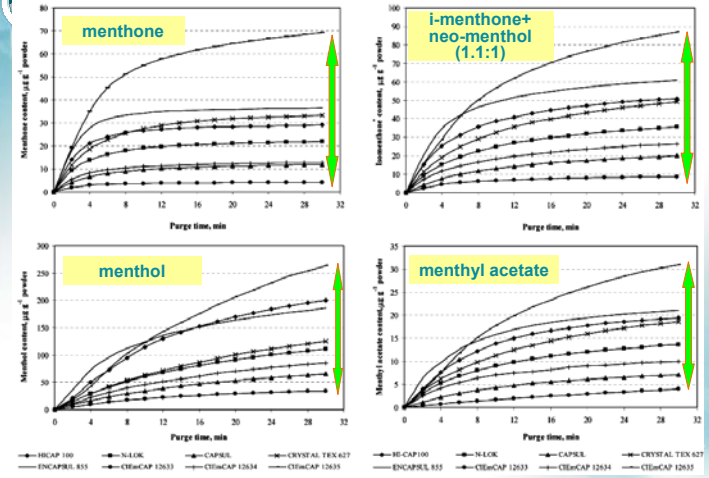
COST865 Spring 2009 Meeting, Luxembourg, April 24-25

Release of caraway volatiles by different matrixes during powders storage



Bylaité et al., 2001

Amounts of major volatiles released from microencapsulated peppermint EO products by DHS analysis



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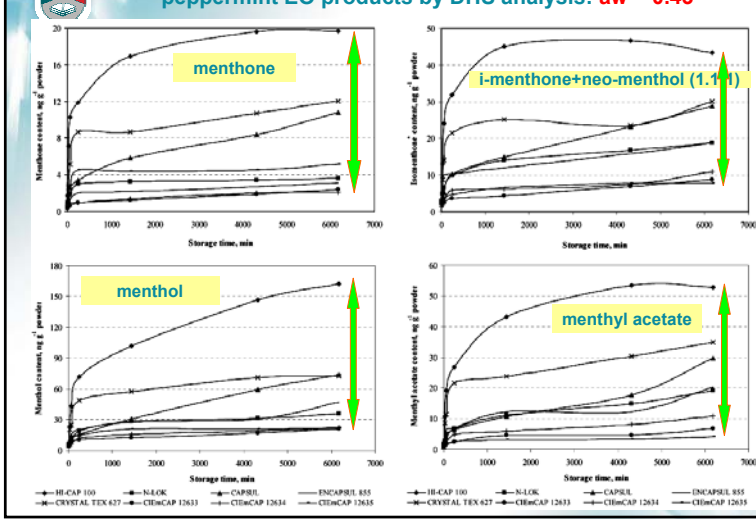
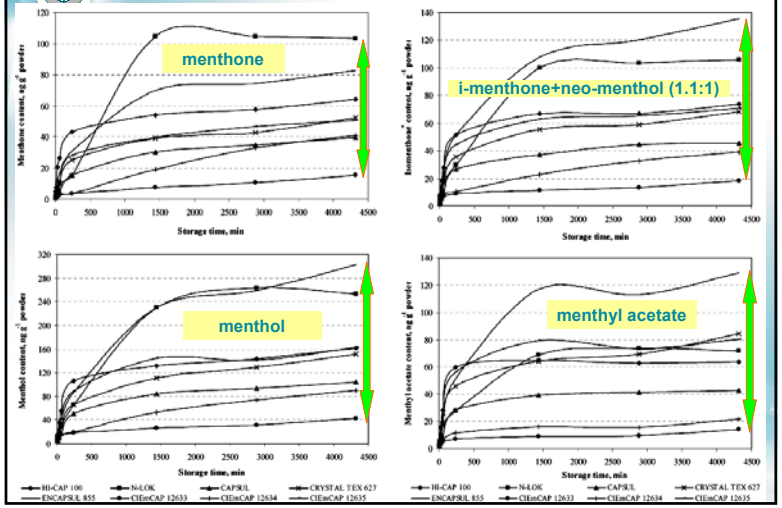
Baranauskienė et al., 2007

Amounts of major volatiles released from microencapsulated peppermint EO products by DHS analysis: aw = 0.43



Amounts of major volatiles released from microencapsulated peppermint EO products by DHS analysis: aw = 0.75



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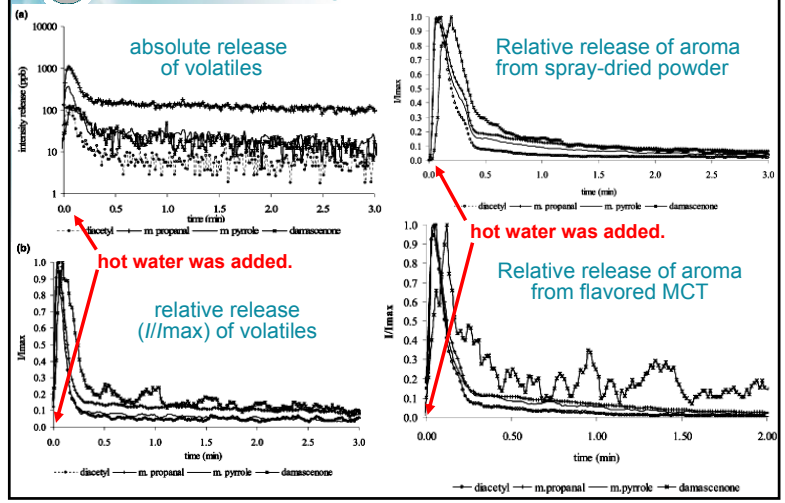
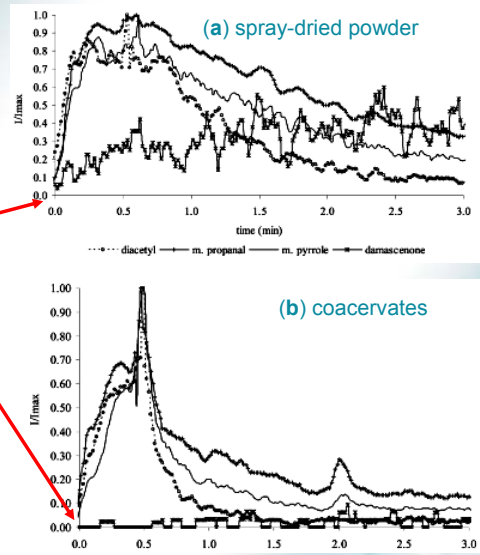
Coacervate microcapsules, cross-linked and intermediate wall thickness (made with 80 g of oil)

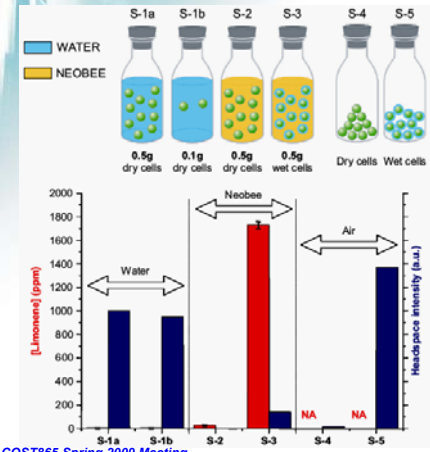


Relative release of volatiles at room temperature (air and water)

water (room temperature) was added



Flavour-encapsulation and flavour-release performances of a commercial yeast-based delivery system



Limonene release intensity in different solvents, water, Neobee or air (red) or in the headspace over the solution (blue)

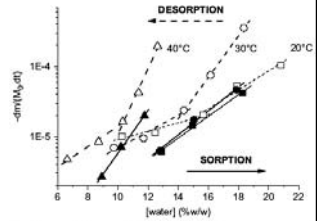
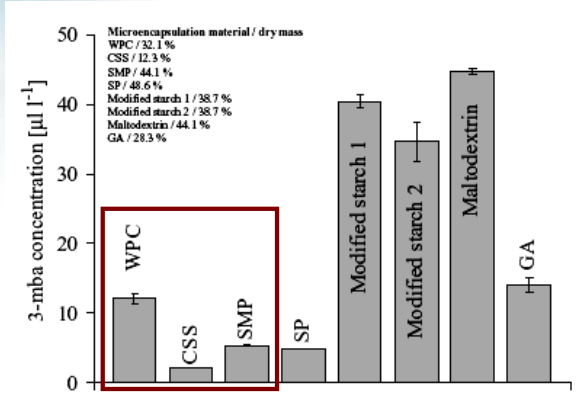


Fig. 3. Normalized rate of limonene loss at different temperatures (20 (squares), 30 (circles) and 40 °C (triangles)) extracted from DVS isotherms of sorption (plain lines) and desorption (dashed lines). Semi-logarithmic representation. Linear fits are shown to guide the eye.

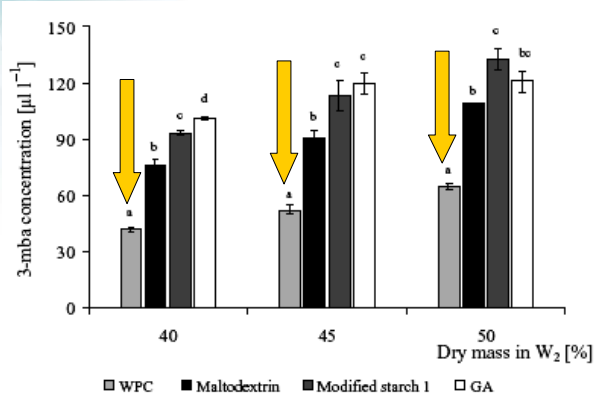
Dardelle et al. 2007

Concentration of 3-methylbutyraldehyde released from different microcapsules after 120 min lipase treatment



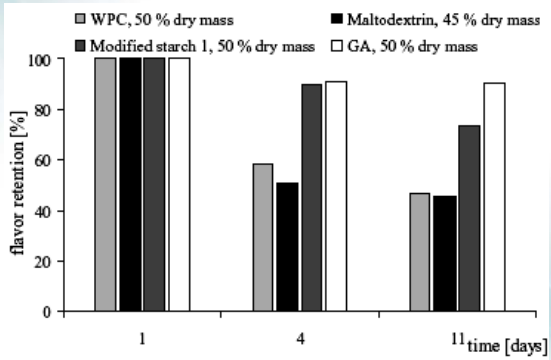
Bruckner et al., 2007

Released conc. of 3-mba from hydrated as a function of carrier material and dry mass in the second aqueous phase W2 at 90 ◦C



Bruckner et al., 2007

Flavor retention as a function of carrier material and time

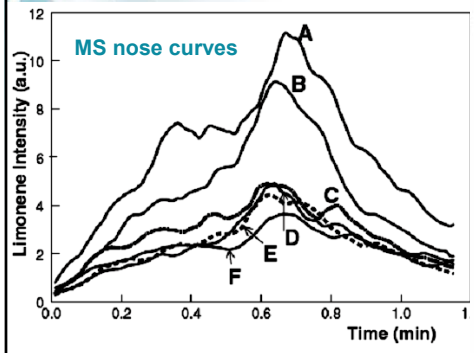


The mechanistic of flavour-controlled release

Encapsulation technique	*Controlled release mechanistic*
Simple coacervation	Prolonged release
Complex coacervation	Prolonged release (diffusion) and started release (pH, dehydration, effect mechanical, dissolution or enzymatic effect
Spray drying	Prolonged release and started release
Fluid bed drying	Started release (pH or heat treatment)
Extrusion	Prolonged release

Richard & Benoit, 2000

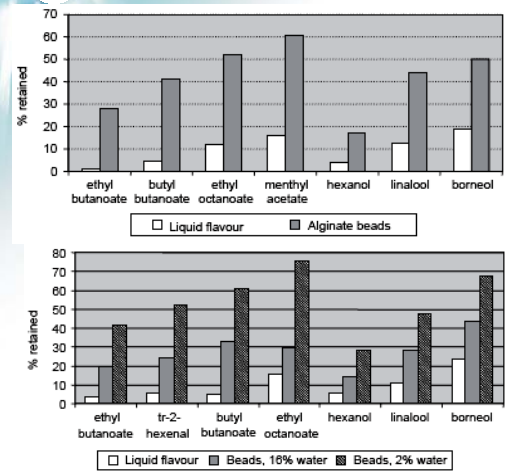
Average flavour release from cheeses containing limonene capsules



- A: large capsule, blank pH 7
- B: large capsule; WP/GA pH 4; not cross-linked
- C: small capsule; WP/GA pH 4; not cross-linked
- D: small capsule, blank pH 7
- E: small capsule; WP/GA pH 4; cross-linked
- F: large capsule; WP/GA pH 4; cross-linked

Weinbreck et al., 2004

Flavour retention in alginate gel beads during baking of crackers

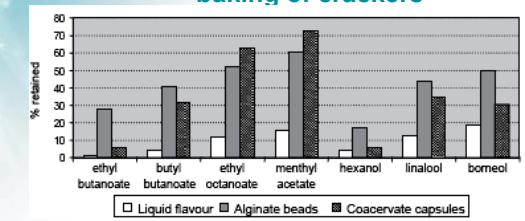


Effect of flavour encapsulation

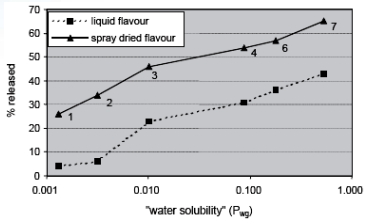
Effect of moisture content

De Roos, 1999

Effect of capsule type on flavour retention during baking of crackers



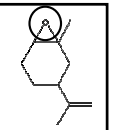
The relatively high retention of volatile compounds by the alginate gel beads is due to their bigger size (about 1mm versus 250 mm for the coacervate microcapsules.

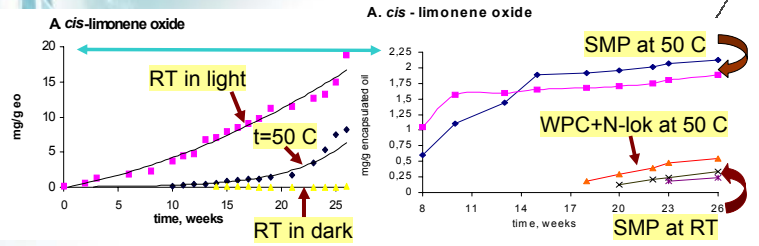


Effect of encapsulation on flavour release from sugar based stick gum measured as percentage released after 5 min of chewing

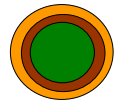
De Roos, 2003

Formation of oxidation products in caraway oil during storage at different conditions: 50 °C, room temperature (RT) with/ without light



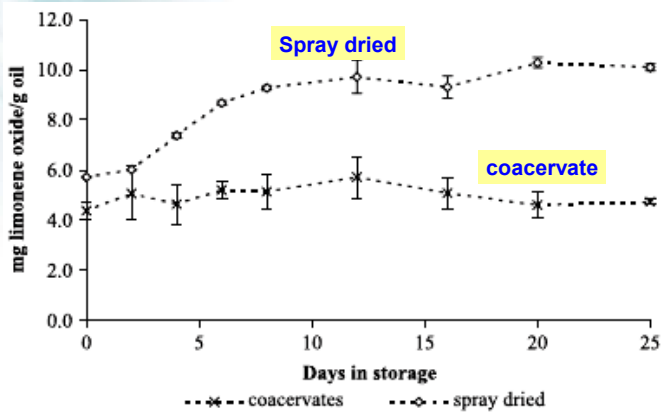


WPC+N-lok forms double layer coating ?



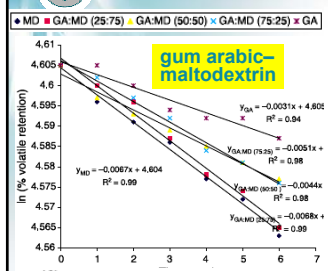
Bylaité et al., 2001

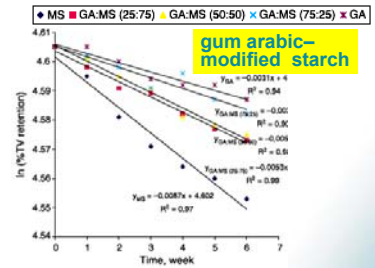
Influence of encapsulation method on storage stability of limonene

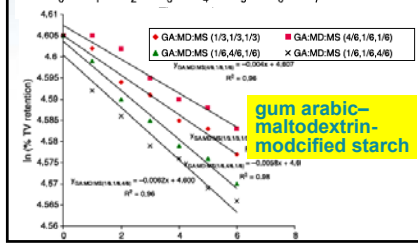


Leclercq et al, 2008

Stability of entrapped aromas in microencapsulated cardamom oleoresin



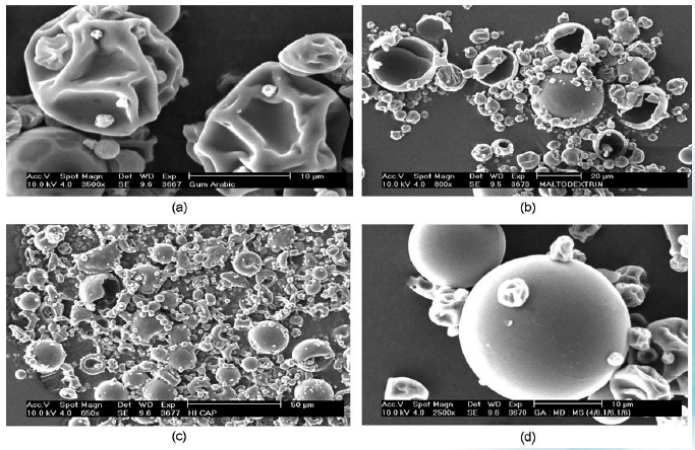




A 4/6,1/6,1/6 blend of GA:MD:MS offered a protection, better than GA as seen from the $t_{1/2}$, time required for a constituent to reduce to 50% of its initial value.

Krishnan et al., 2005

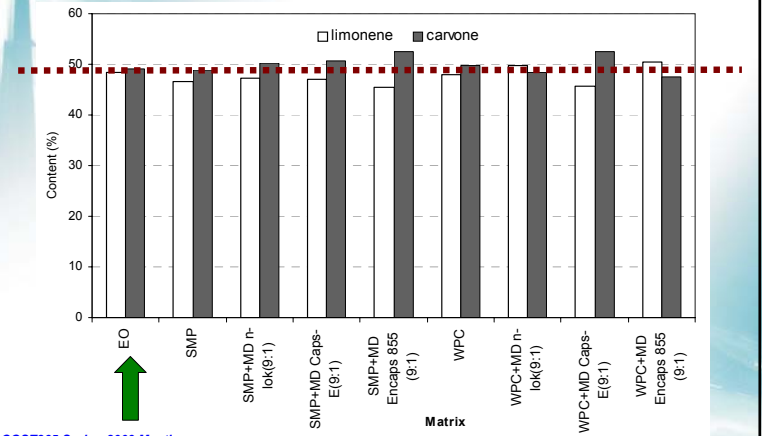
SEM of the microcapsules prepared from (a) gum arabic, (b) maltodextrin, (c) modified starch HiCap100 and (d) the blends of all the three GA:MD:MS (4/6,1/6,1/6).



Krishnan et al., 2005

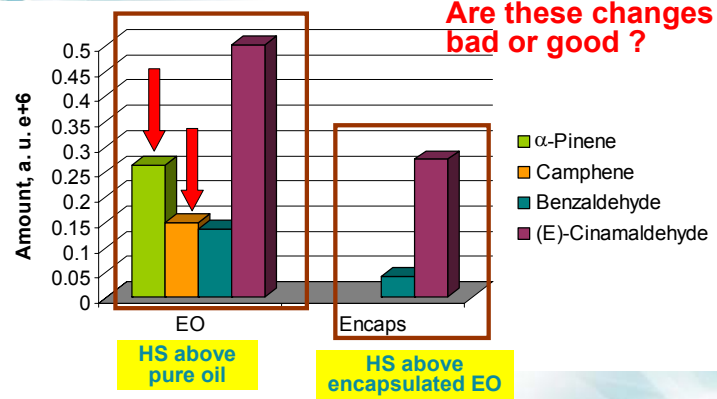
Differences in the composition of aroma in the initial material (e.g. essential oil) and in the microencapsulated products

Content of limonene and carvone in pure caraway essential oil (EO) compared to retention in different matrixes



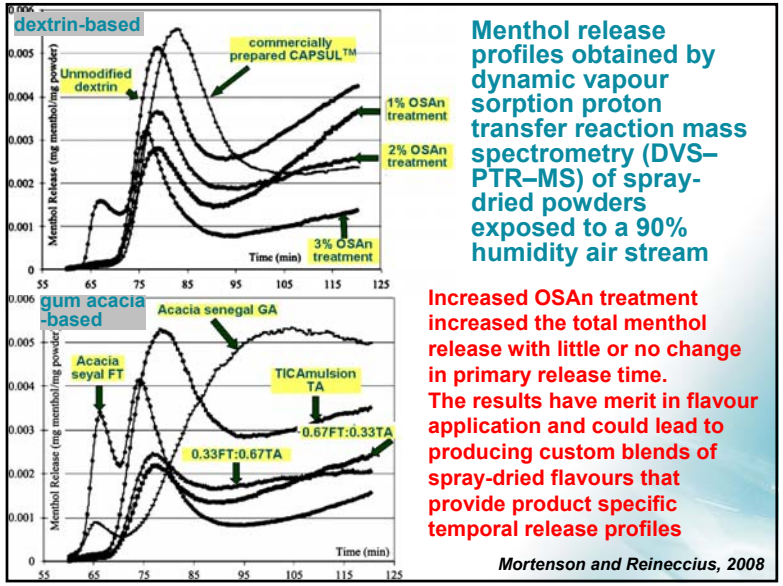
Amount of main cassia constituents in headspace (HS) of pure essential oil and encapsulated product

Are these changes bad or good ?



HS above pure oil

HS above encapsulated EO

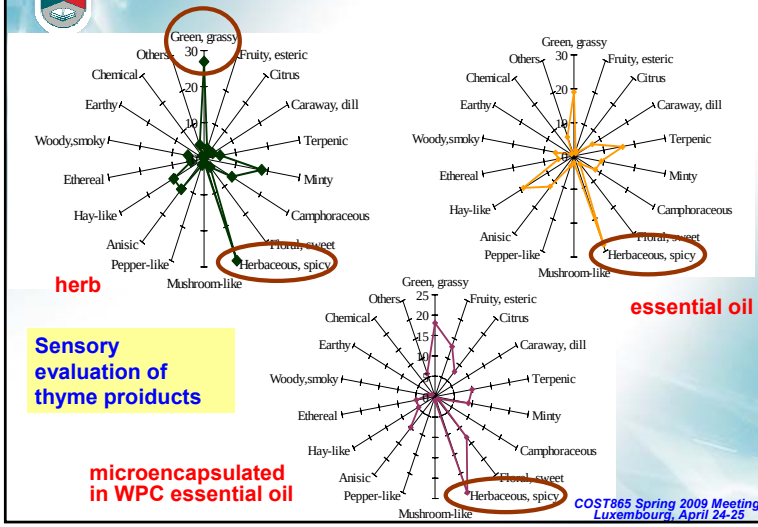


Menthol release profiles obtained by dynamic vapour sorption proton transfer reaction mass spectrometry (DVS–PTR–MS) of spray-dried powders exposed to a 90% humidity air stream

Increased OSAn treatment increased the total menthol release with little or no change in primary release time.
The results have merit in flavour application and could lead to producing custom blends of spray-dried flavours that provide product specific temporal release profiles

Mortenson and Reineccius, 2008

Chages in aroma profile after microencapsulation.



Metal oxide sensor responses to oregano oil encapsulated in different matrices