Formulating Nano-particles into Robust Particle-Stabilized Emulsions

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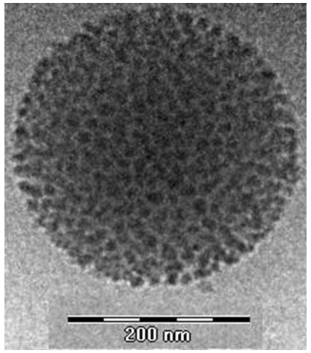

- Particle Stabilized Emulsions
- Preparation of Particle Stabilized O/W Nanoemulsions
- Stability of PS Nanoemulsions.
- Spray-drying of PS Nanoemulsions

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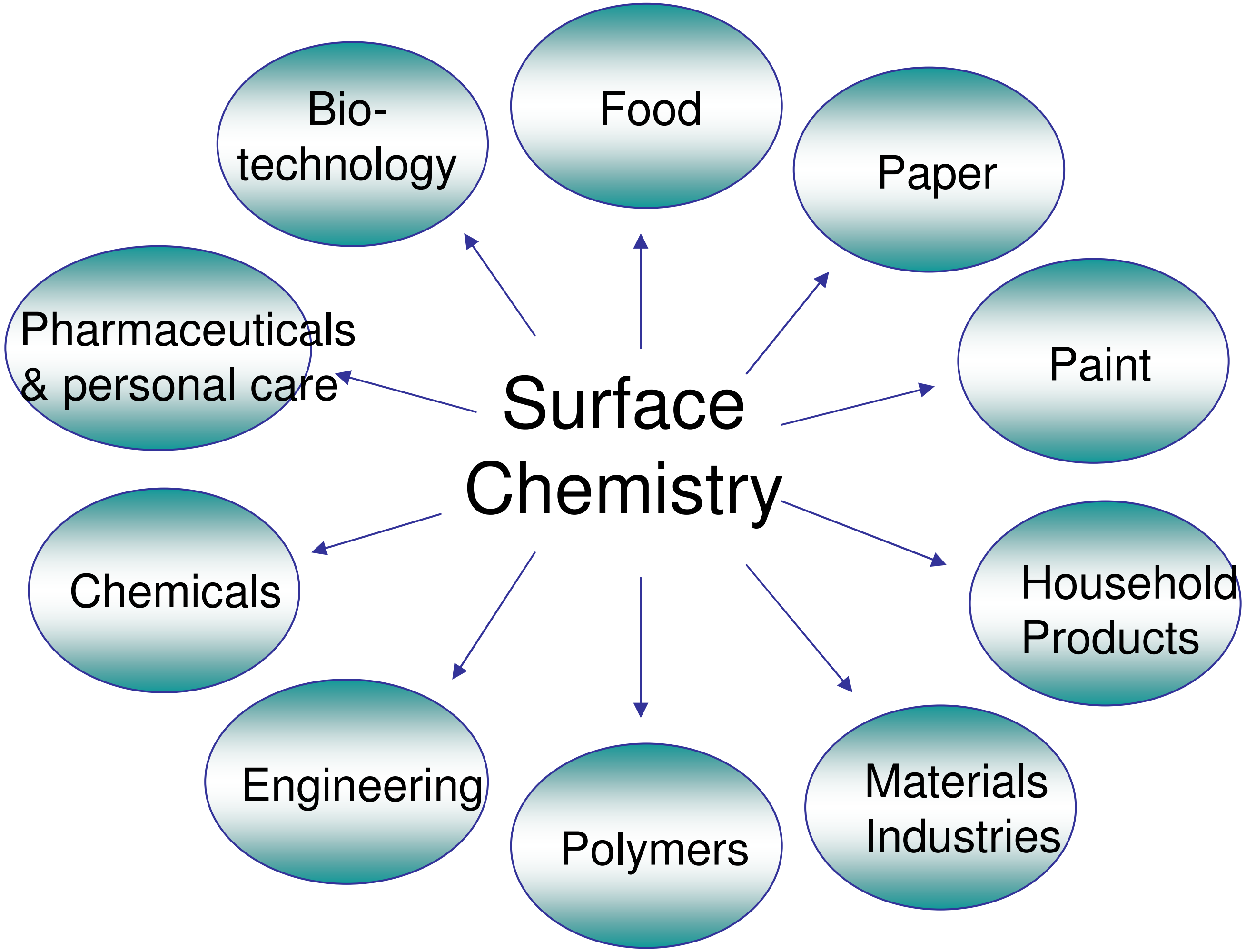

Some of the Member Companies…..

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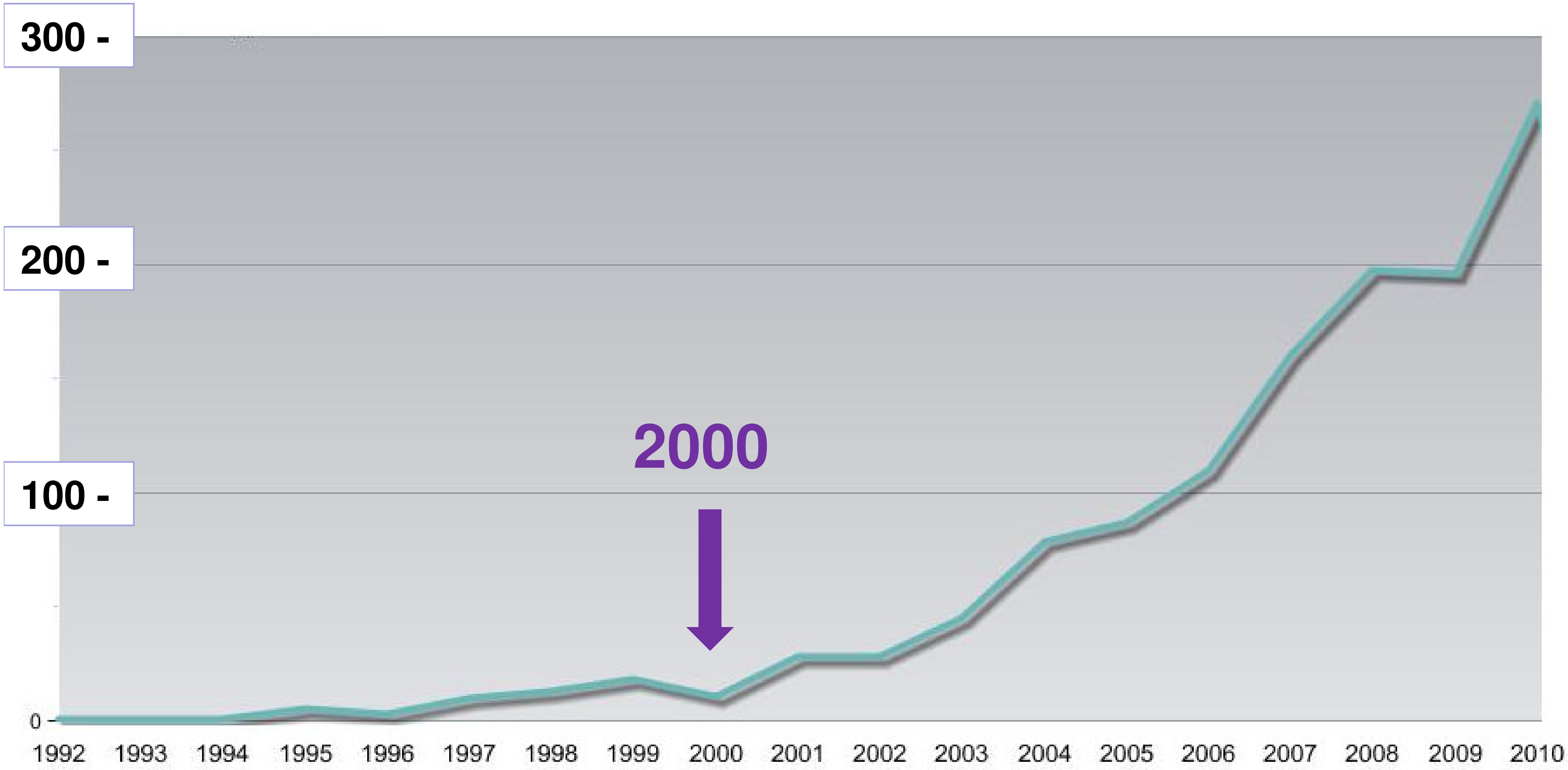
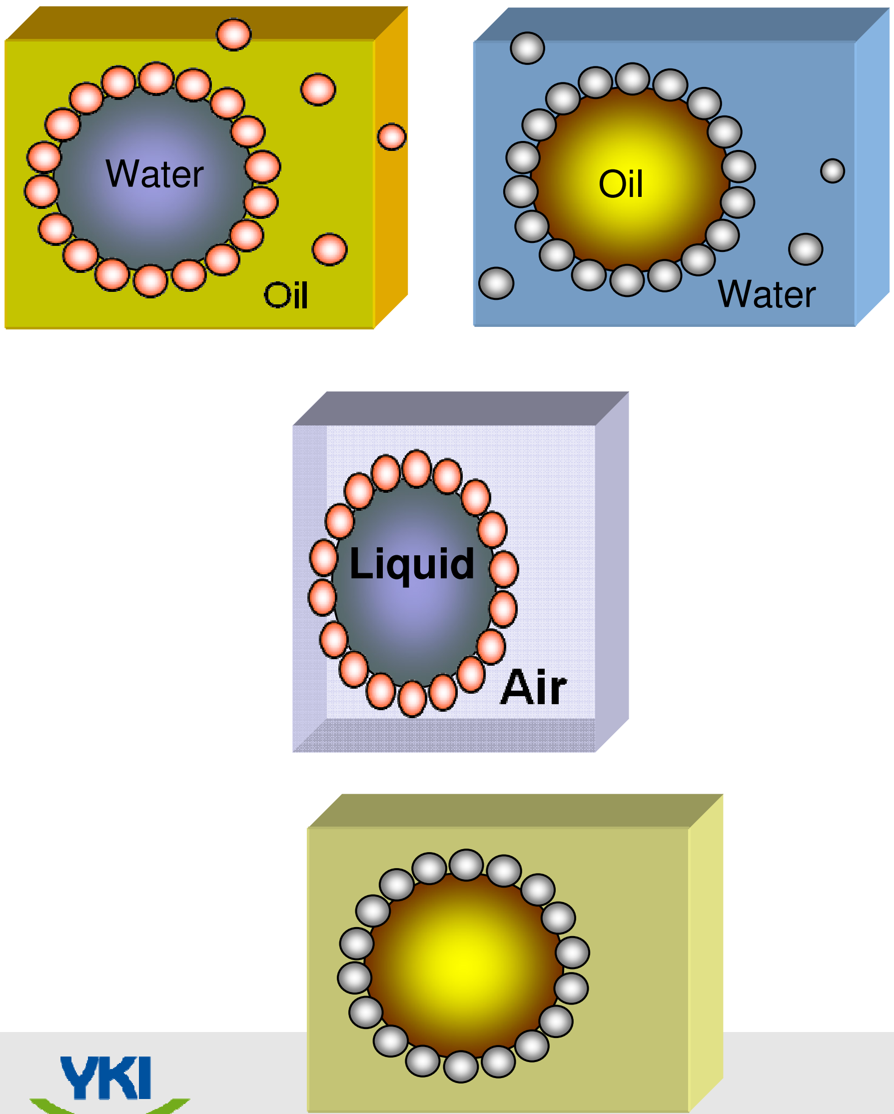
Pickering and Particle Stabilized Article Publishing Trends



Source: Thomson Innovation®, www.thomsoninnovation.com

Particle Stabilized Structures



Types of emulsions

W/O and O/W/O

O/W and W/O/W

Liquid marbles

Dry water

Microcapsules

Colloidosomes

Applications

Nano-particle design

Synthesis

Nanocomposites

Porous materials

Nano-particle vehicles

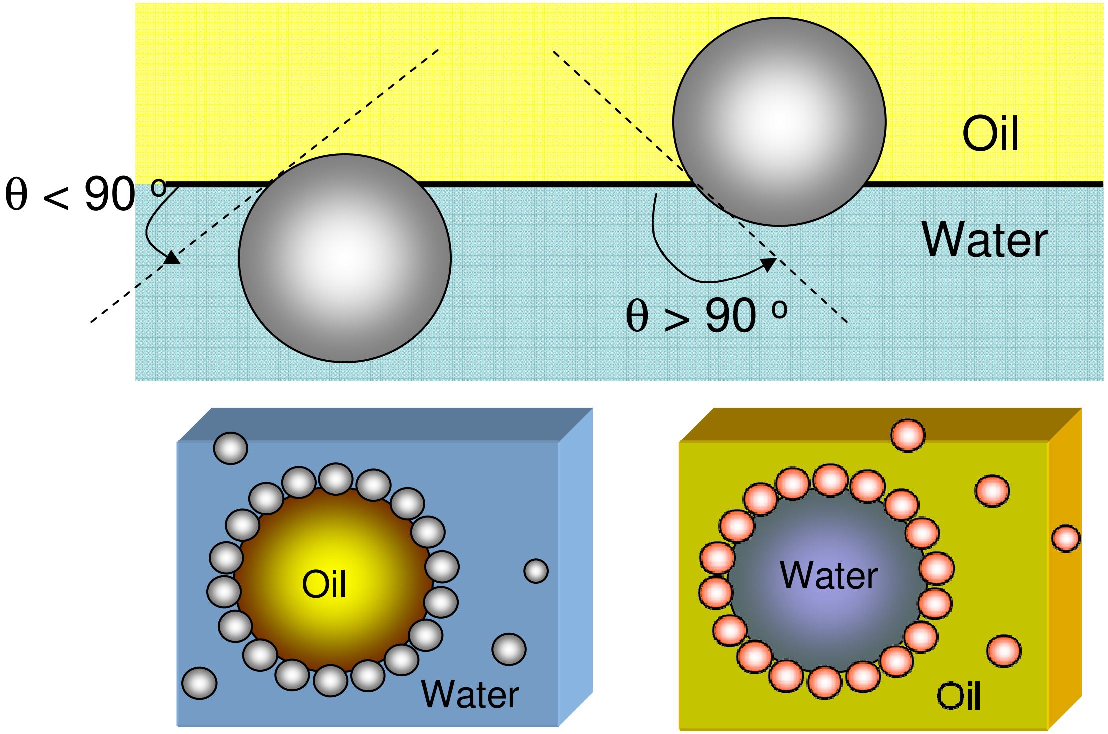
Alternative penetration profiles

New delivery systems

Particle Stabilized Emulsions: Formulation

I. Physicochemical Aspects

Particle wettability determines preferred emulsion type



Wettability determined by:

- ► Nature of the particle
- ► Nature of the oil and aqueous phase

Binks, B.P., Curr. Opin. Colloid Interface Sci. ***7****, 21-41 (2002).*

Particle Stabilized Emulsions: Formulation

Stabilization energy of a particle
Energy required to remove particle from oil-water interface is given by

$$-E = \pi \mathbf{r}^2 \gamma (1 \pm \cos \theta)^2$$

E proportional to R^2 →

Larger particles are generally more effective

For 90 ° contact angle:

1 µm particle E ~ 10^7 kT

10 nm particle E ~ 10^3 kT

1 nm particle E ~ 10 kT

Globular proteins E ~ a few kT

Surfactants E ~ 1 kT

Pieranski, P. *Physical Review Letters* **1980**, 45, 569-572.

Binks, B. P.; Lumsdon, S. O., *Langmuir* **2001,** 17, 4540-4547.

Other Variables Affecting the Outcome of Emulsification

II. Composition

- Amount
- Ratios
- Order of addition

III. Emulsification protocol

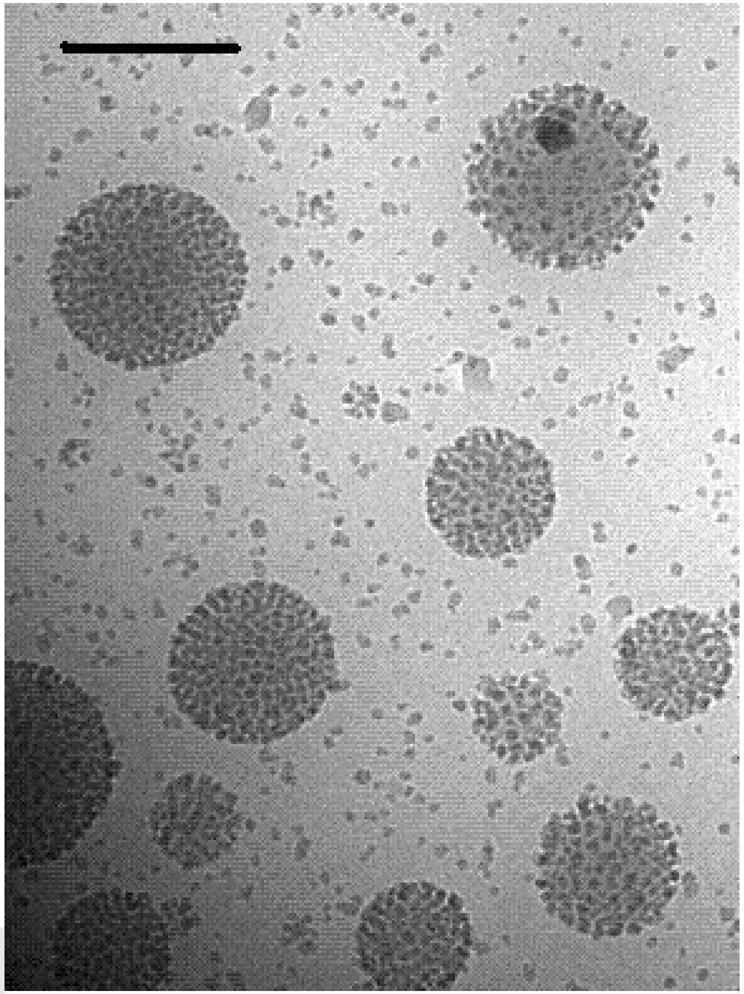
- Shear (turbulence)
- Mixer geometry (turbine, blade)
- Energy (intensity, duration)

…the properties of an emulsion depend on a complex interplay of factors!

Novel Development:
Robust Particle-stabilized Nanoemulsions

- Colloidal Pickering emulsions
- Ultra-stable droplets
  - *Temperature, electrolyte, surfactants, etc*

200 nm



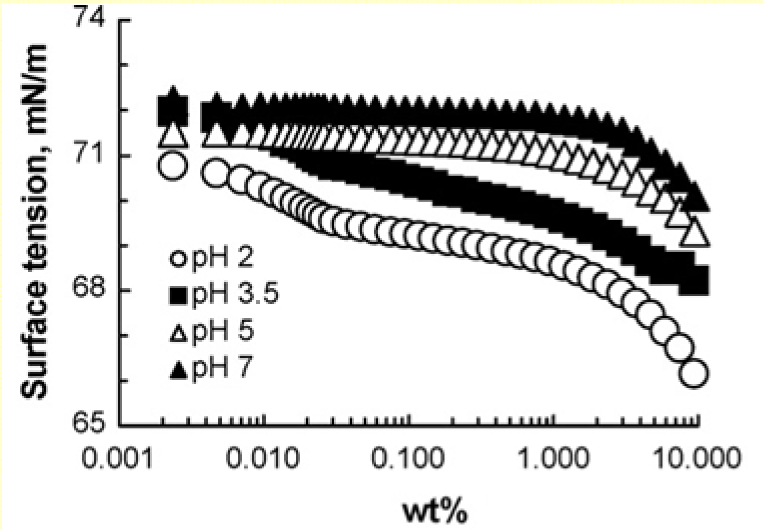
The Particles: Commercial Silica Sol

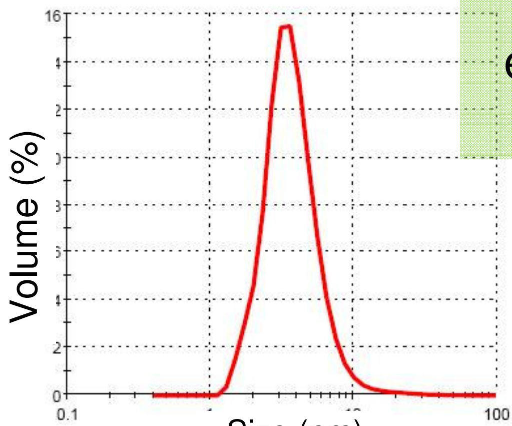
Silica Sol

- ►Hydrophobically modified (methoxysilanated or ethoxysilanated) silica particles
- ►Aqueous dispersion (pH 7.5, 30% w)
- ►Particle diameter: 7 nm

Stabilization of O/W emulsions

Surface activity





Size distribution by volume as determined by dynamic light scattering

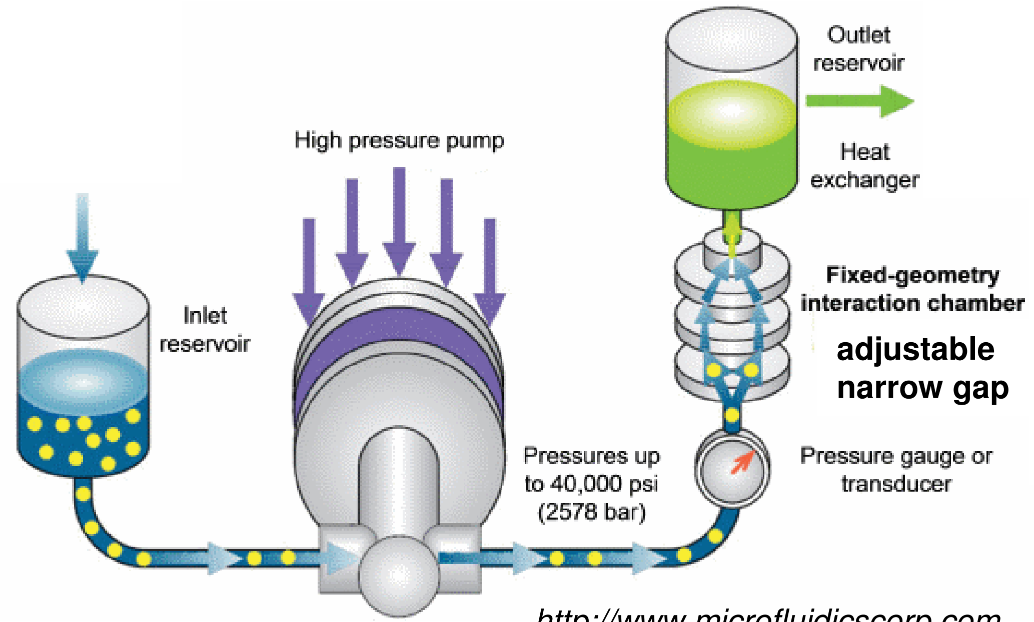
I. Blute et al. / Colloids and Surfaces A: Physicochem. Eng. Aspects 337 (2009) 127–135

Preparation of Particle Stabilized O/W Nanoemulsions

Emulsification Protocol

► Ultra shear device - High pressure homogenizer type

► Production of extremely fine emulsion (drops in nanometer size range)

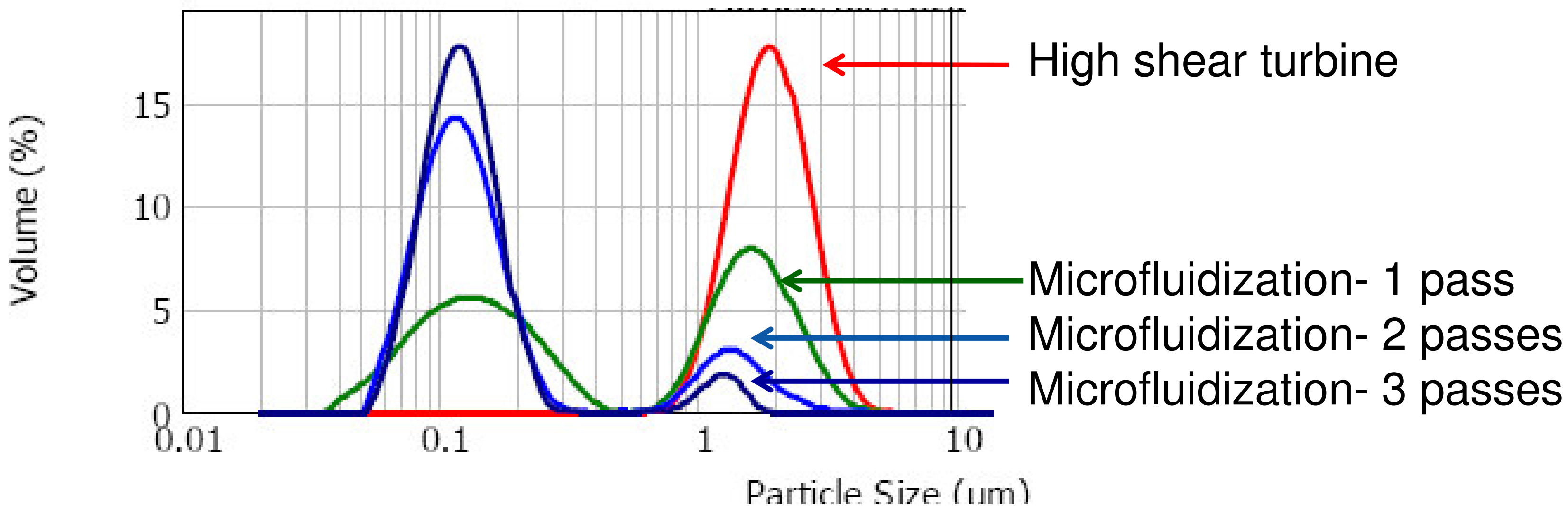


http://www.microfluidicscorp.com

Preparation of Particle Stabilized O/W Nanoemulsions

Emulsification Protocol Studies

Oil phase: Hexadecane (C16)
Particle concentration: 30% w/v

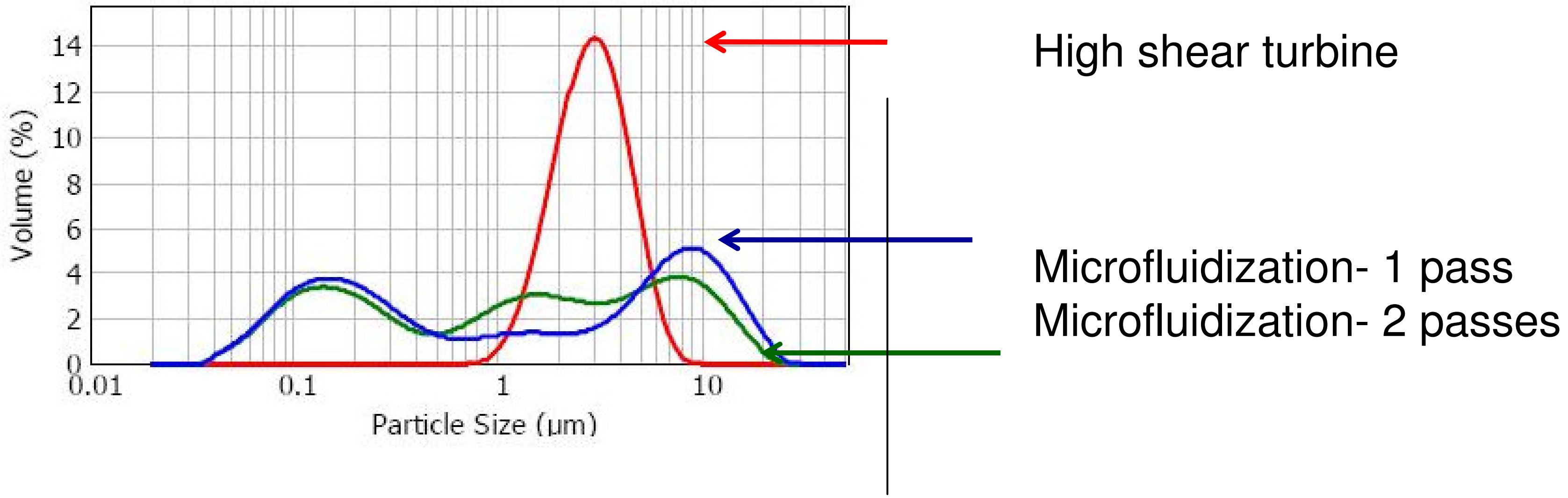


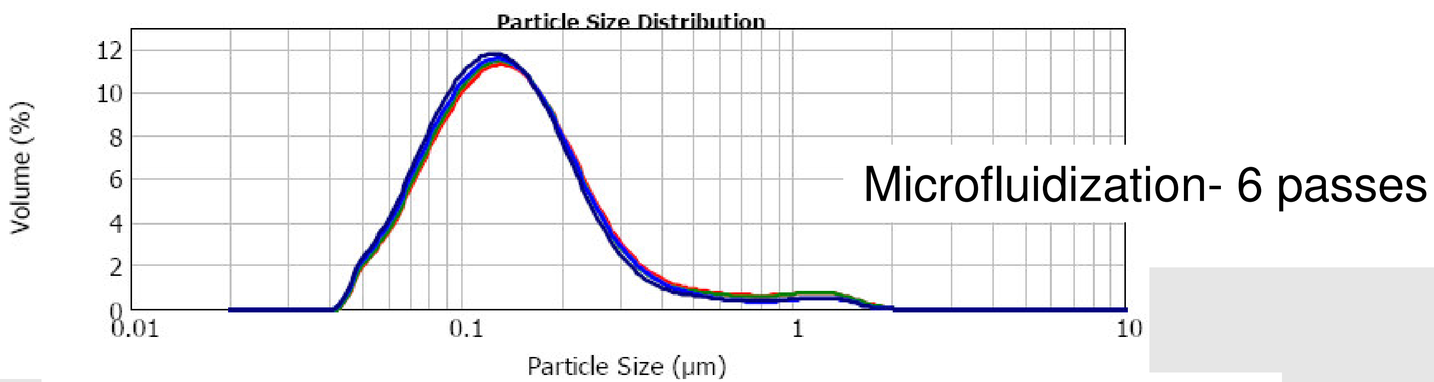
Particle size distribution of freshly prepared emulsions

Preparation of Particle Stabilized O/W Nanoemulsions

Emulsification Protocol Studies

Oil phase: Hexadecane (C16)
Particle concentration: 10% w/v

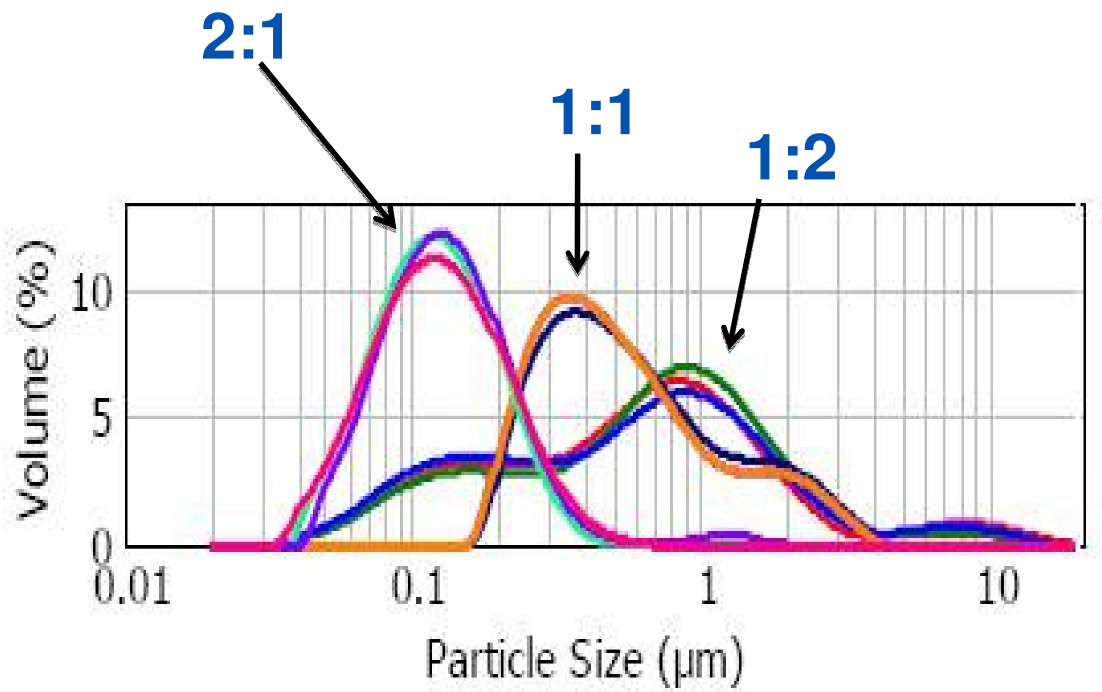




Particle size distribution of freshly prepared emulsions

Nanoemulsions of Food Oils

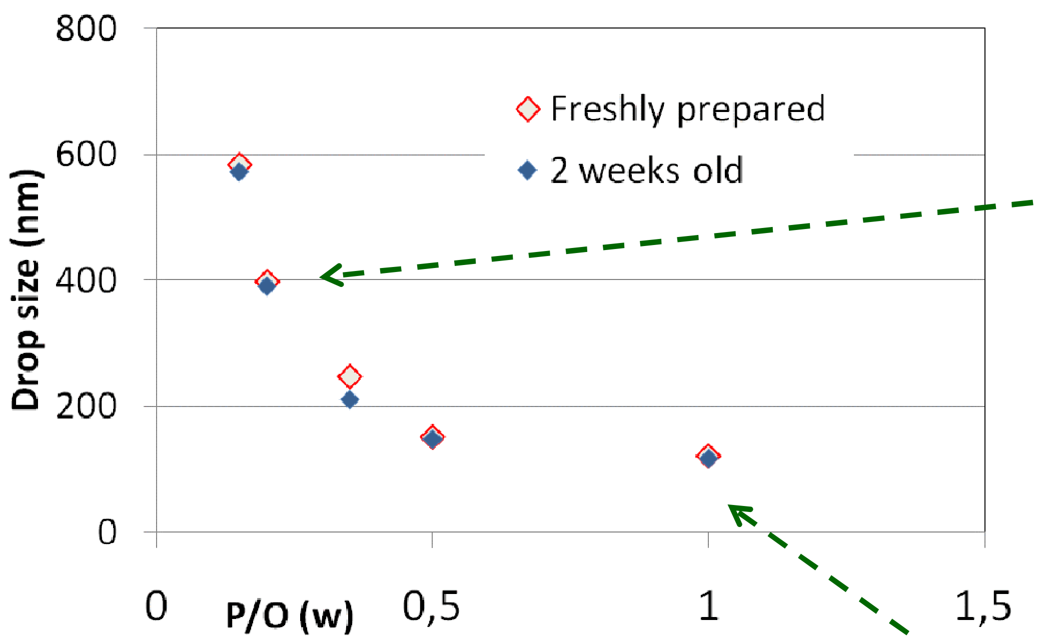
Effect of particle : rapeseed oil ratio

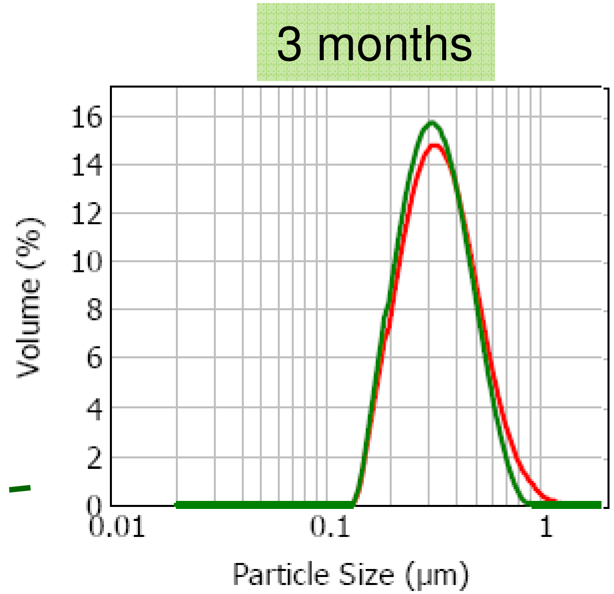


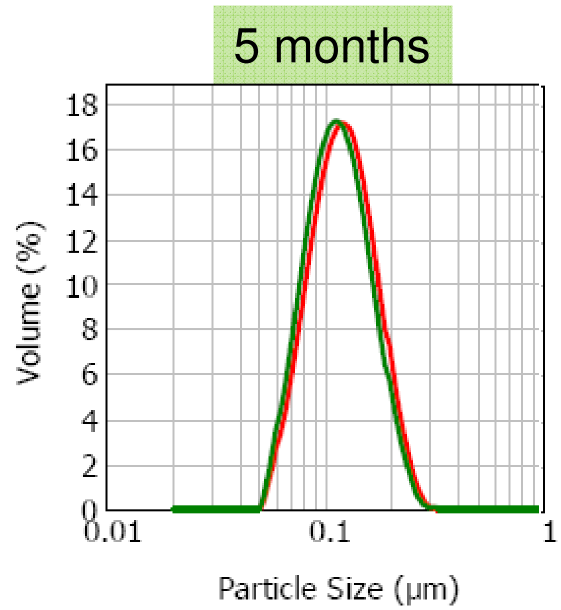
Droplet size as a function of processing time at 4.5 bar pressure.
↑ 5 ,10 and 15 minutes for the systems

Stability Studies: Time

Oil phase: Squalene (10% w/v)
P/O ratio: 0.15-1







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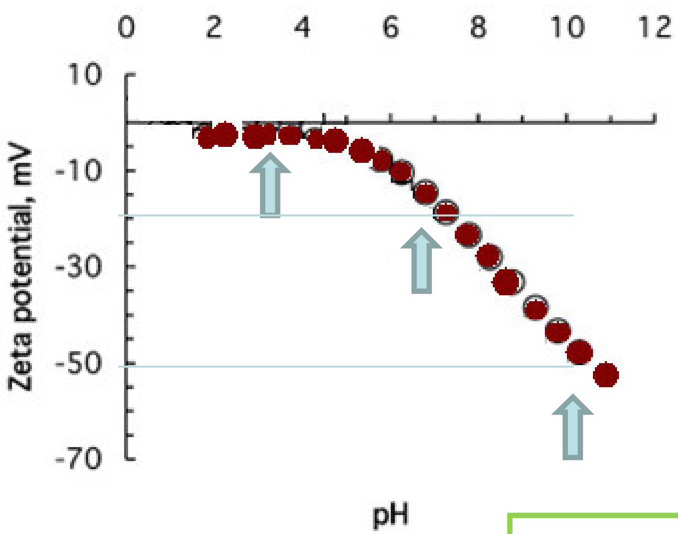
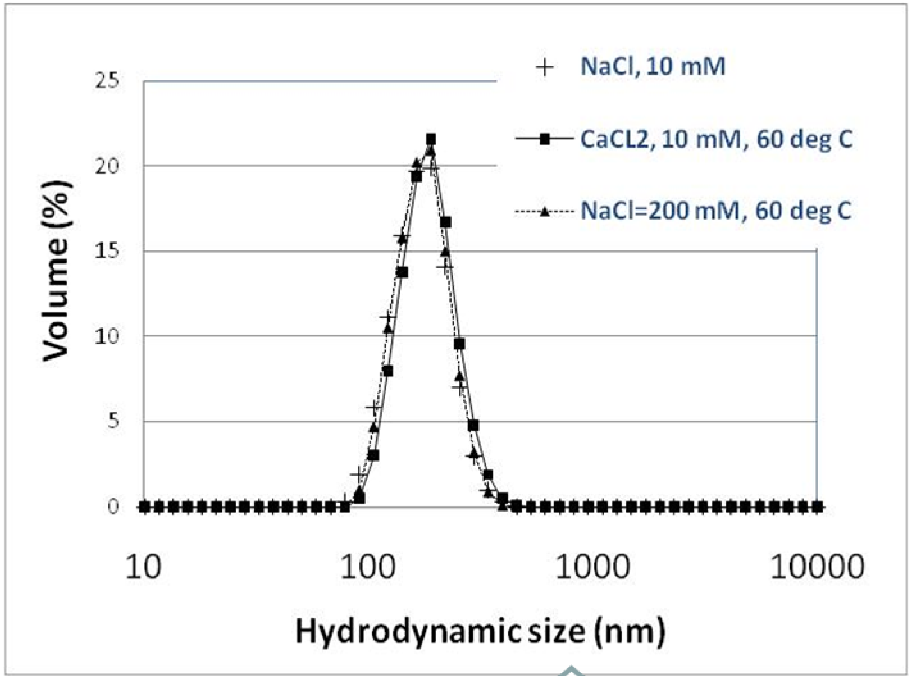
Stability Studies: Temperature, pH, Surfactants and Electrolytes

	SDS	Tween 80	Dotab
pH	1 w/w%	1 w/w%	1 w/w%
3			
7			
10			



	CaCl2
pH	20 mM
3	
7	
10	



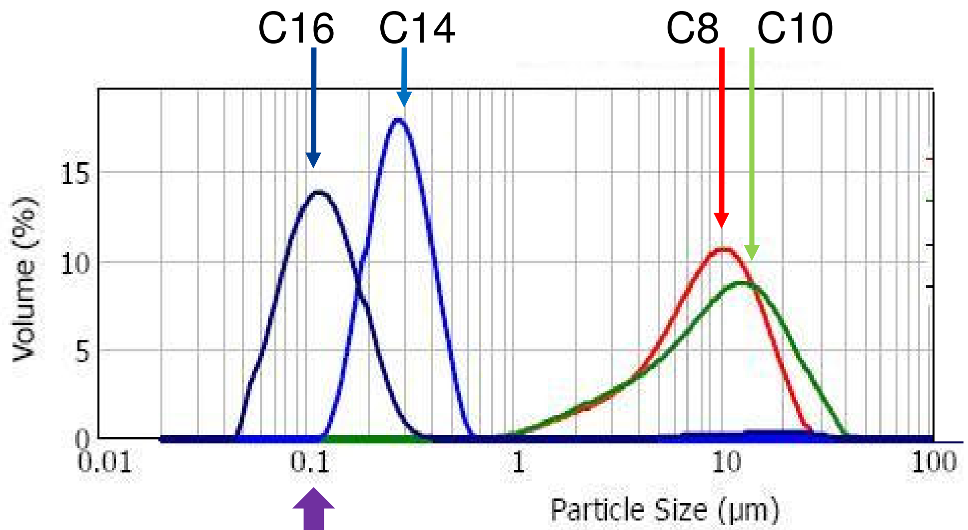
Preserved narrow droplet distribution after several weeks of exposure to electrolytes & elevated temperatures

Low Solubility of Oil in Contineous Phase Needed to Reduce Ostwald Ripening

Droplet size distribution after ***2 weeks storage***

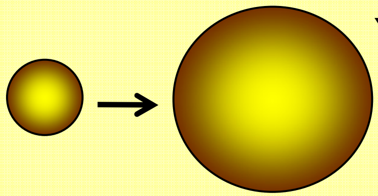
Oil phase: variable
  Linear alkanes (C8, C10, C14, C16)
P/O ratio: 1.2 (10% w/v)

►Effect of Oil Phase



Original drop size

Ostwald Ripening

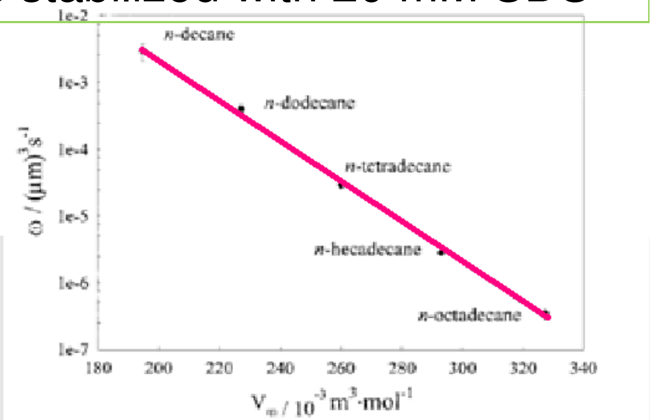


Young - Laplace equation

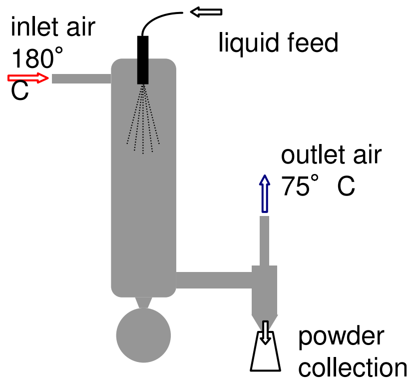
$$\Delta p = \gamma \frac{2}{r}$$

- Molecules of the dispersed phase travel from the small droplets to the larger ones.
- Leads to emulsion breakage

Ostwald ripening rate of linear aloane emulsions stabilized with 20 mM SDS

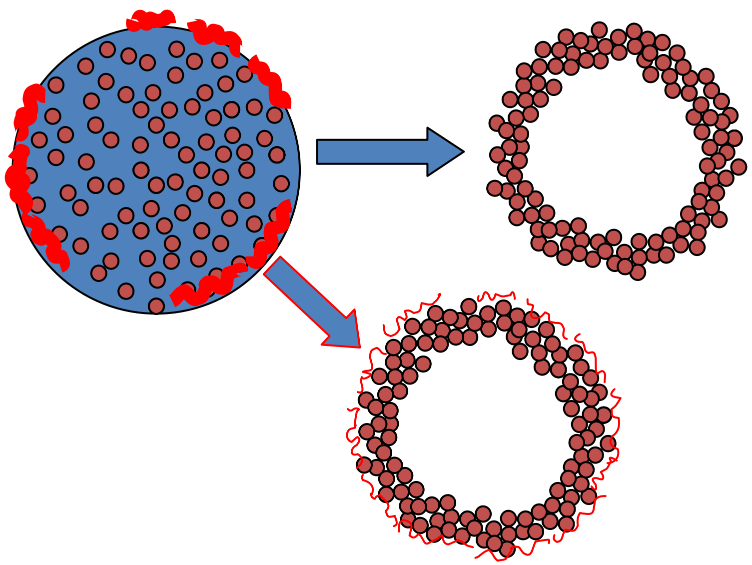


Surface Formation in Spray-dried Suspensions



Mass transport by diffusion and convection

Moisture moves from the interior of the droplet by diffusion and capillary forces

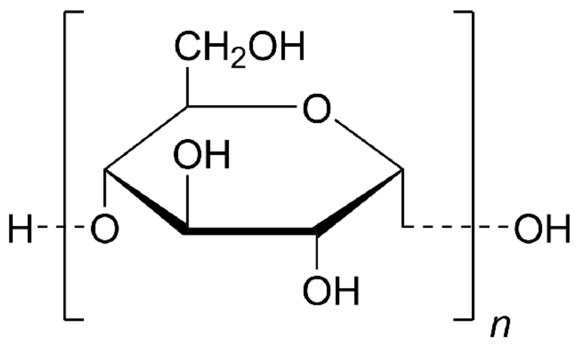


- Solid primary particles
- Binder
- Flocculant
- Non-adsorbed binder may migrate to surface and form a film

Spray-drying of Pickering Emulsions

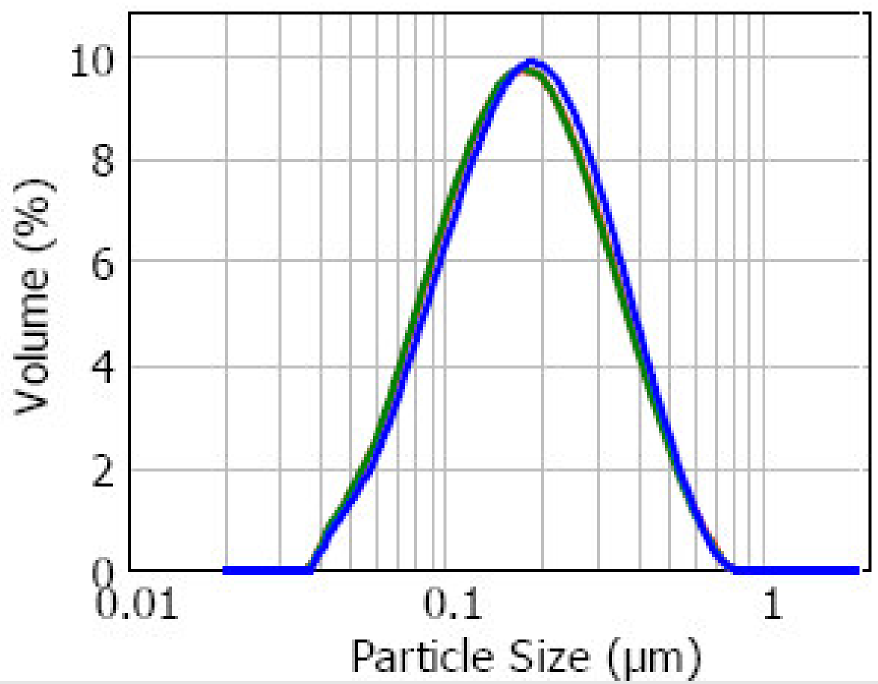
Addition of maltodextrin binder did not change droplet size of original emulsion

10% hexadecane,
3.5% silica particles
3.5% maltodextrins

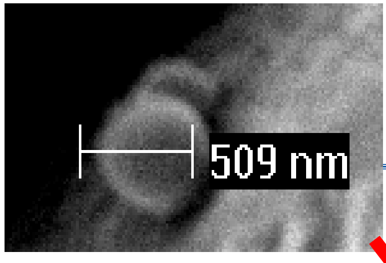


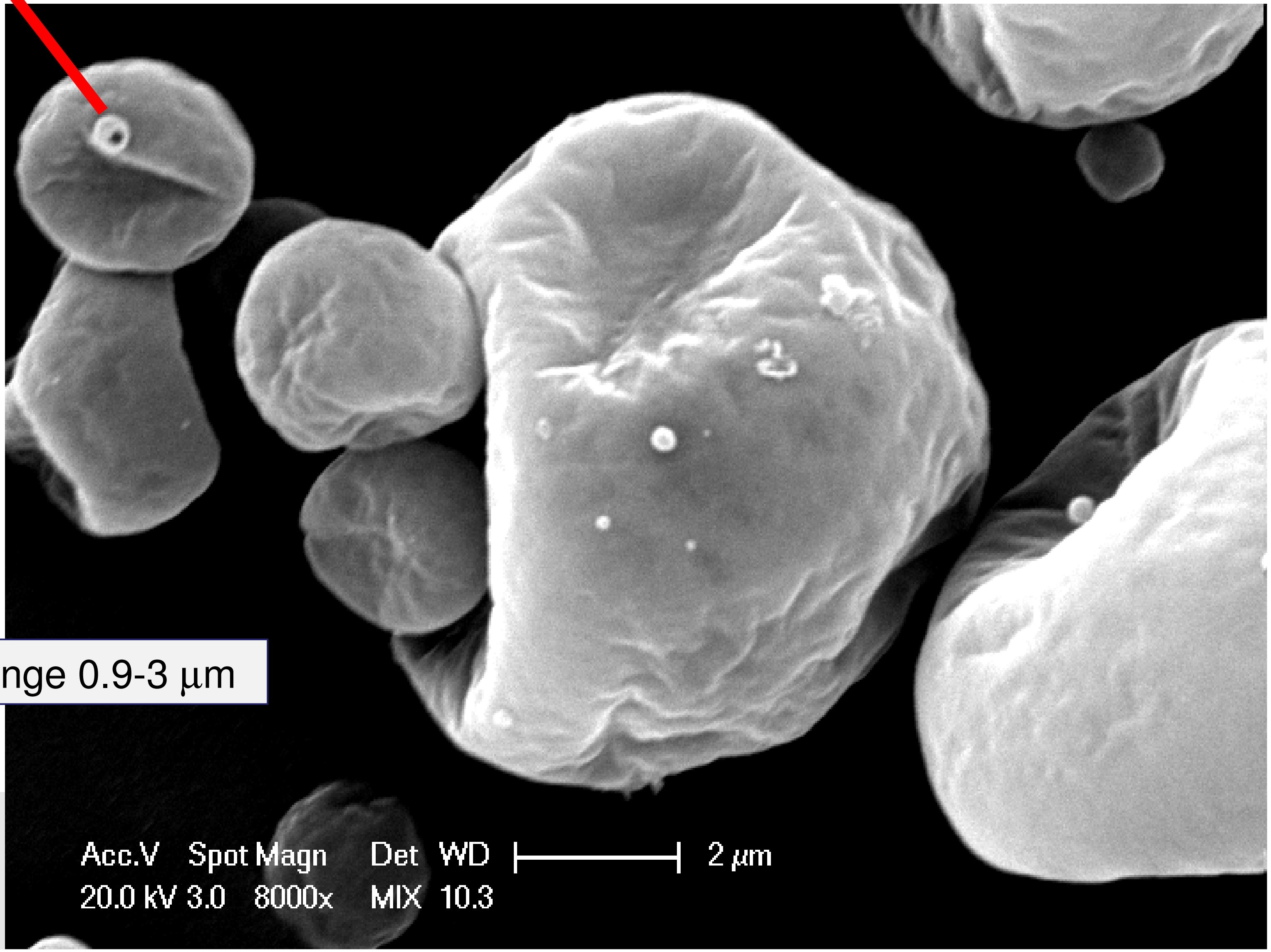
α-1,4

$2 < n < 20$



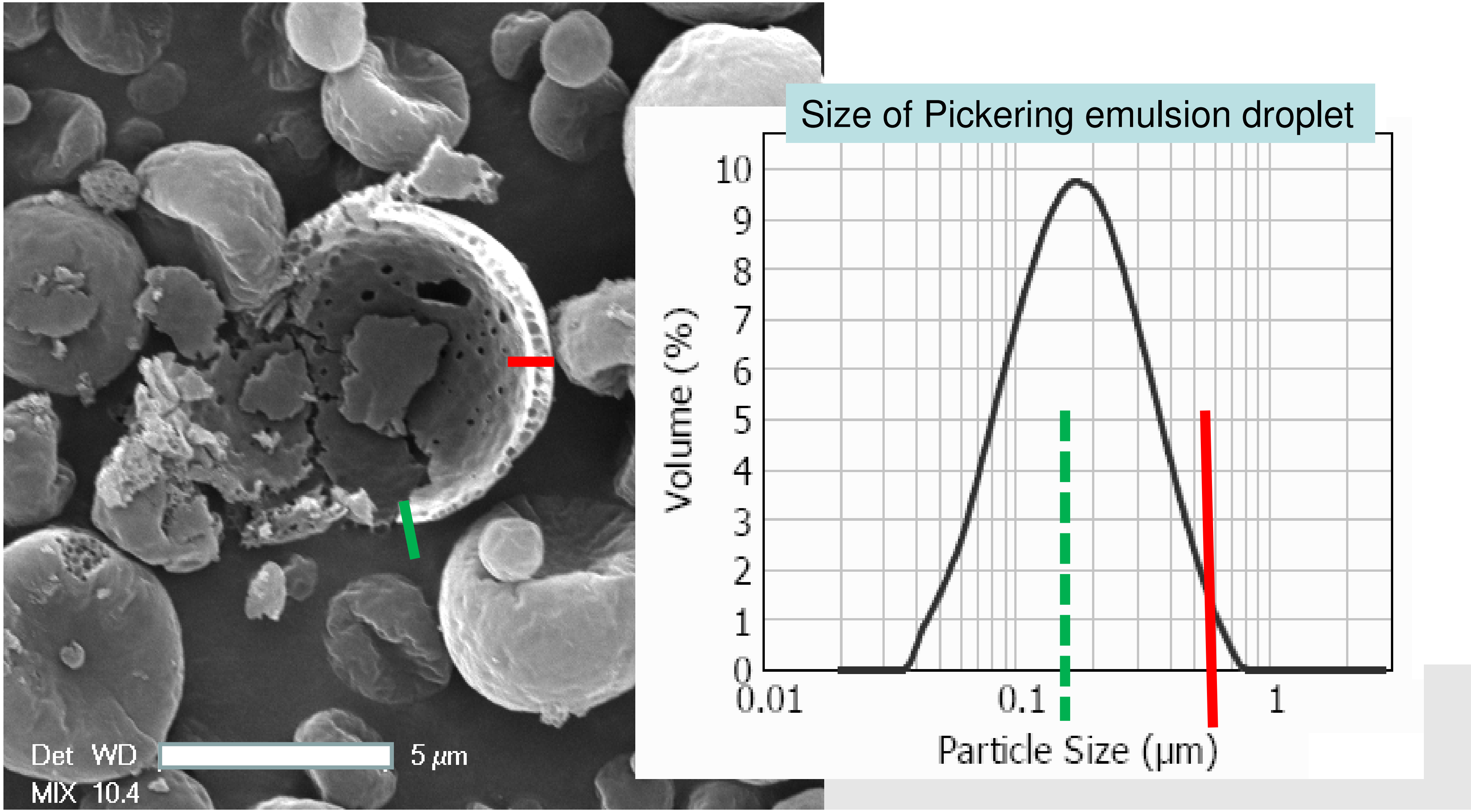
SEM of Spray-dried Emulsion



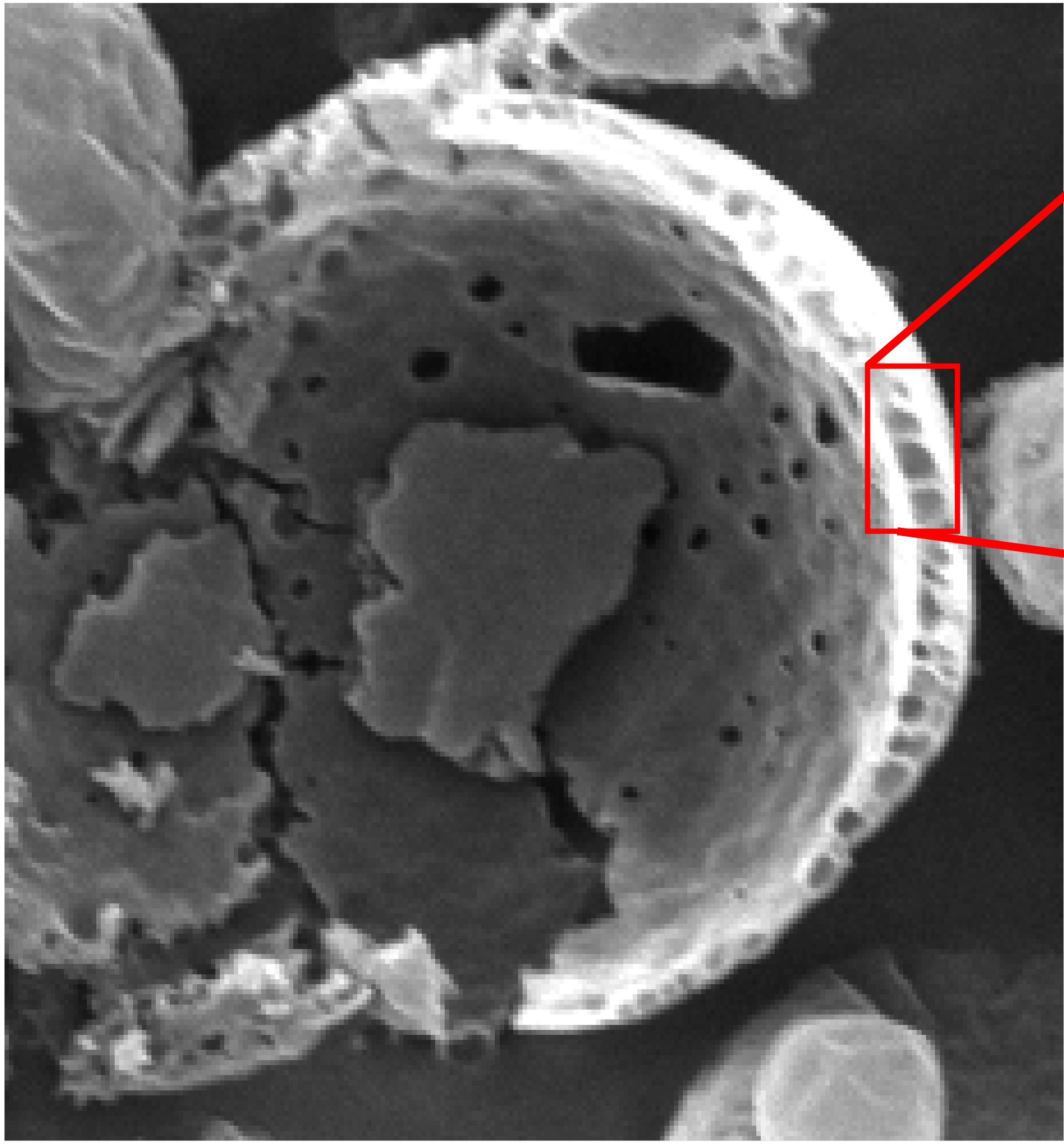


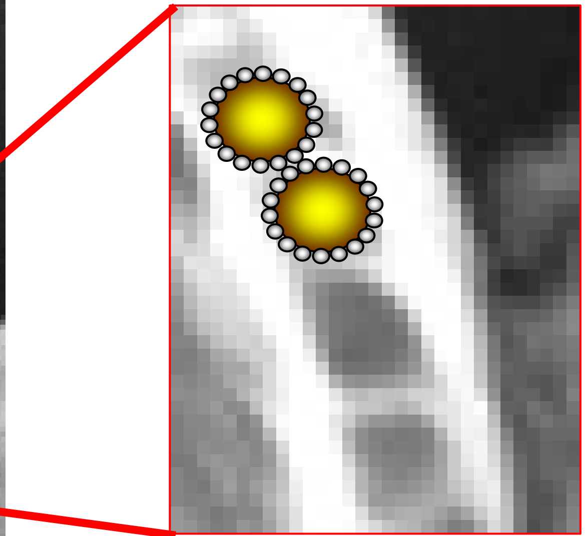
Droplet size range 0.9-3 µm

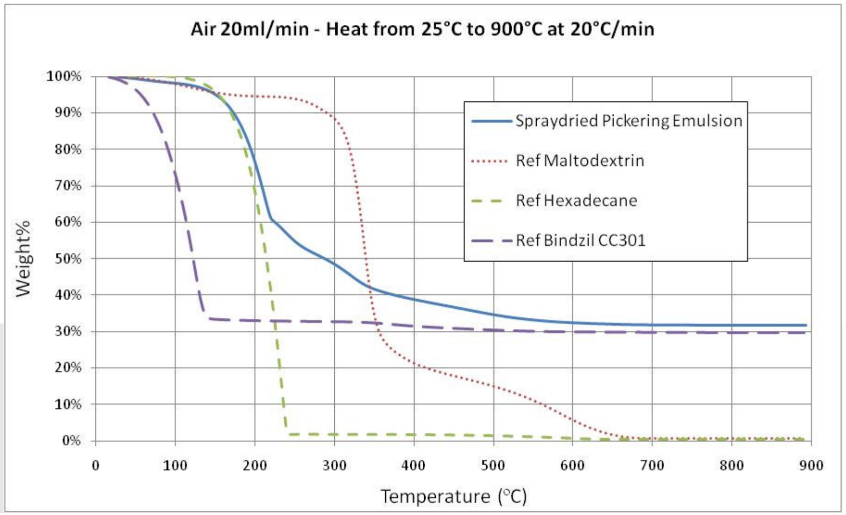
Spray-dried Pickering Emulsion



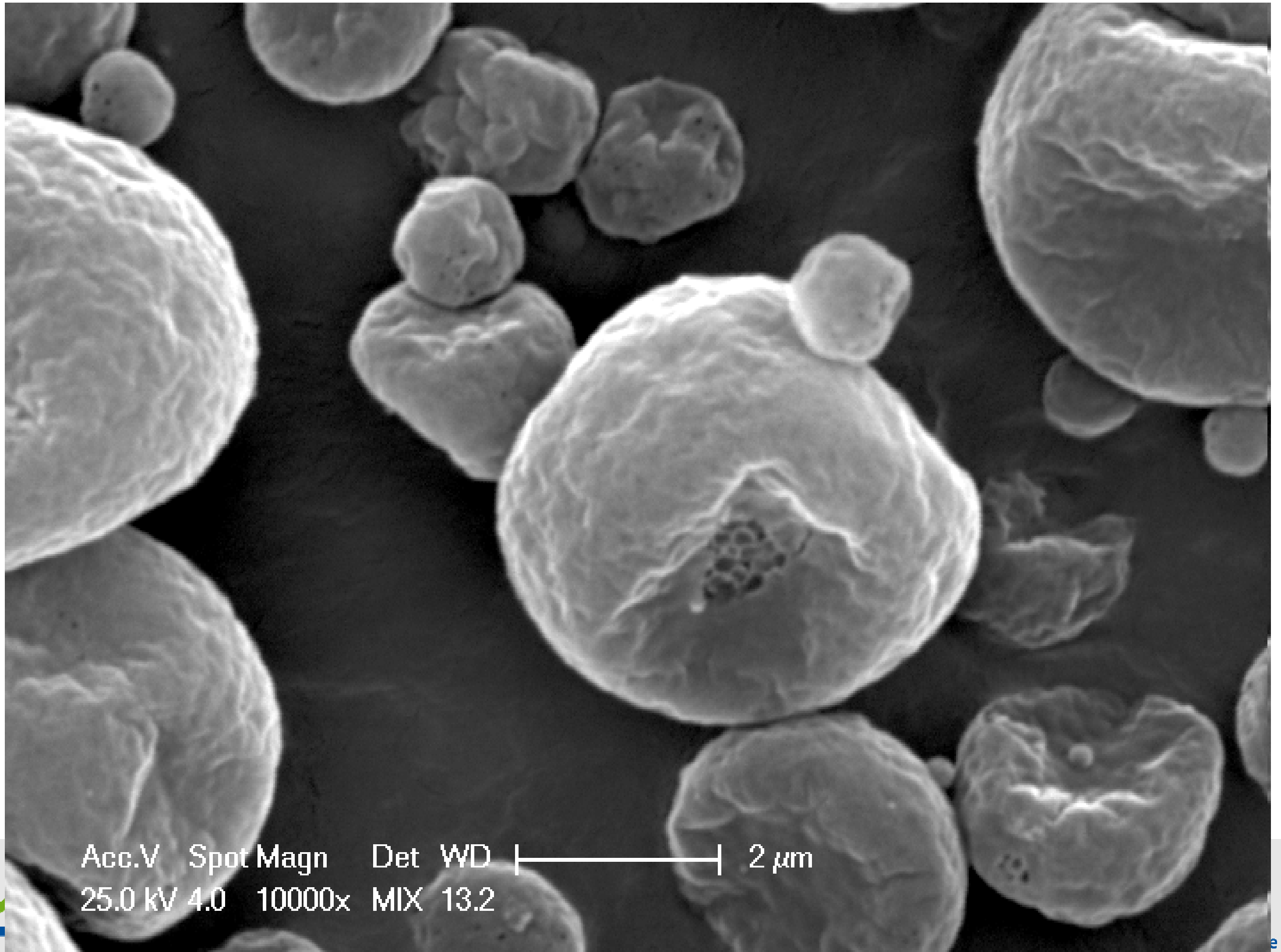
Environmental SEM of Spray-dried Pickering Emulsion







Calcined



Summary

Nano-emulsions with

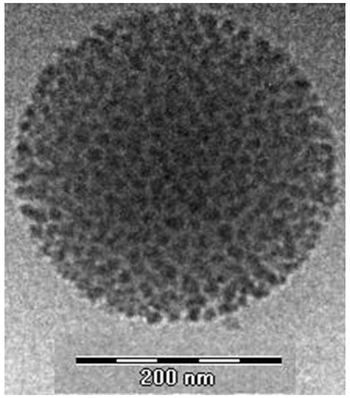
hexadecane, squalene, vegetable oils, silicon oil

Stable against stress

temperature, pH, surfactants, electrolyte

Colloidosome (microcapsules) formation by spray-drying

Cacination of colloidozome



The YKI Pickering emulsion team:

Karin Persson
Anna Fureby
Isabel Mira
Adam Feiler
Eva Sjöström
Johan Andersson
Irena Blute
Hans Ringblom

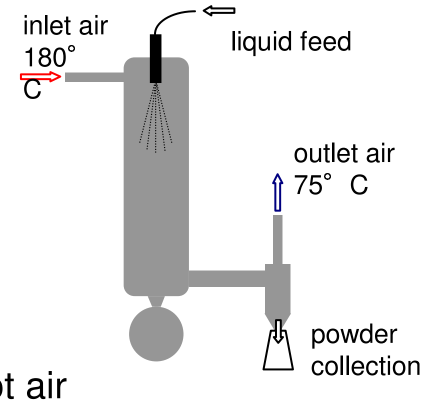
Thank you for your attention!

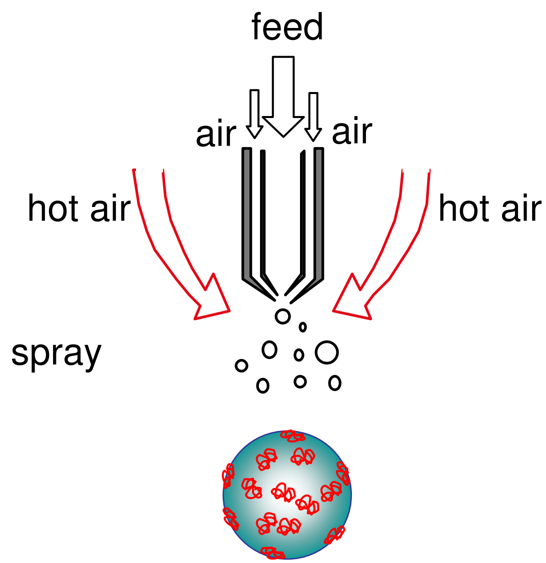
Surface Formation in Spray-drying

- Surface-active substances adsorb at the air/liquid interface of the spray-droplet
- This surface is conserved during spray-drying

ð The surface composition reflects the composition of the spray-droplet surface

ð The extent of surface excess of a substance depends on adsorption kinetics and efficiency of the substance and any competing components in the drying liquid

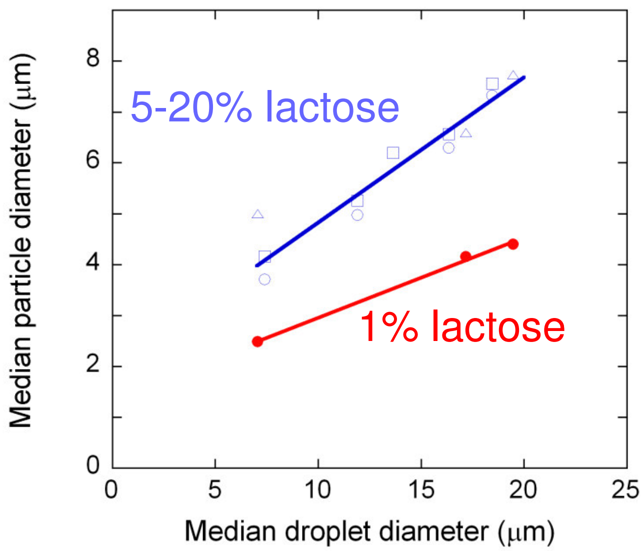


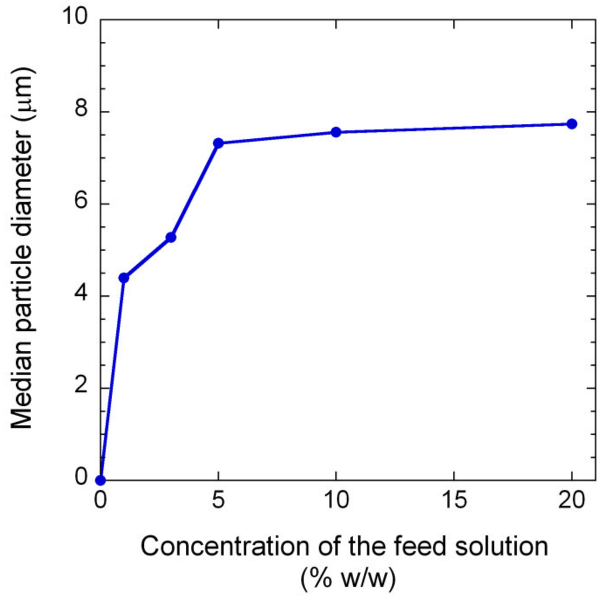


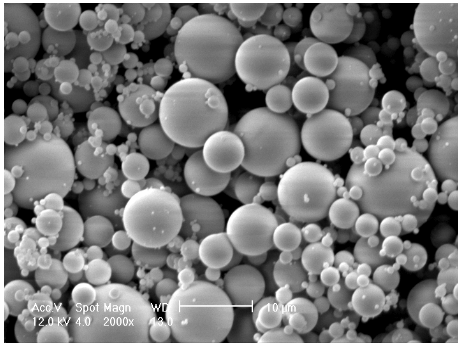
Spray Drying: Particle Formation

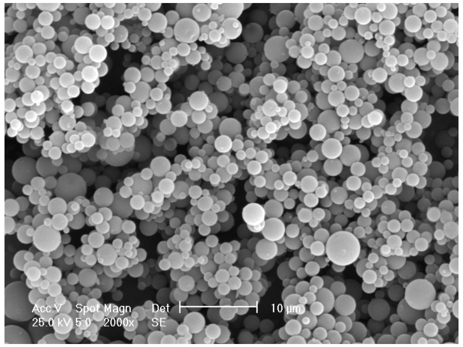
Control of the particle size

Mainly hollow particles







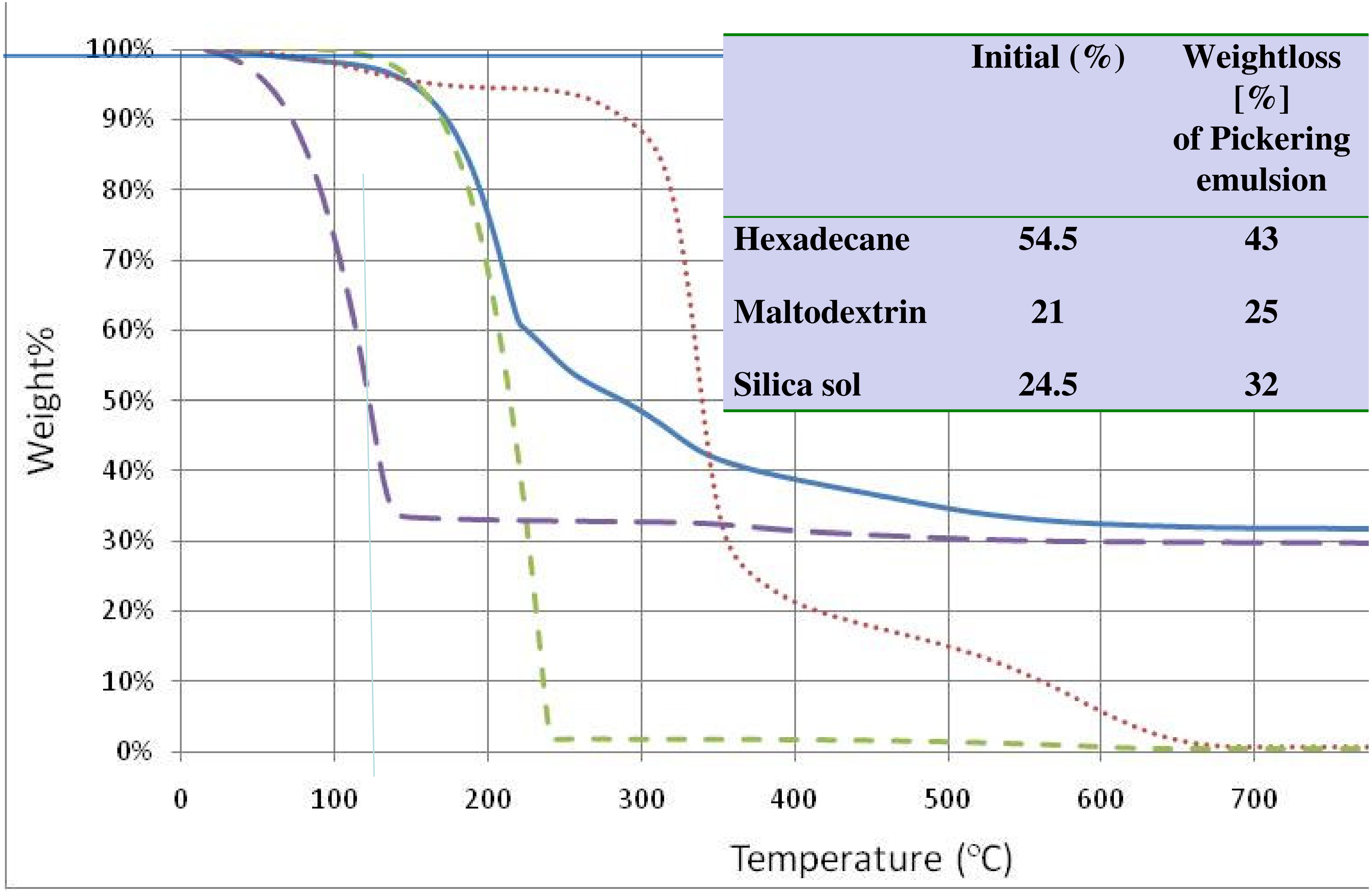


Droplet size
Change nozzle operation

Concentration of the spray solution (little effect on η)

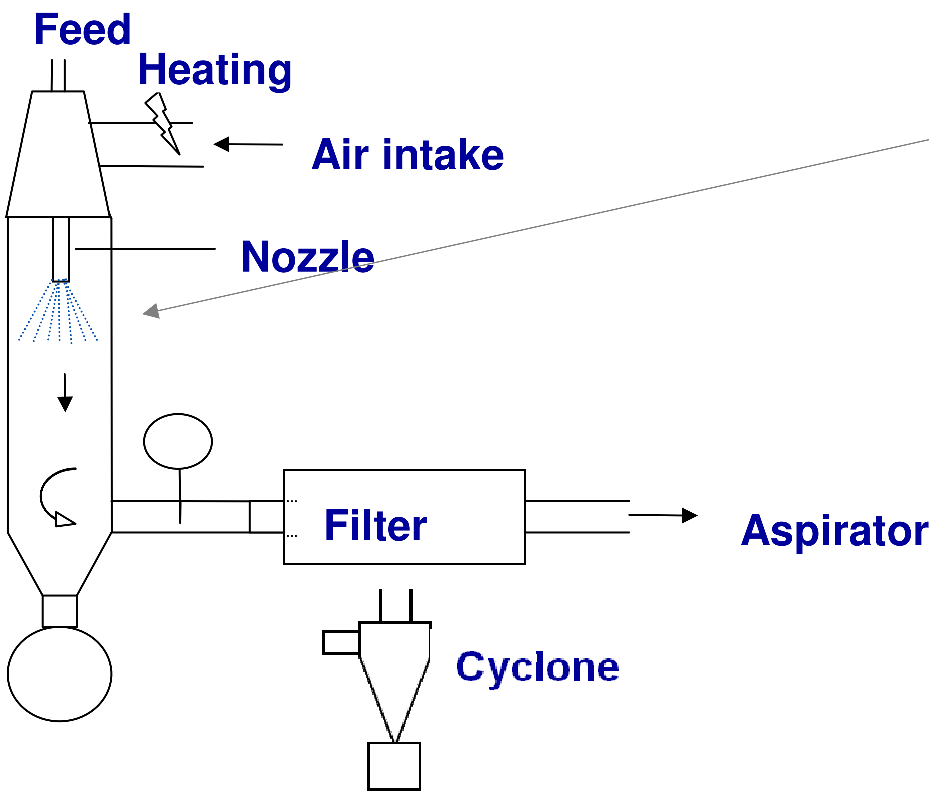
Reduced surface tension

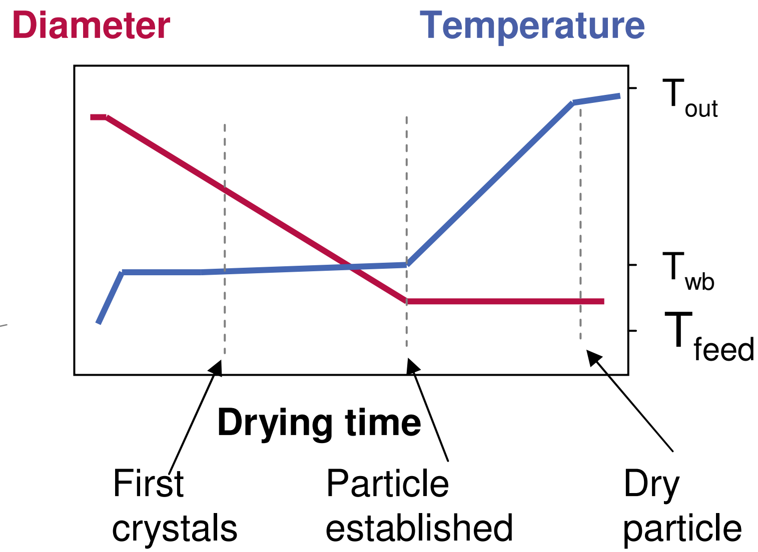
Content of Emulsion Retained During Spray-drying



	Initial (%)	Weightloss [%] of Pickering emulsion
Hexadecane	54.5	43
Maltodextrin	21	25
Silica sol	24.5	32

Spray-drying Process





Droplet life-time during spray drying

4.5 ms (droplet 10 μm, particle 7 μm)

21 ms (droplet 50 μm, particle 30 μm)

Droplet surface temperature:

$T_{(wb)}$, wet bulb temperature ~45ºC

(at T_{in}=200 ºC and T_{out}=90 ºC)

Residence time in lab dryer:~1sec