CAP.C534

Advanced Supercritical Fluid Process

（超臨界流体プロセス特論）

2. Particle formation using SCF (I)

Department of Chemical Science and Engineering

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2018.10.4 Room 421 of South Buld. 4

Class Schedule

1. 9/27 Fundamental property of SCF
2. 10/4 Particle formation using SCF (I)
3. 10/11 Particle formation using SCF (II)
4. 10/18 Porous material formation using SCF (I)
5. 10/25 Porous material formation using SCF (II)
6. 11/1 Composite formation using SCF
7. 11/8 Film formation using SCF

11/22 Final report submission

Class document will be upload in OCW

Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)

Ultraheavy oil*

- ✓ Canada : Oilsand
  333 Billion Barrel
- ✓ Venezuela : Oinoco Tar
  289 Billion Barrel
- ✓ Current Oil : 1000 Billion Barrel


Oilsand
（Canada）

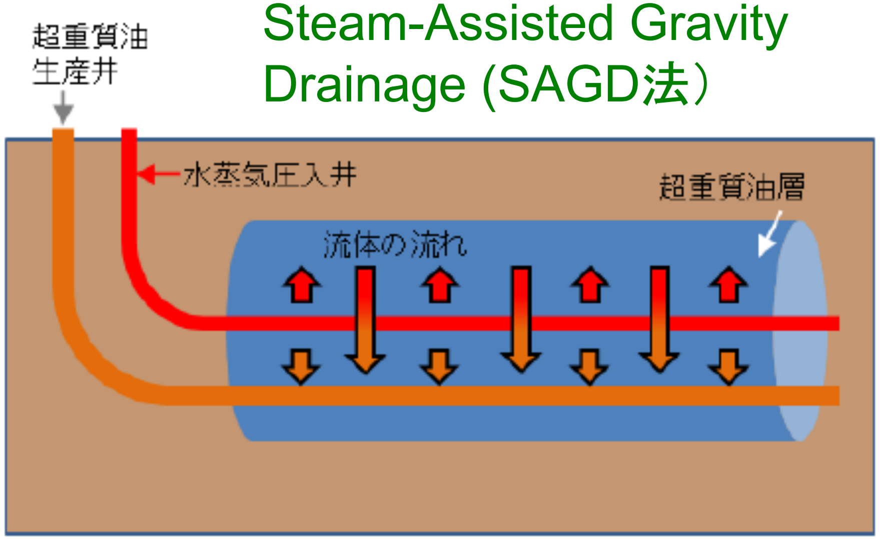

Orinoco Tar
（Venezuela）

Upgrading of Ultraheavy oil*

SAGD : Using high–temperature and pressure water

Upgrading : reduction of viscosity, light oil production, desulfarization

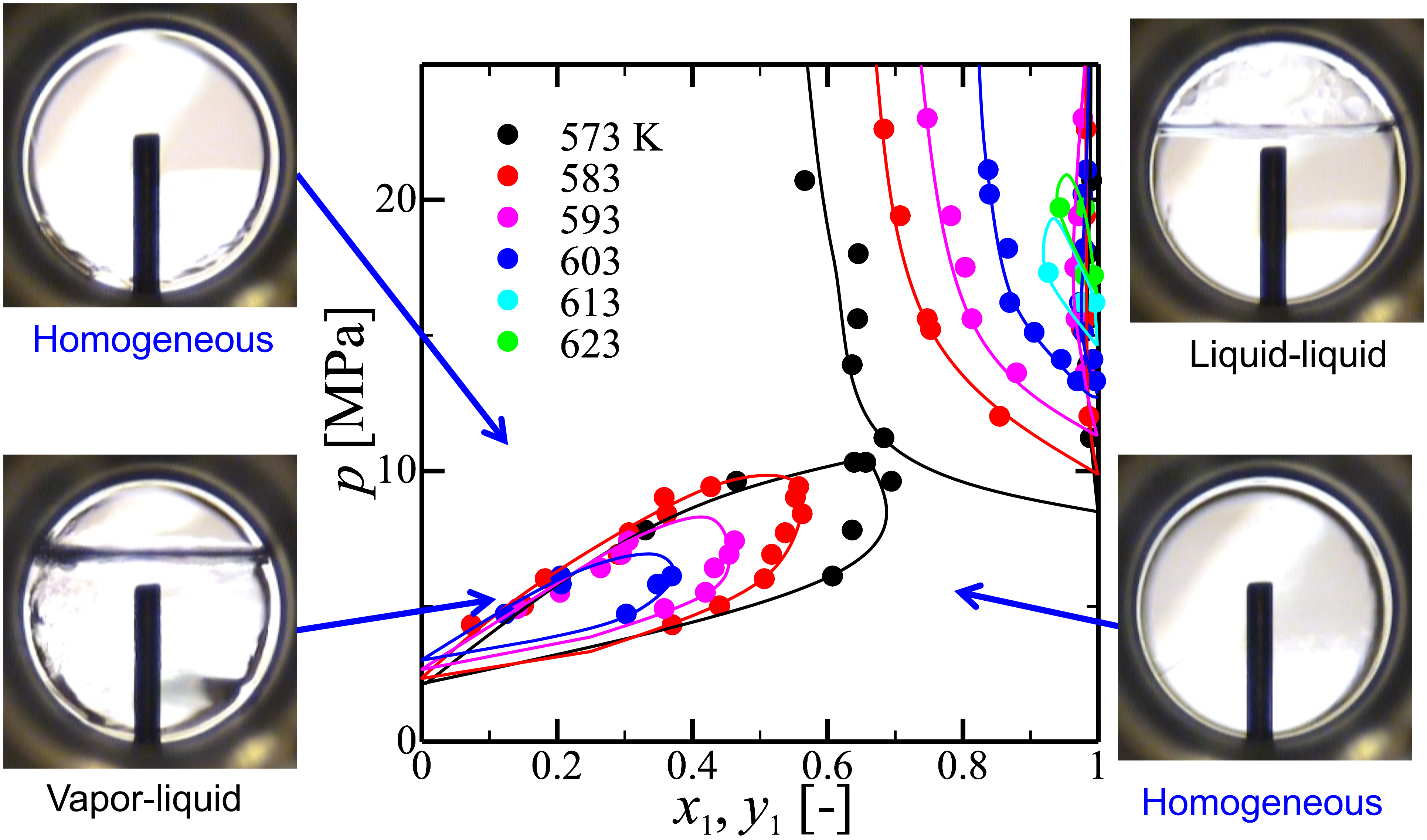
Steam-Assisted Gravity Drainage (SAGD法）



＊石油天然ガス・金属鉱物資源機構　技術部開発技術課報告書 (2011)

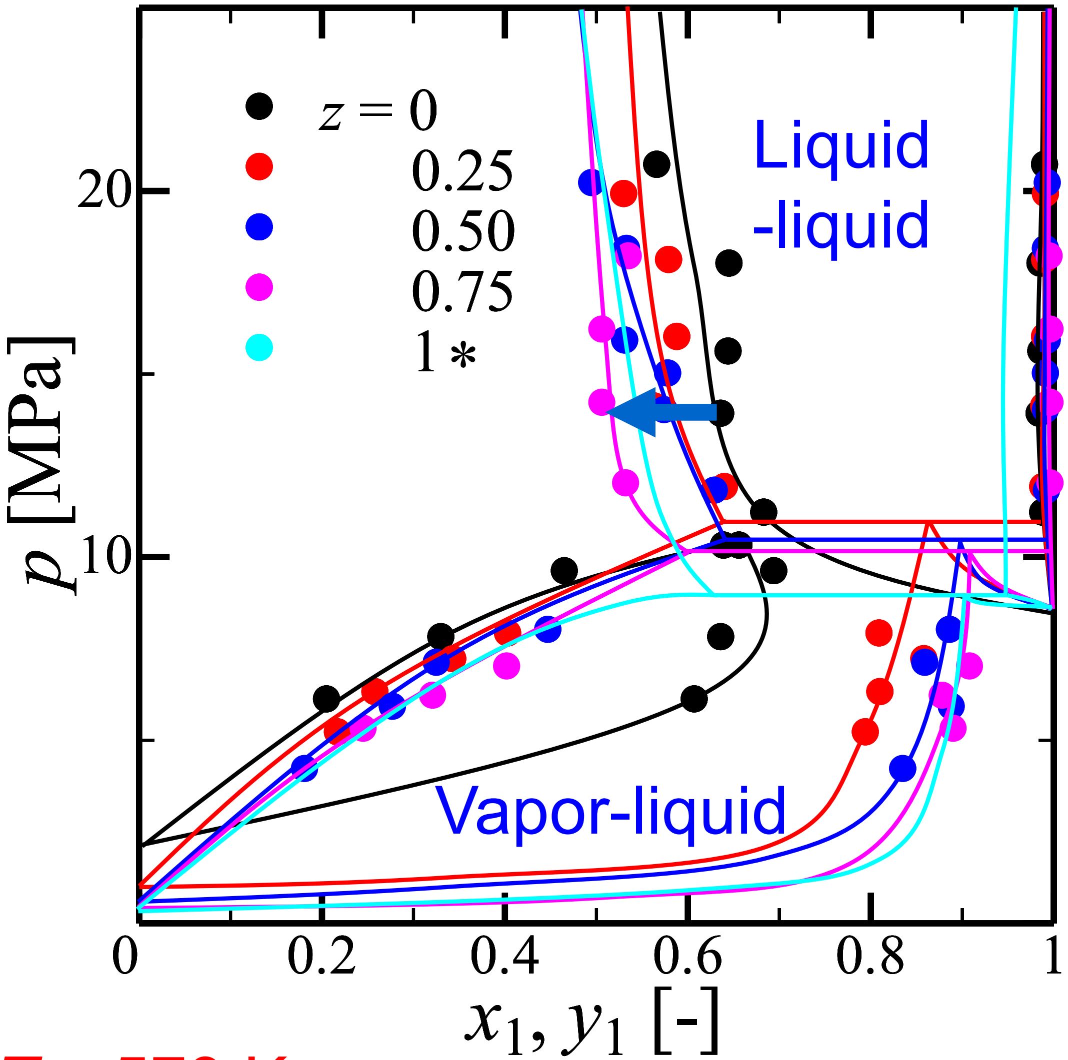
Fundamental Property of SCF

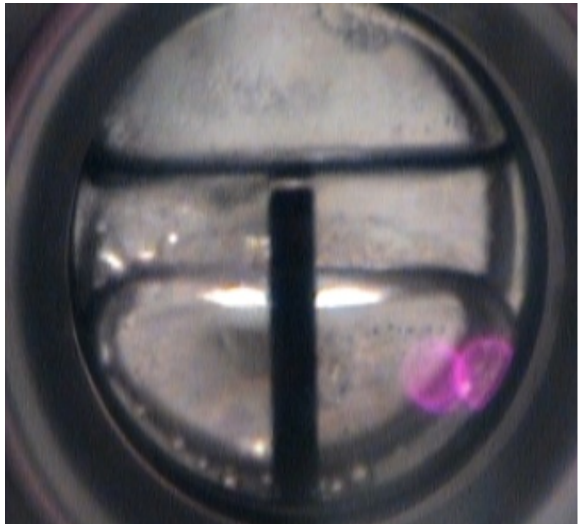
- Supercritical water (high temperature and pressure water)



Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)





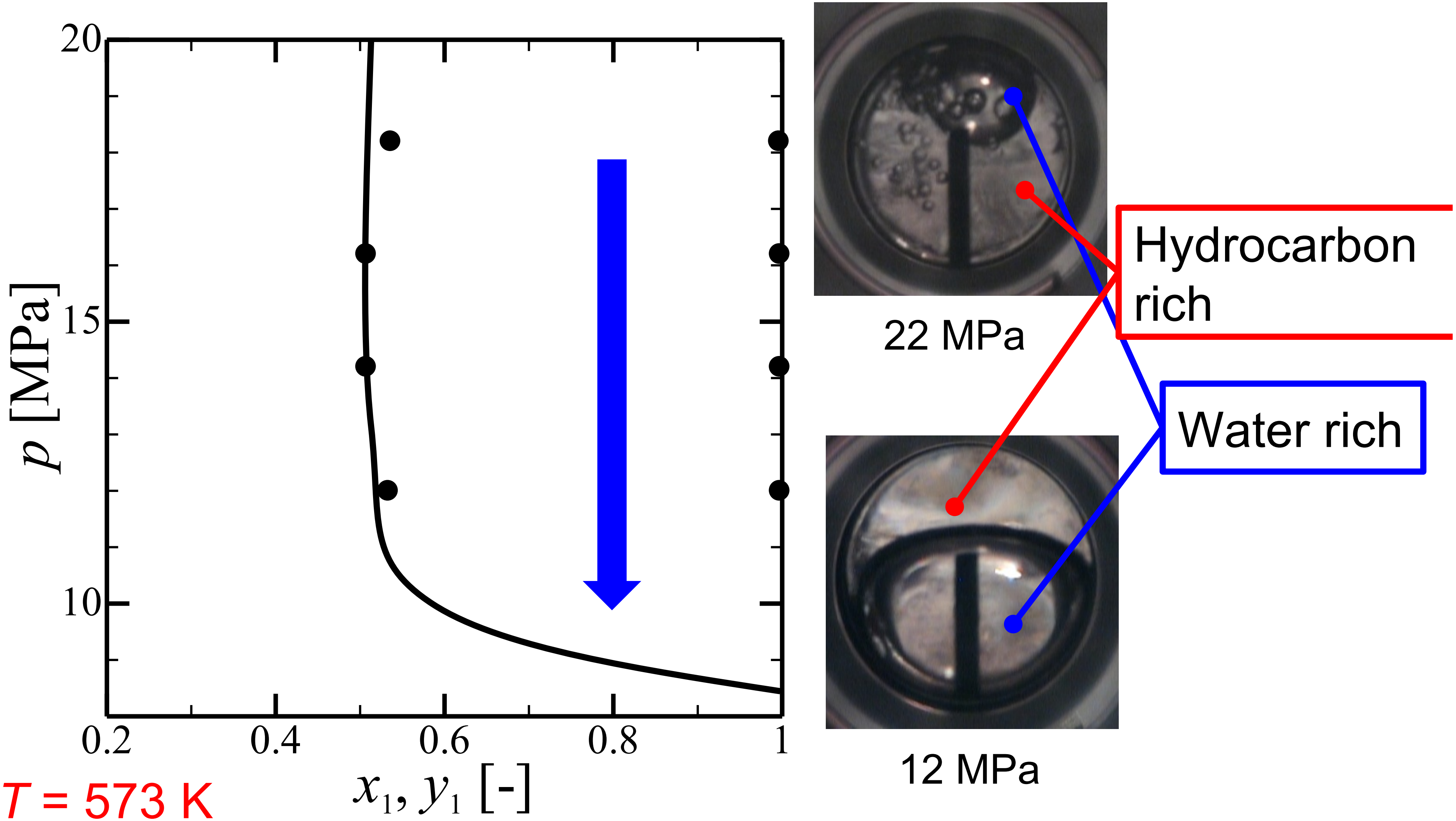
Vapor-liquid-liquid (VLLE)

T = 573 K

Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)

Phase transition on liquid-liquid equilibria



T = 573 K

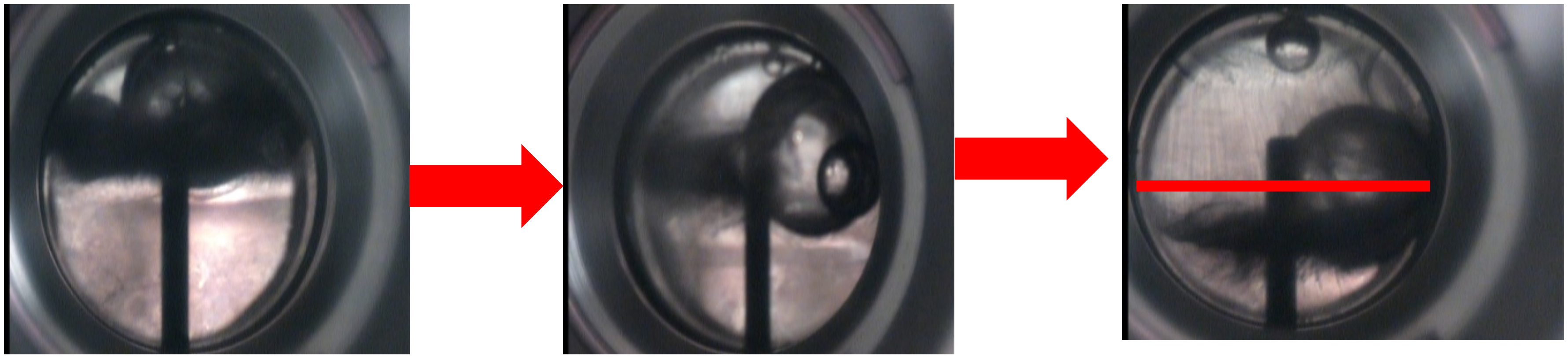
Fundamental Property of SCF

➢ Supercritical water (high temperature and pressure water)

Mole ratio heavy oil / light oil = 0.75

25.0MPa 24.5MPa 24.4MPa

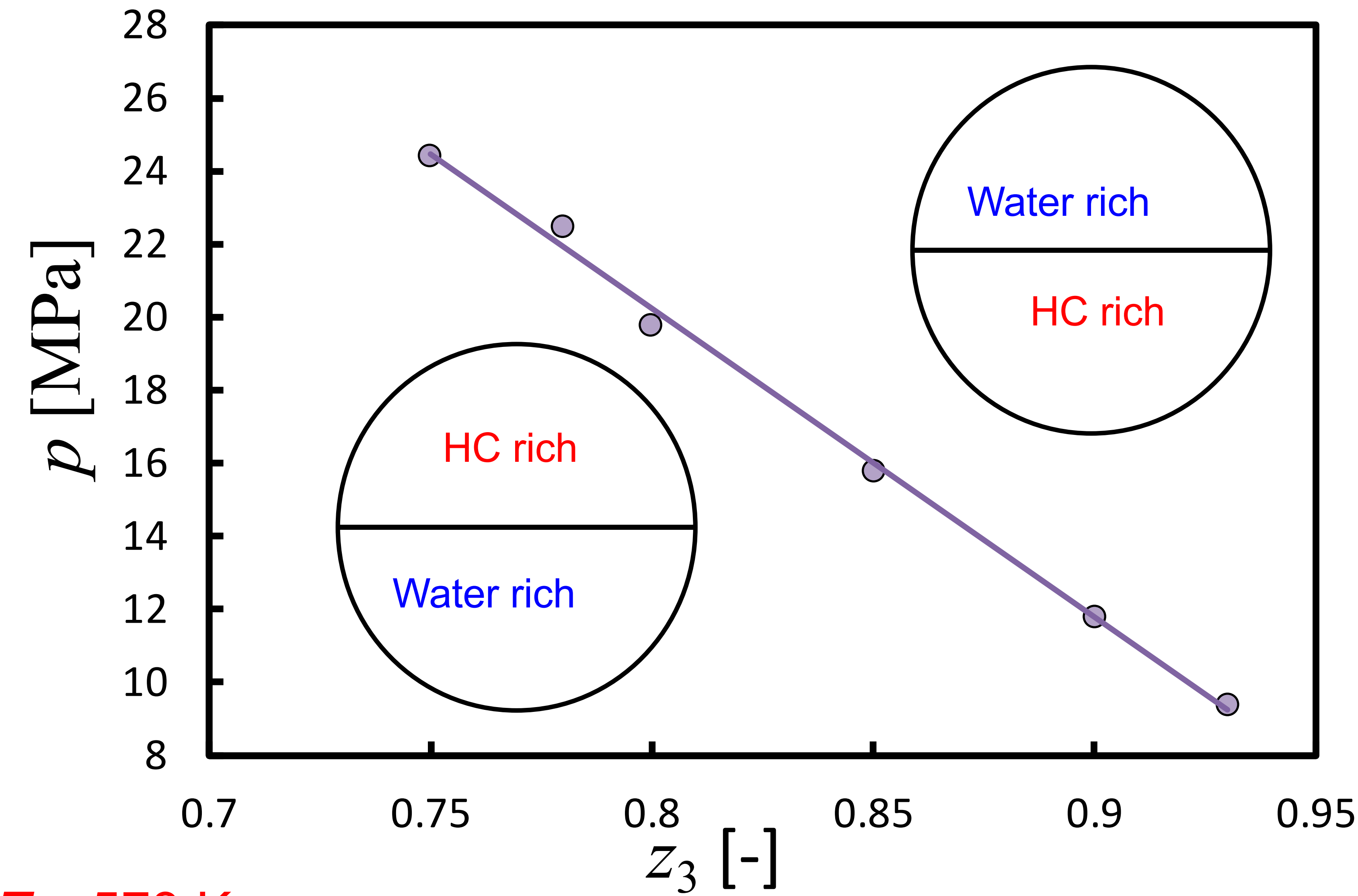
Mole ratio heavy oil / light oil = 0.80



20.5MPa 20.1MPa 19.9MPa

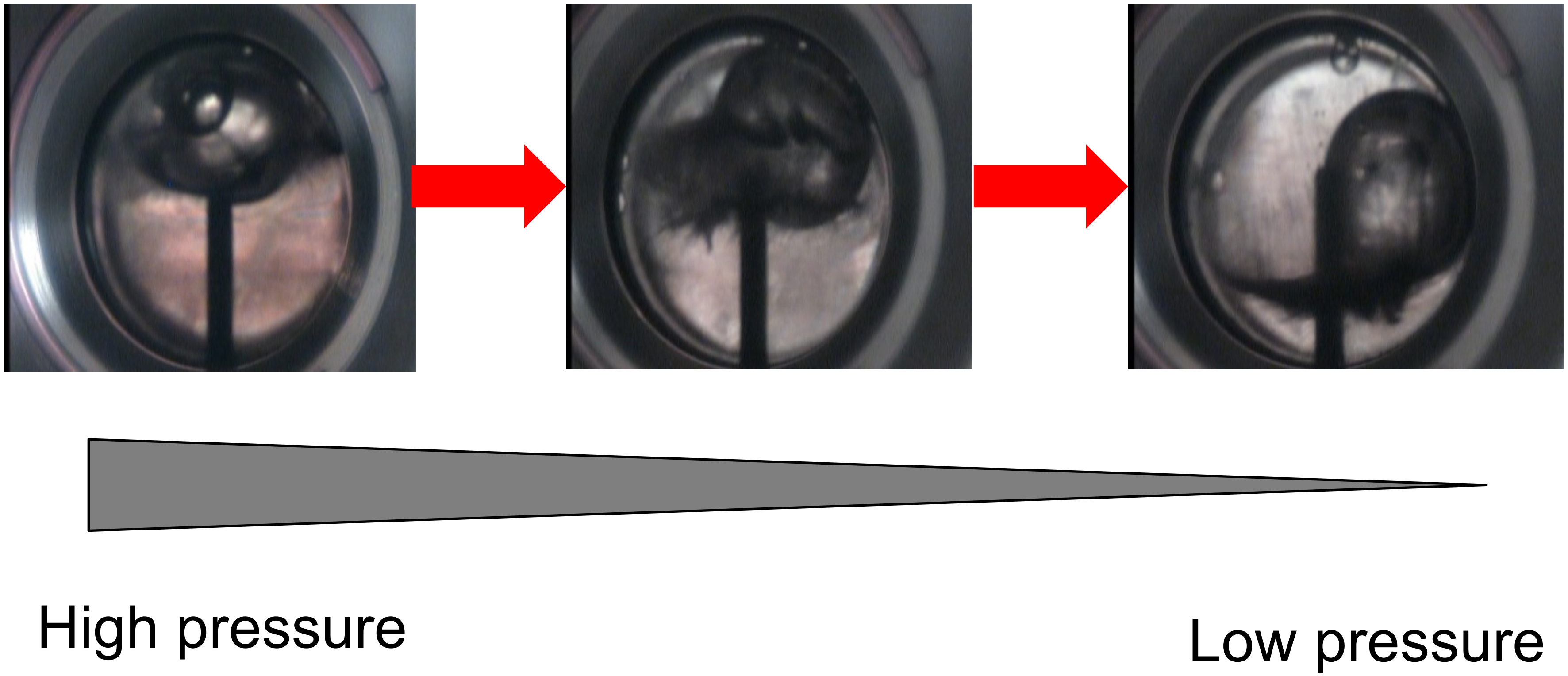
Fundamental Property of SCF

- Supercritical water (high temperature and pressure water)



T = 573 K

Q. 1-4 : Why is this phase transition on liquid-liquid two phase region formed?



Fundamental Property of SCF

A. 1-4 :

Particle formation using SCF

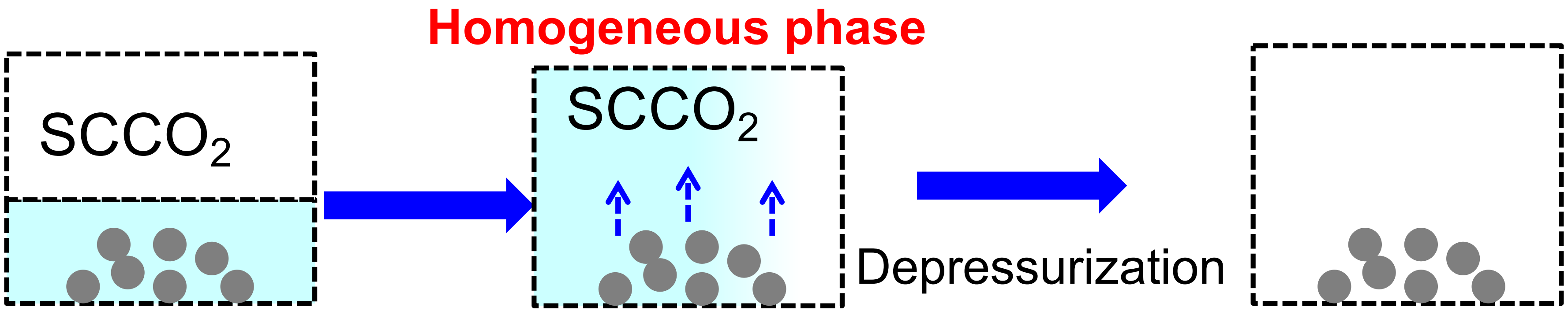
- Material process in physical method

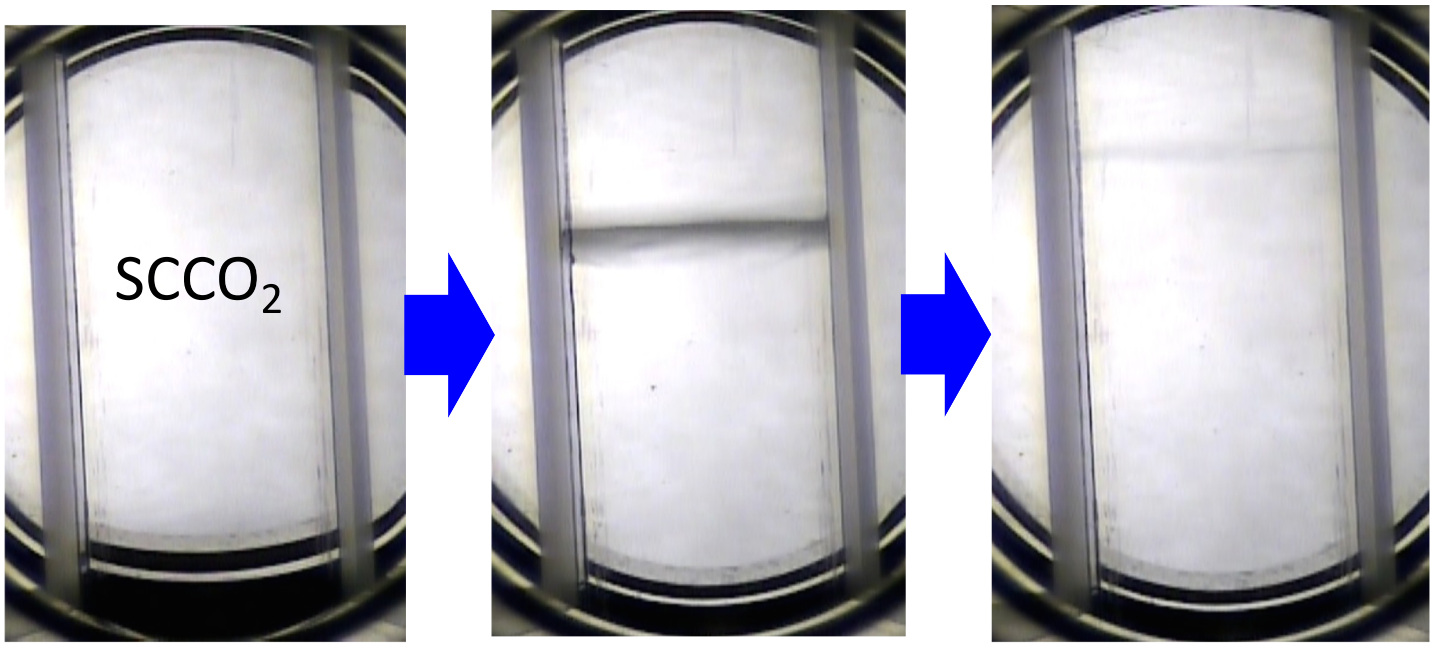
SCF as solvent
- Supercritical drying
- Supercritical fluid extraction of emulsion
- Supercritical solvent impregnation
- Rapid expansion of supercritical solution

SCF as antisolvent
- Supercritical antisolvent
- Solution-enhanced dispersion of solids

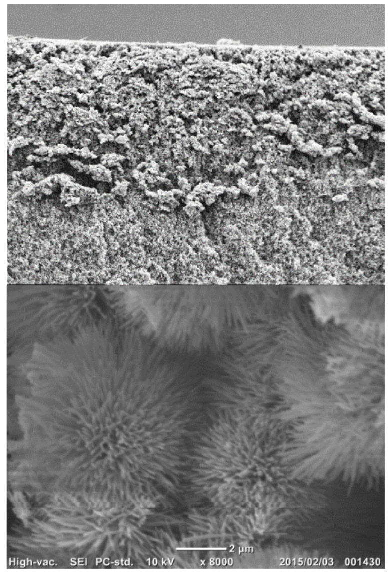
Material process using supercritical CO_2 as solvent

Supercritical drying





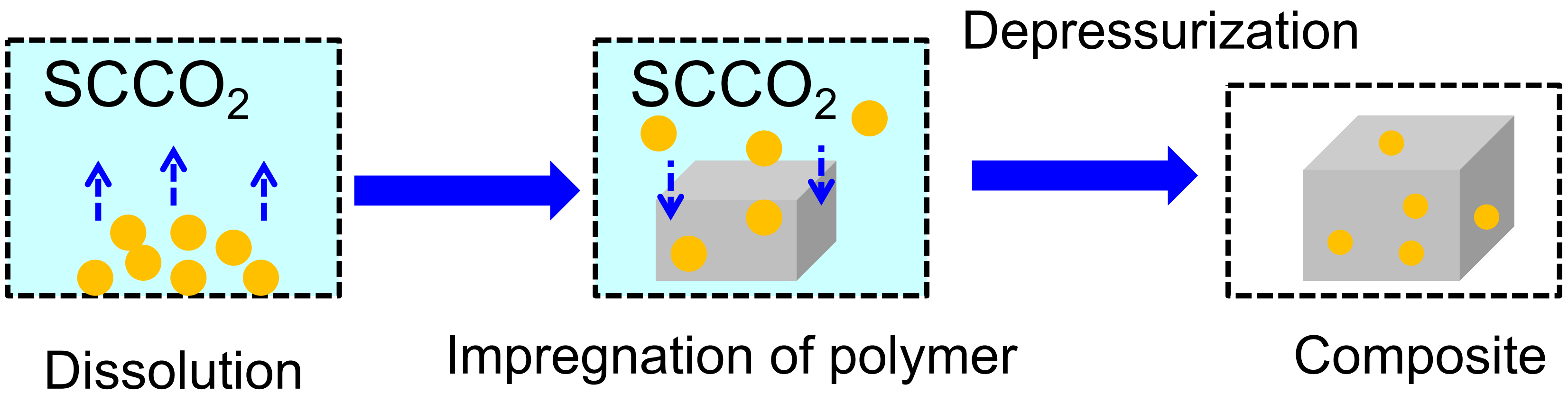
Porous material



Ultra-low interface tension during removing solvent

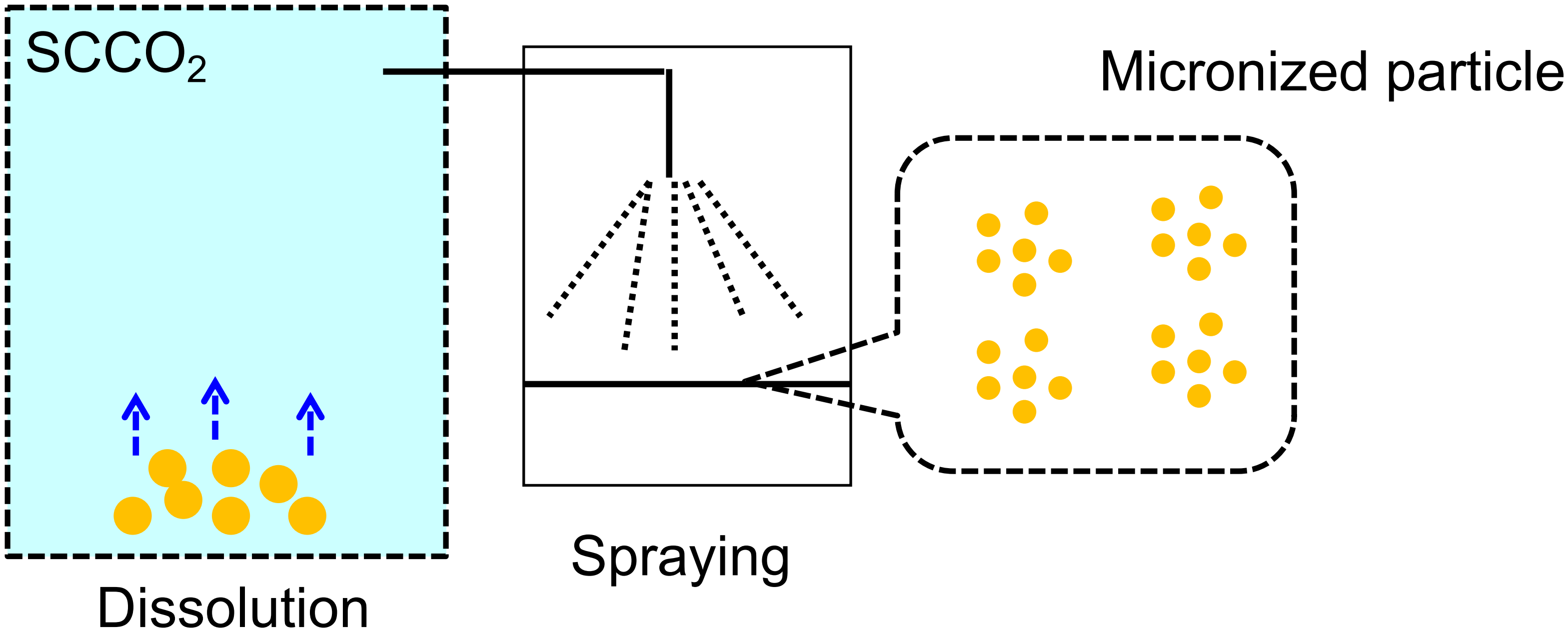
Material process using supercritical CO_2 as solvent

Supercritical solvent impregnation



- ✓ To control loading amount of solute into polymer by solubility in supercritical CO_2
- ✓ This can be applied for fabrication of composite of catalyst / supporting material and drug delivery system

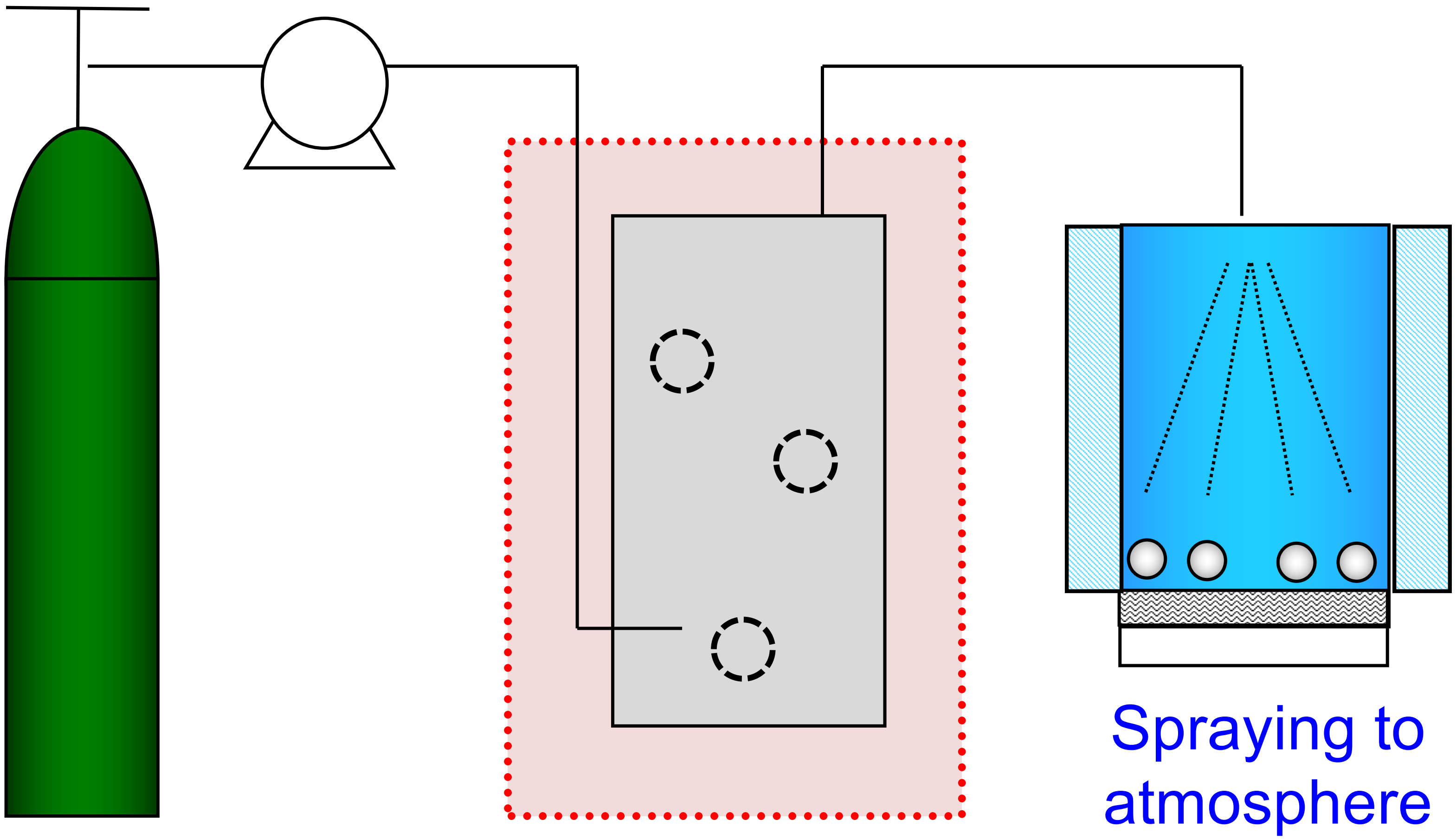
Rapid Expansion of Supercritical Solution



- ✓ To control particle size by solubility in supercritical CO_2
- ✓ This can be applied for micronization of pharmaceutical or bioactive compound particles.

Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS



Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS

How to control particle size in RESS process

↑

Design of nucleation

↑

Controlling supersaturation

↑

Solubility in $SCCO_2$

↑

Design of crystal growth

↑

Temperature and velocity distribution inside jet flow

↑

How to set up spraying unit and set the condition

Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS

How to control particle size in RESS process

Design of nucleation

Controlling supersaturation

Solubility in $SCCO_2$

Critical radius of nuclei

$$r^* = \frac{2\sigma v_2}{kT \ln S}$$

σ ; surface free energy
v_2 ; molar volume of solute
k ; Boltzmann constant
T ; temperature

Supersaturation

$SCCO_2$

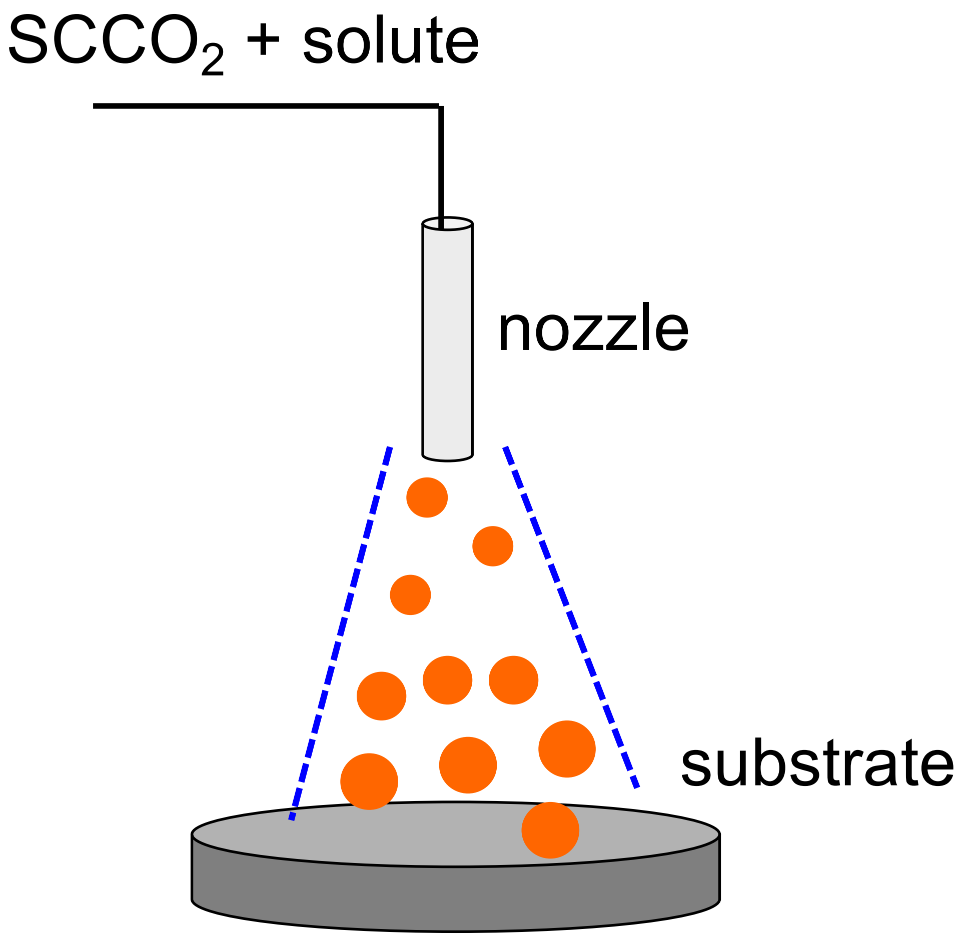
$$S = \frac{\phi\left(T, p, y_2\right) y_2\left(T, p\right)}{\phi\left(T, p, y^*\right) y^*\left(T, p\right)}$$

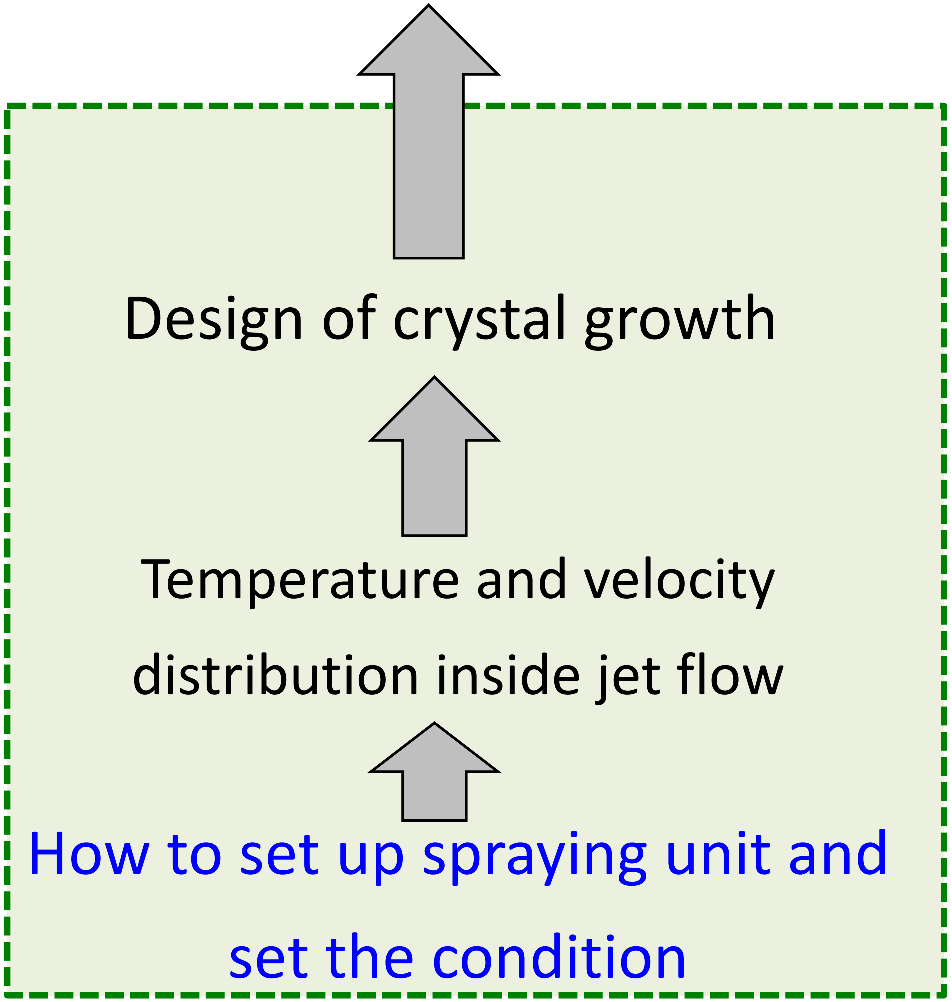
1 atm

Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS

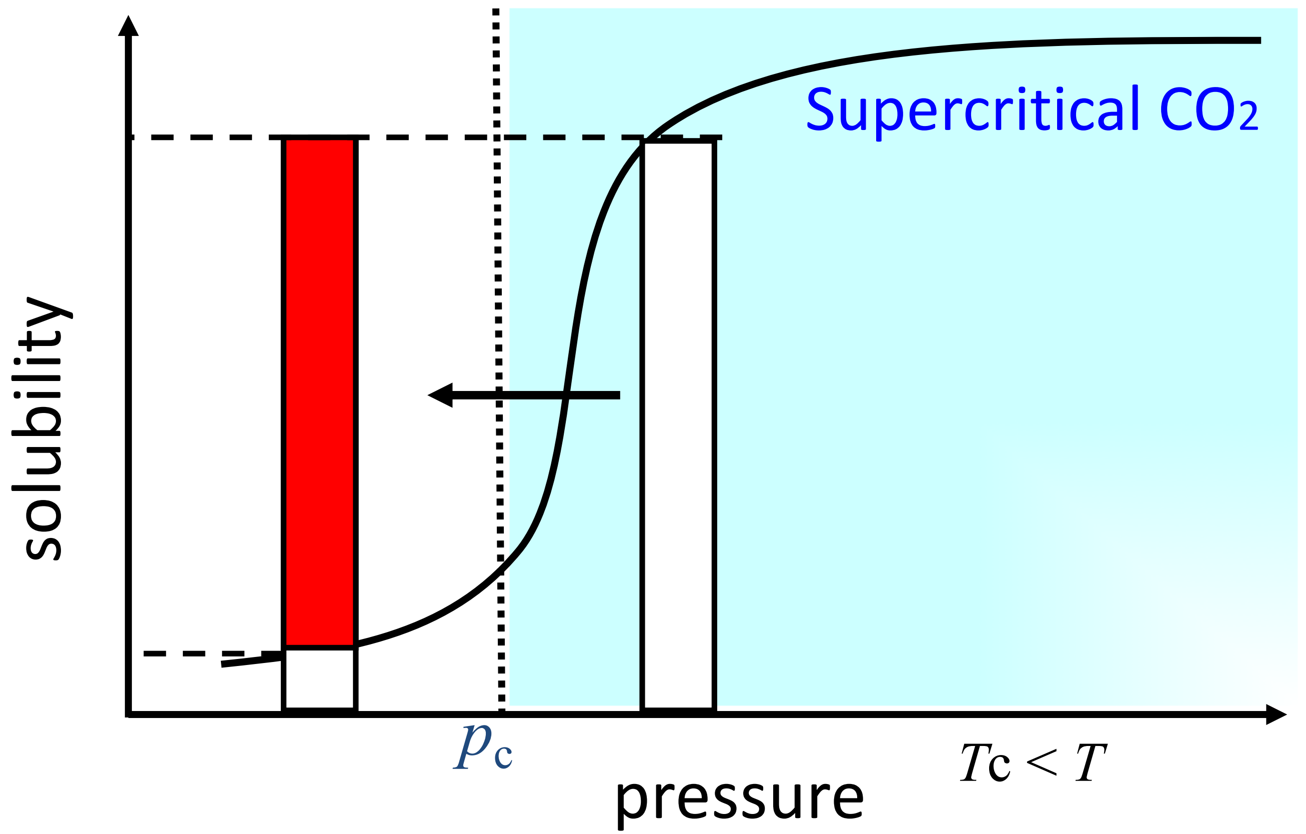
How to control particle size in RESS process





Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS



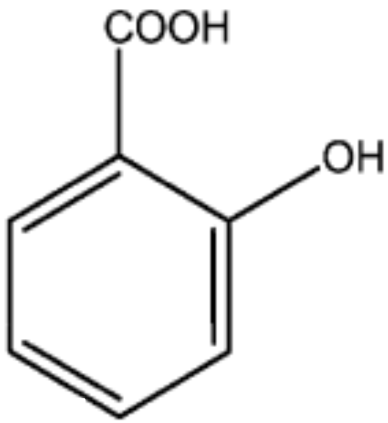
Solubility in supercritical CO_2

Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS

- Micronization of salicylic acid

Yildiz, N. et al., J. Supercrit. Fluids, 41 (2007) 440 – 451.



Salicylic acid

Anti-inflammatory agents

Before

34 – 171 μm

＜RESS condition＞

Supercritical fluid: CO_2

Dissolution into $SCCO_2$:

Temperature 45 – 60 ℃

Pressure 15 – 25 MPa

Spraying nozzle

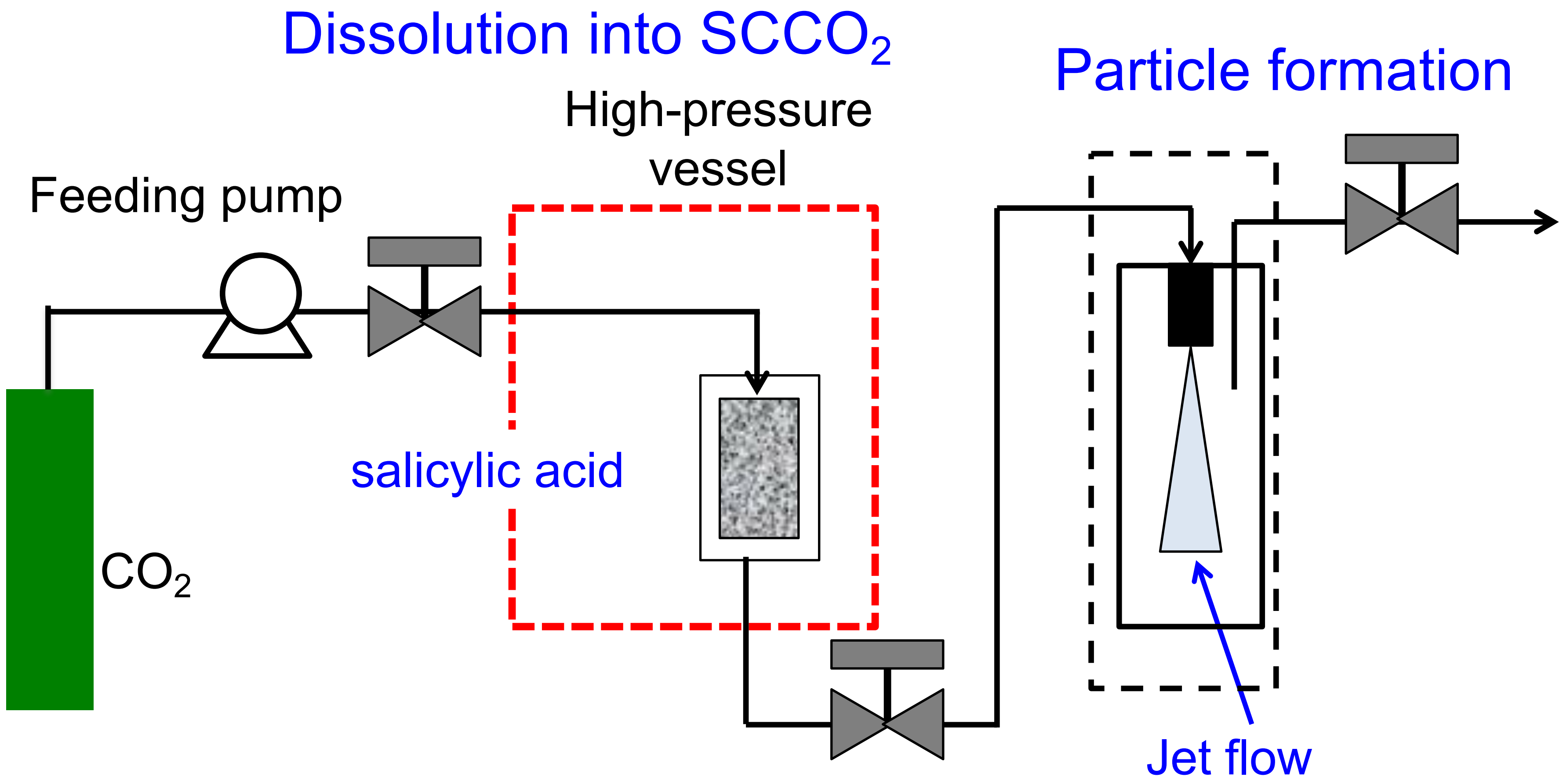
Inside diameter : 50 μm

Length : 3 – 4 mm

Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS

➢ Setup for RESS process using $SCCO_2$



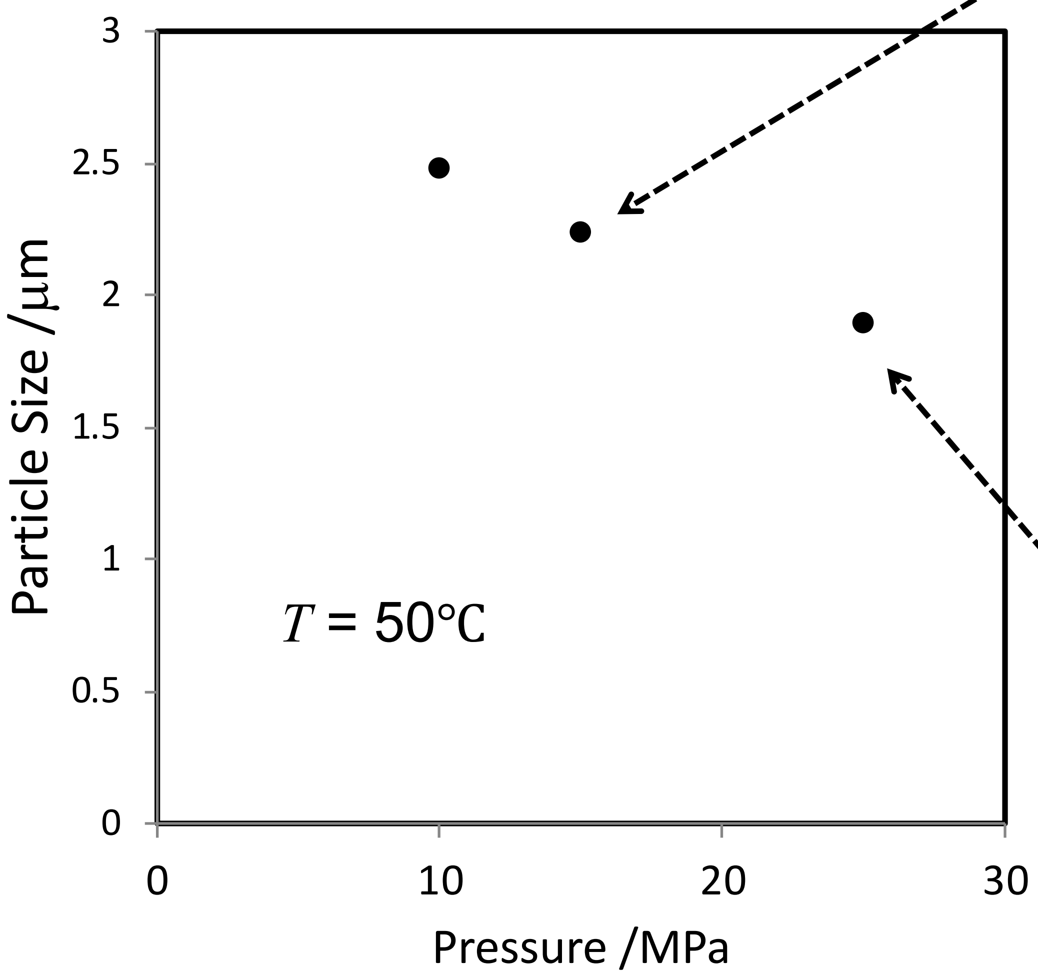
Yildiz, N. et al., J. Supercrit. Fluids, 41 (2007) 440 – 451.

Particle formation using SCF

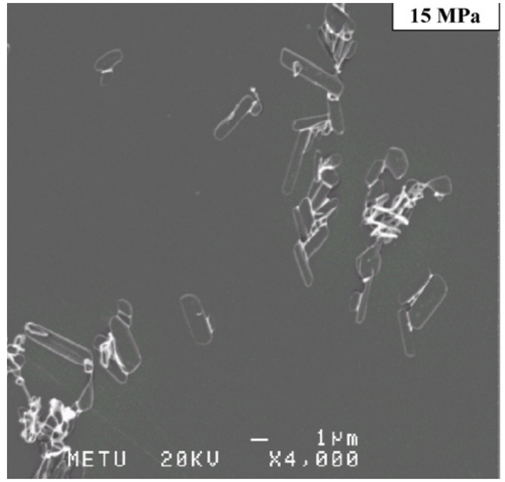
- Micronization of salicylic acid

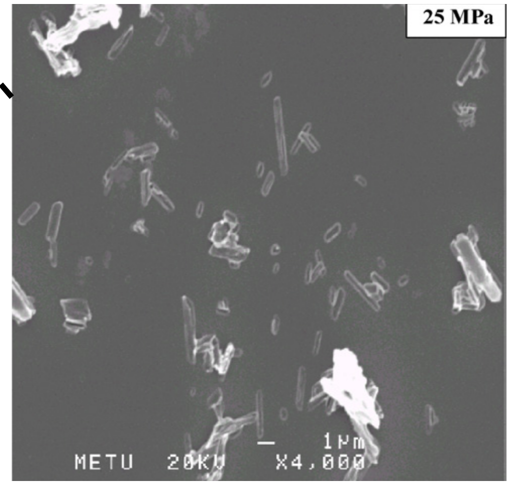
Before

34 – 171 μm



After RESS 2.2 μm





After RESS 1.9 μm

Yildiz, N. et al., J. Supercrit. Fluids, 41 (2007) 440 – 451.

Particle formation using SCF

Q. 2-1

Give the reason why high pressure dissolution into $SCCO_2$ leads to the smaller particle formation.

Particle formation using SCF

A. 2-1

Yildiz, N. et al., J. Supercrit. Fluids, 41 (2007) 440 – 451.

Particle formation using SCF

A. 2-1

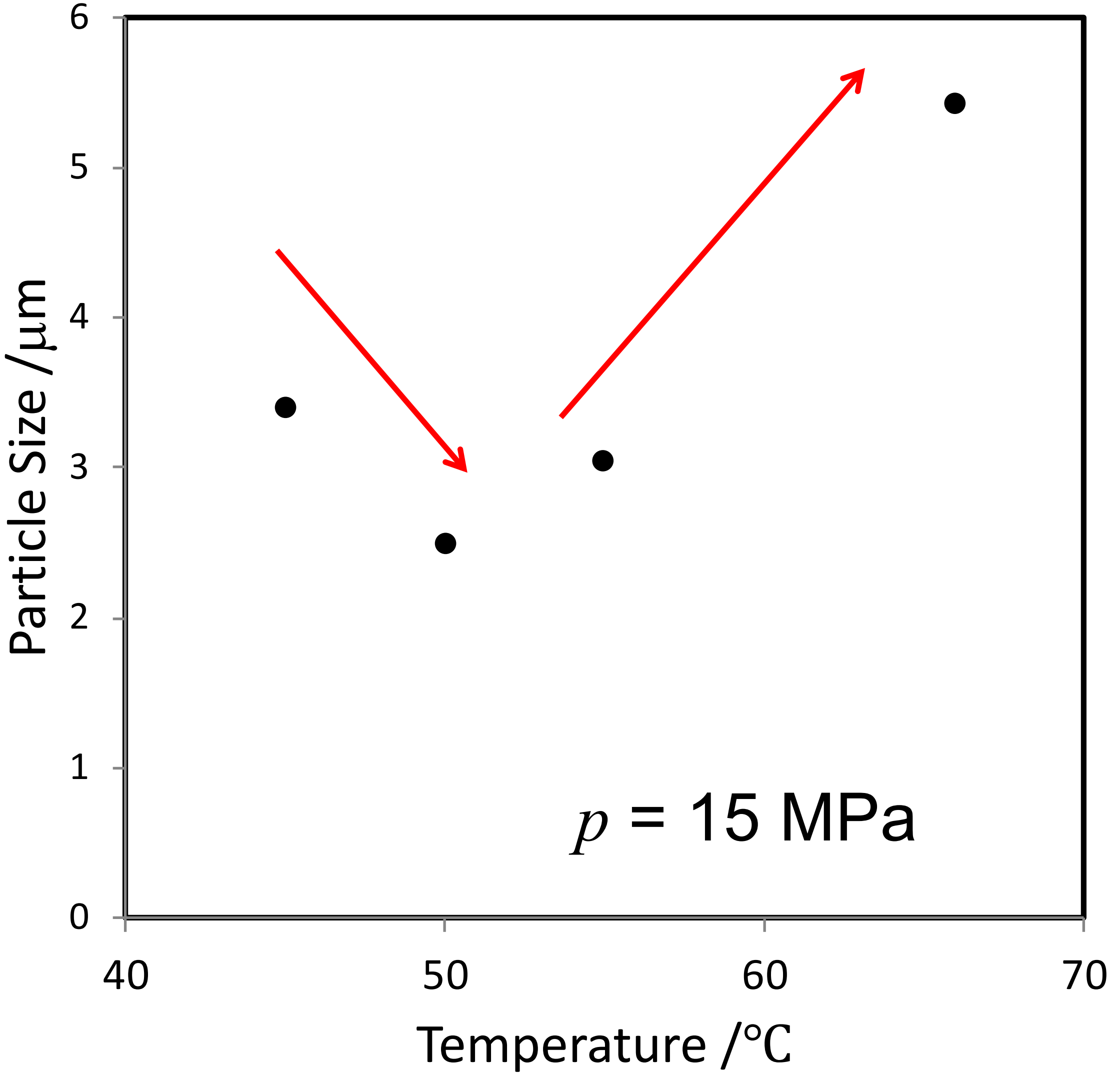
Yildiz, N. et al., J. Supercrit. Fluids, 41 (2007) 440 – 451.

Particle formation using SCF

- Micronization of salicylic acid

Before

34 – 171 μm



Yildiz, N. et al., J. Supercrit. Fluids, 41 (2007) 440 – 451.

Particle formation using SCF

Q. 2-2

Give the reason why temperatures over 65℃ results in the particle size increasing with temperature

Particle formation using SCF

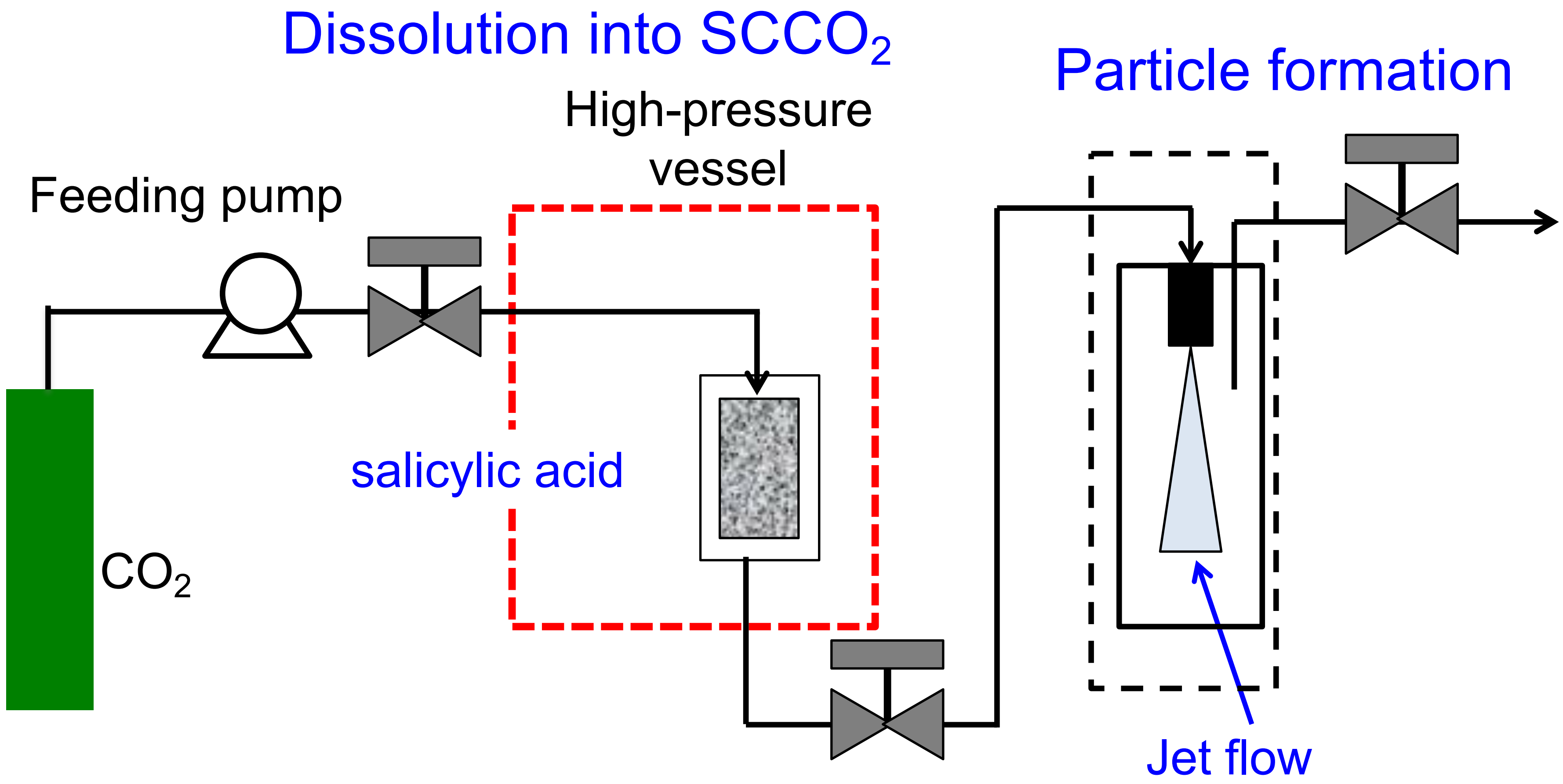
A. 2-2

Yildiz, N. et al., J. Supercrit. Fluids, 41 (2007) 440 – 451.

Particle formation using SCF

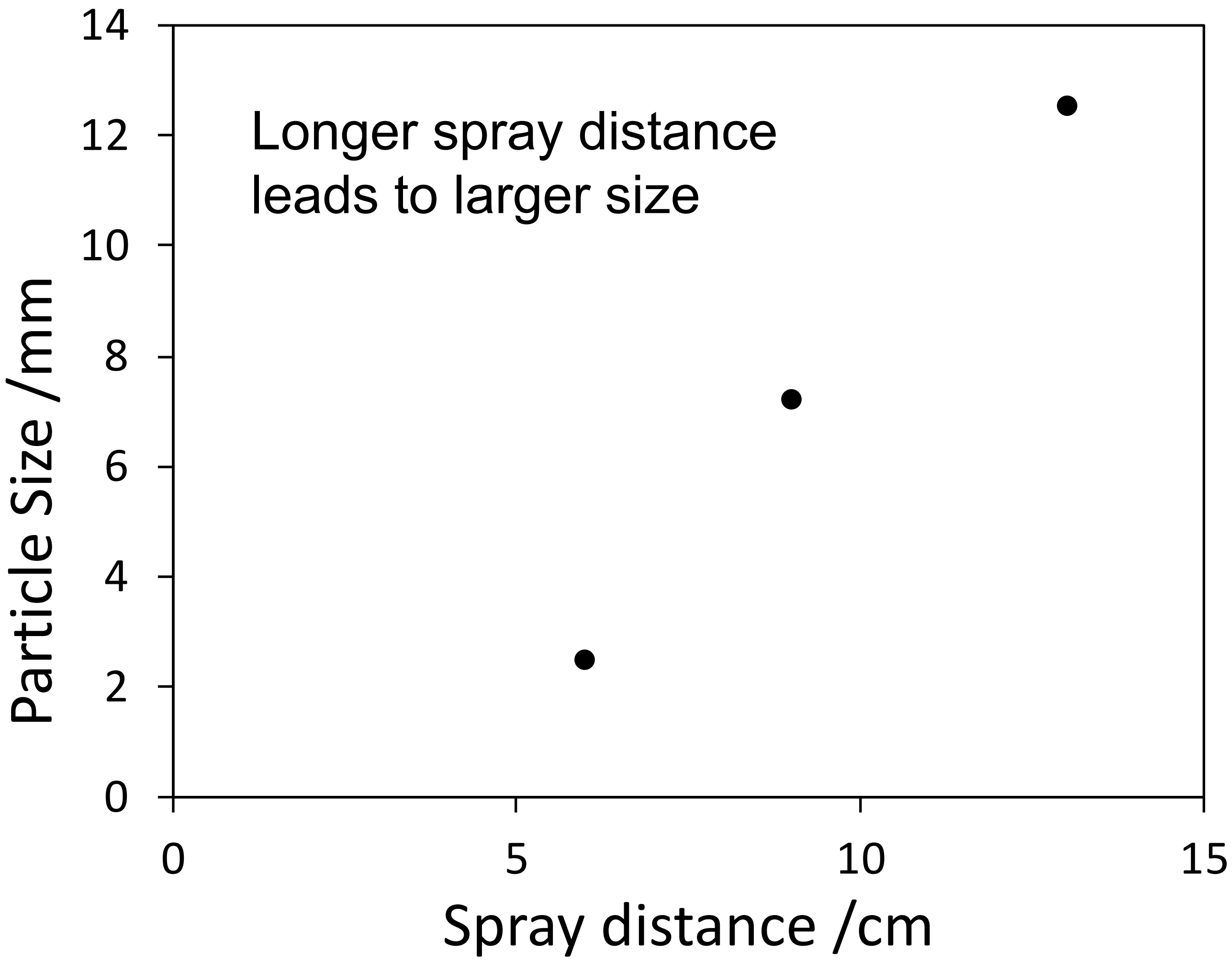
Rapid Expansion of Supercritical Solution : RESS

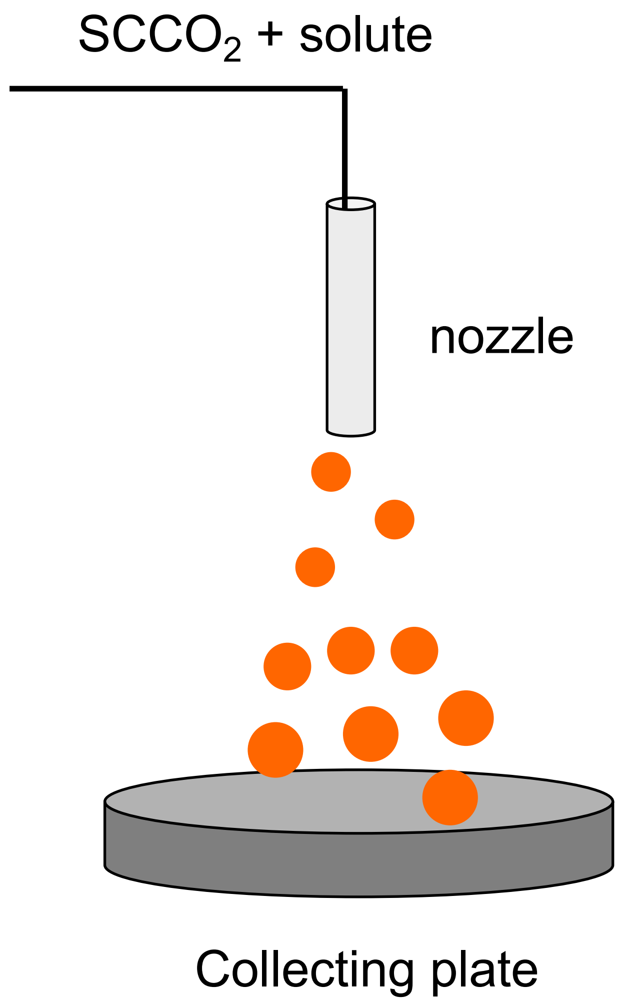
- Setup for RESS process using $SCCO_2$



Yildiz, N. et al., J. Supercrit. Fluids, 41 (2007) 440 – 451.

- Effect of spray distance on particle size





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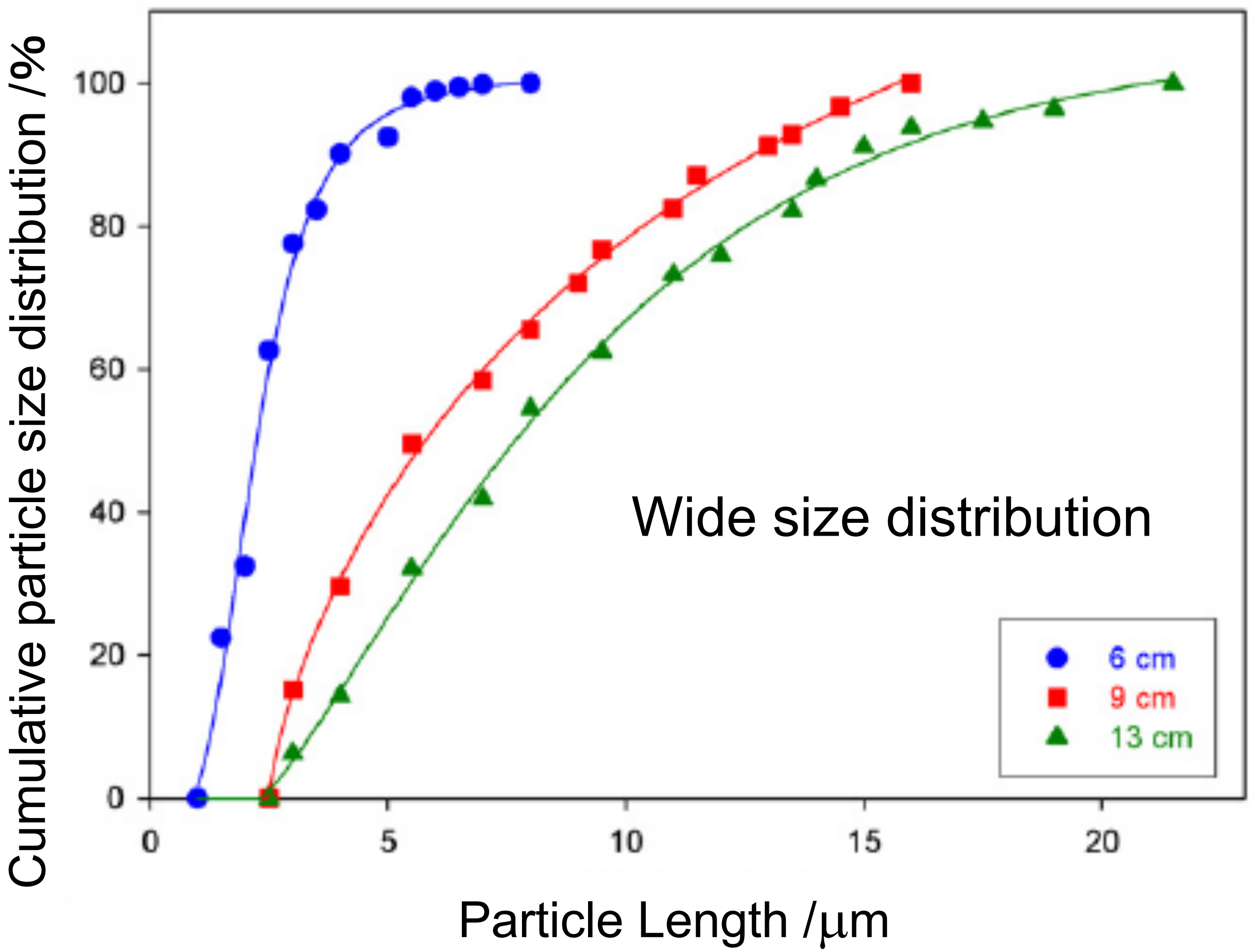
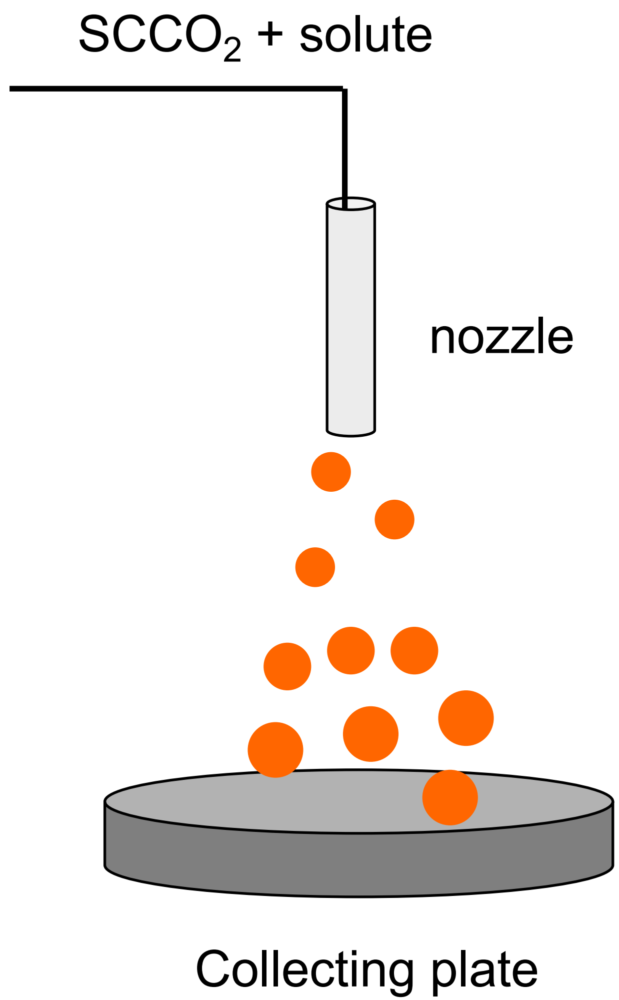
Particle formation using SCF

- Effect of spray distance on particle size



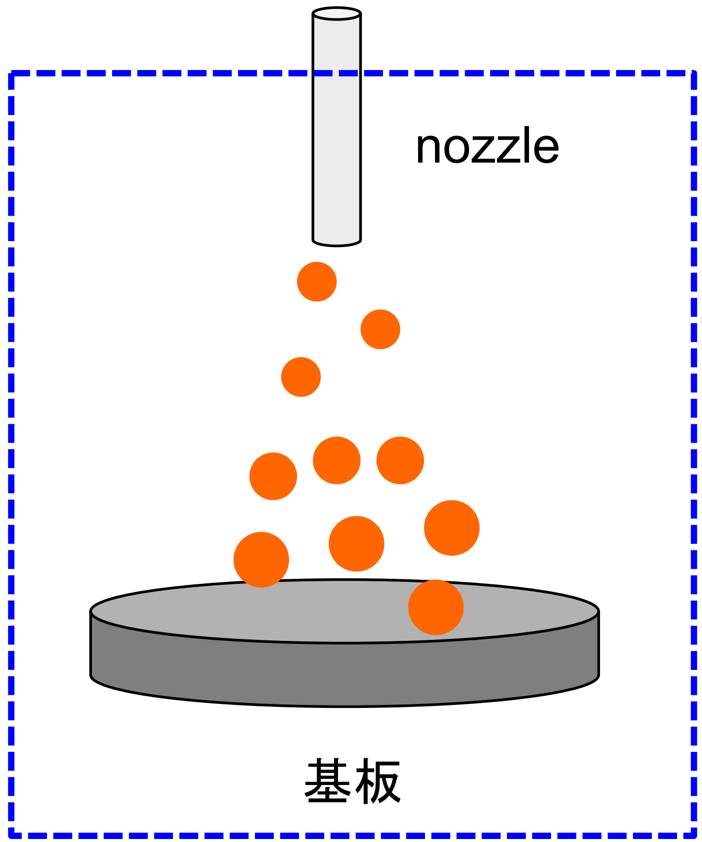


Yildiz, N. et al., J. Supercrit. Fluids, 41 (2007) 440 – 451.

Particle formation using SCF

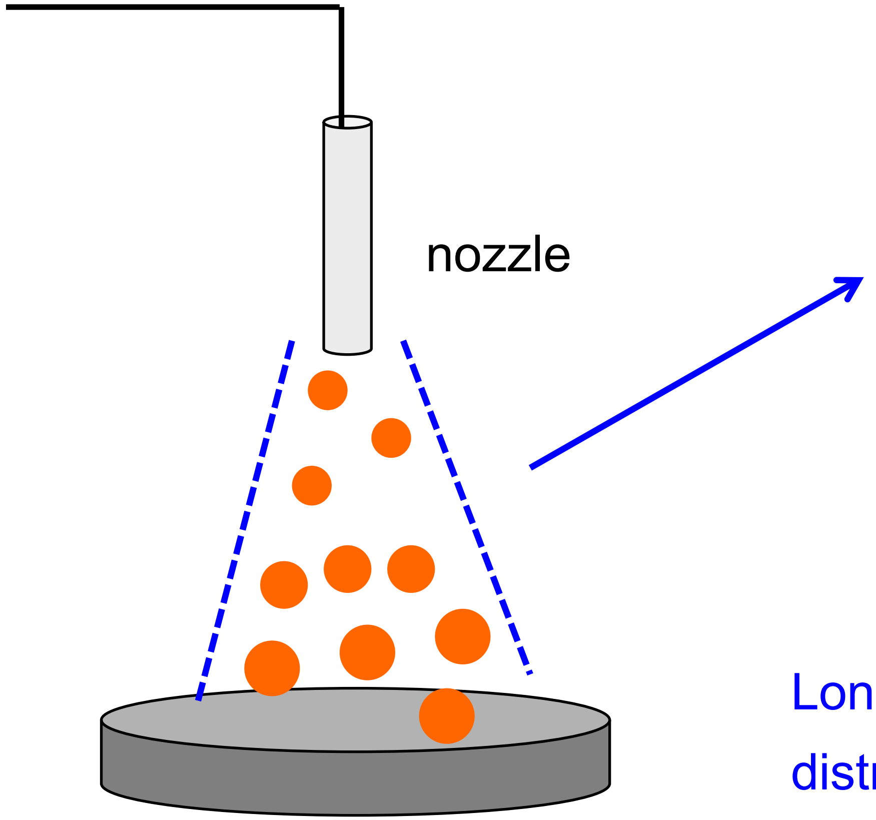
Q. 2-3

Give the mechanism why the longer spray distance results in the larger particle size and wide size distribution.

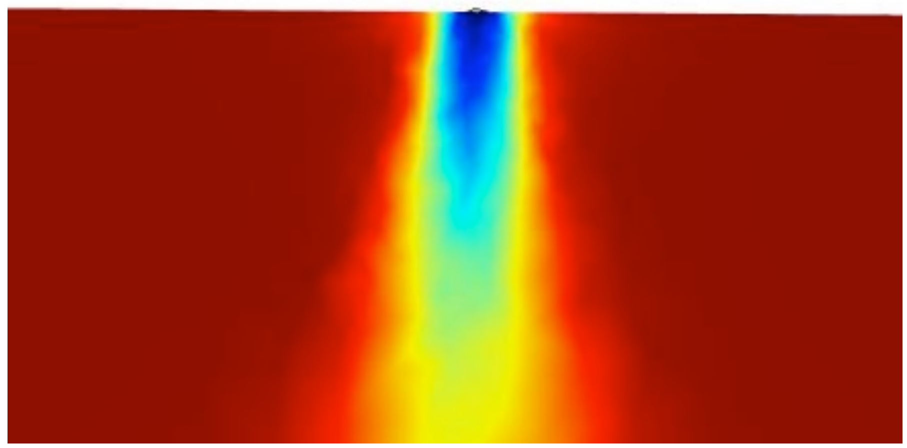


Particle formation using SCF

A. 2-3



Temperature distribution
(from CFD simulation)



Long spray distance allow the wide temperature distribution on the collecting plate.

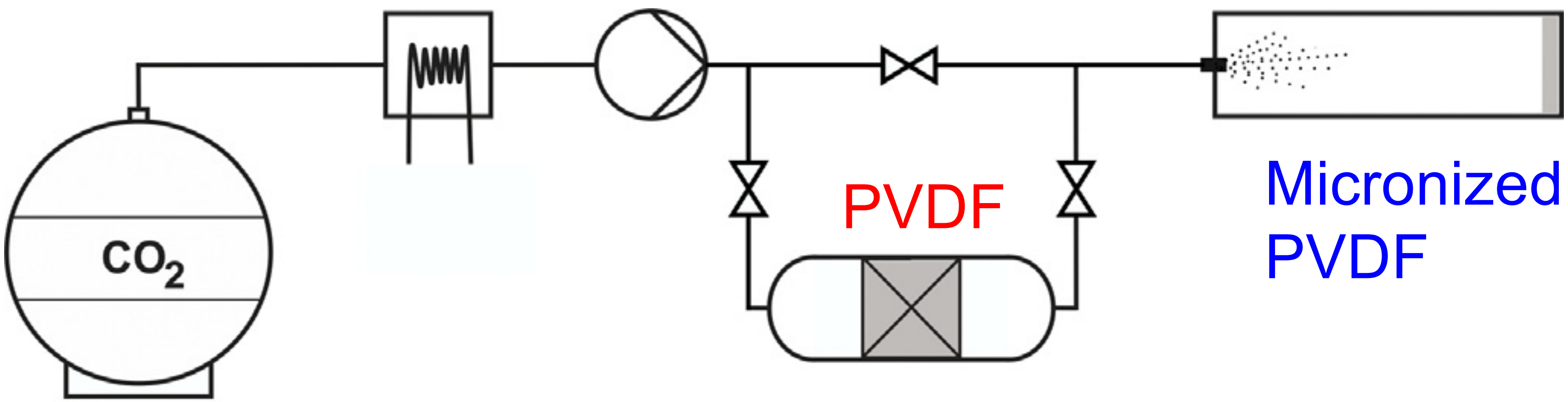
Particle formation using SCF

A. 2-3

Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS

- Poly(vinylidene fluoride) (PVDF) micronization
  - >> semicrystalline polymer
  - >> α and β phases (other three phases) are known.
  - >> β phases has piezo-, pyroelectric property.

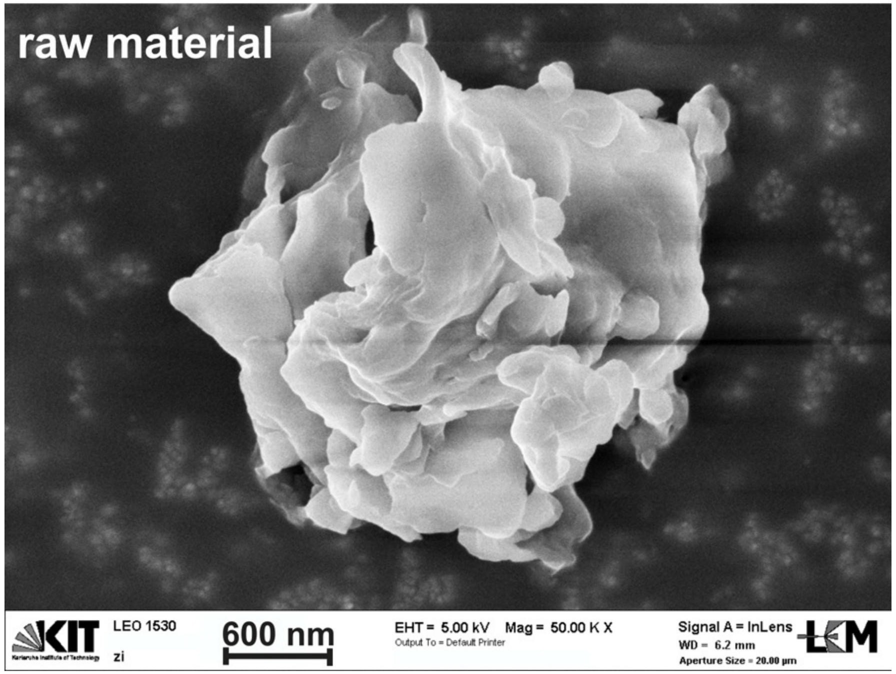


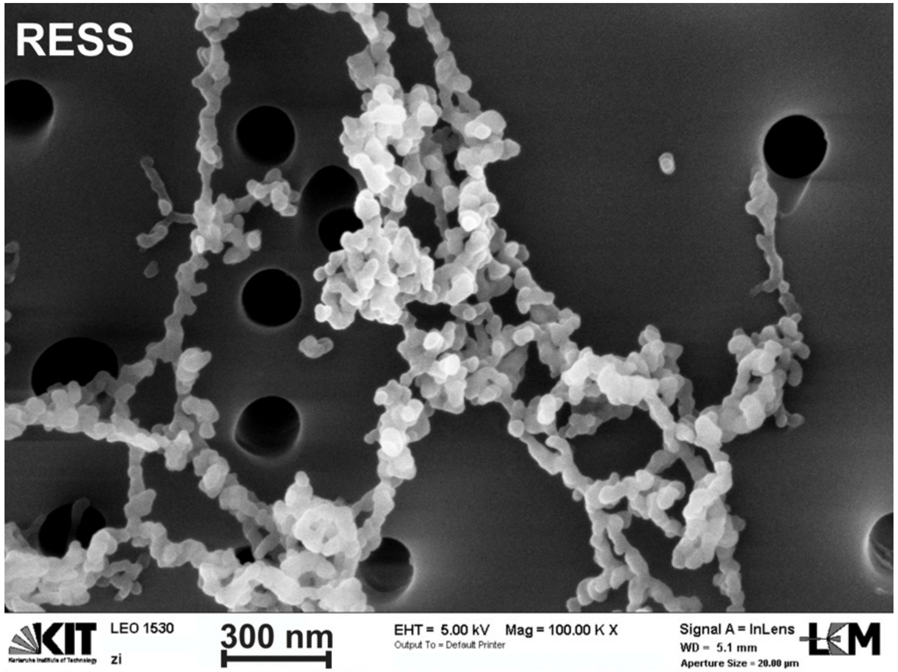
J. Supercrit. Fluids 117 (2017) 18-25.

Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS

- Poly(vinylidene fluoride) (PVDF) micronization





PVDF can be microparticle from RESS process

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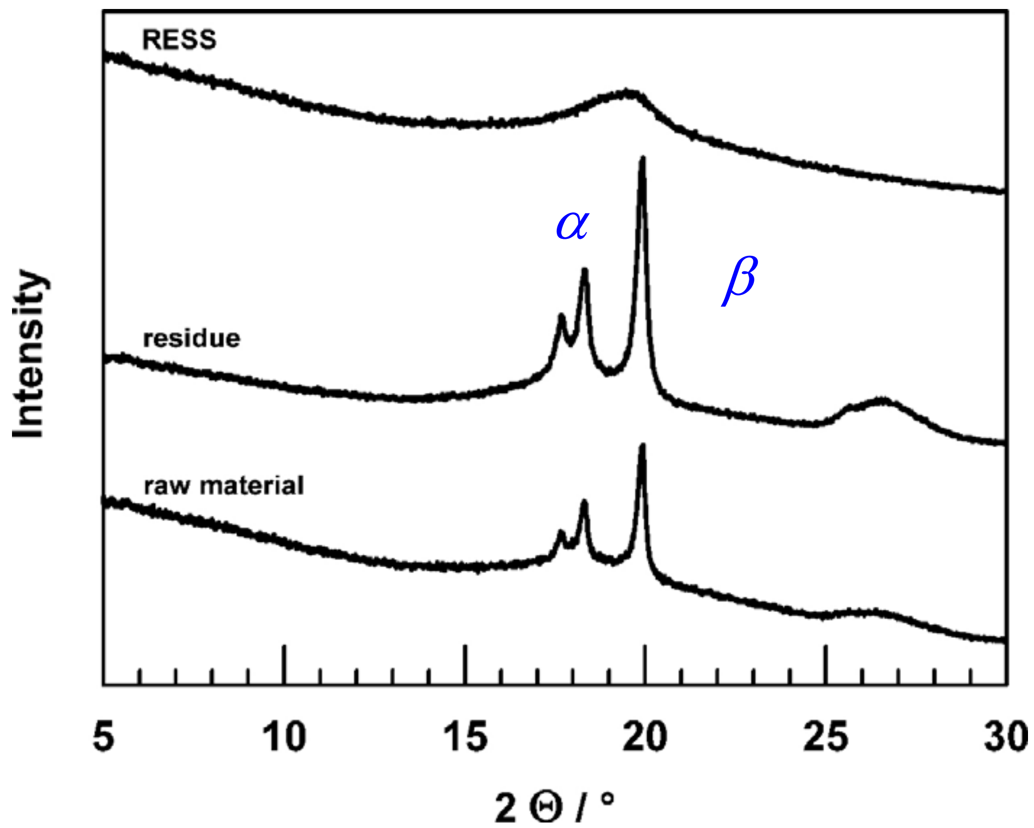
Particle formation using SCF

Rapid Expansion of Supercritical Solution : RESS

➢ Poly(vinylidene fluoride) (PVDF) micronization

Crystallinity of PVDF residue and produced in RESS process



RESS can produce β phase of PVDF

Dissolution into SCCO2：

>> 50℃, 10 MPa

Nozzle diameter

>> 50 μm

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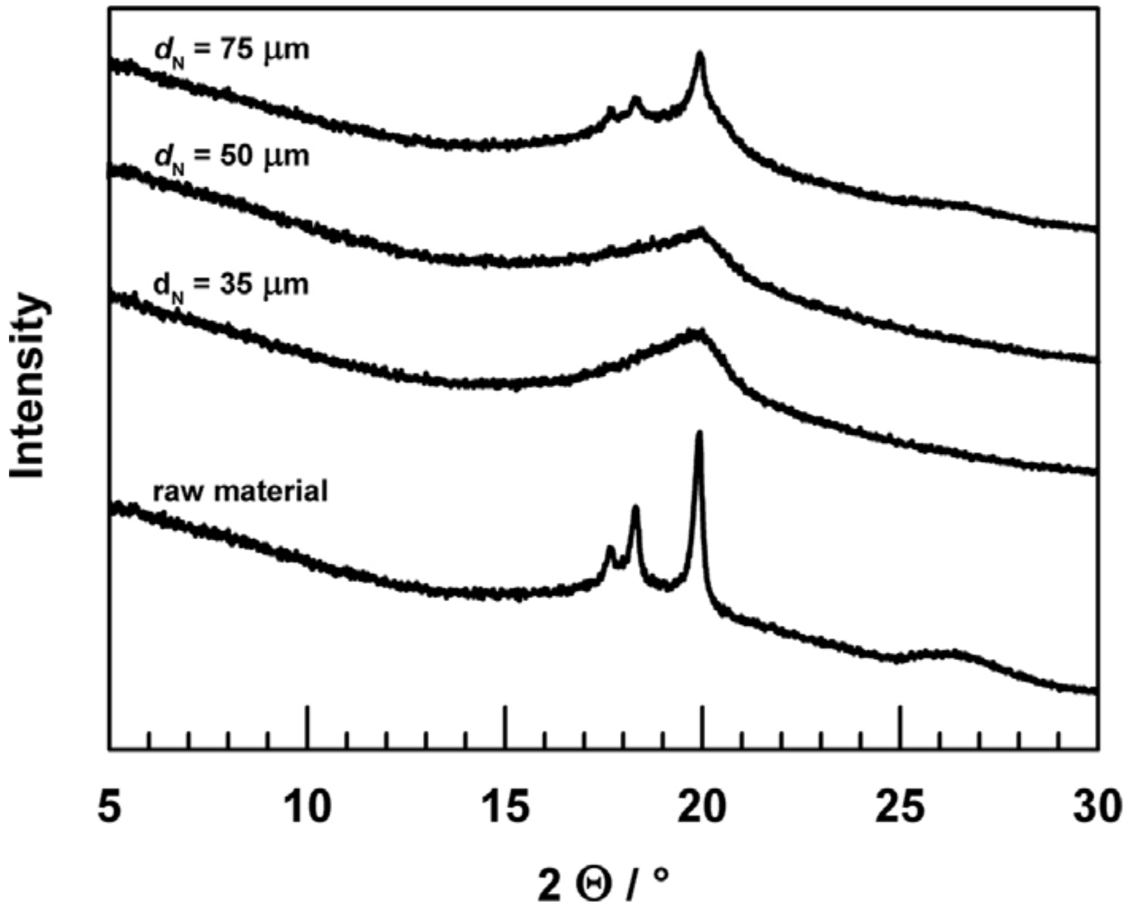
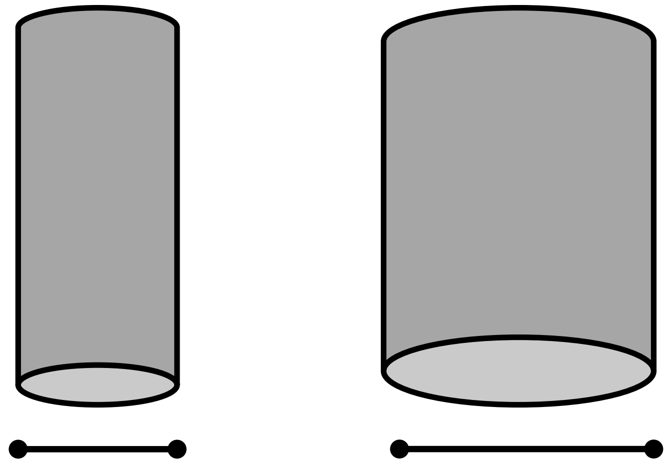
Particle formation using SCF

- Poly(vinylidene fluoride) (PVDF) micronization

Crystallinity of PVDF residue and produced in RESS process





Larger nozzle diameter
→ High PVDF crystallinity

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Q. 2-4

Give the mechanism why large nozzle diameter achieves the high PVDF crystallinity.

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