Towards a better understanding of condensed mode cooling.
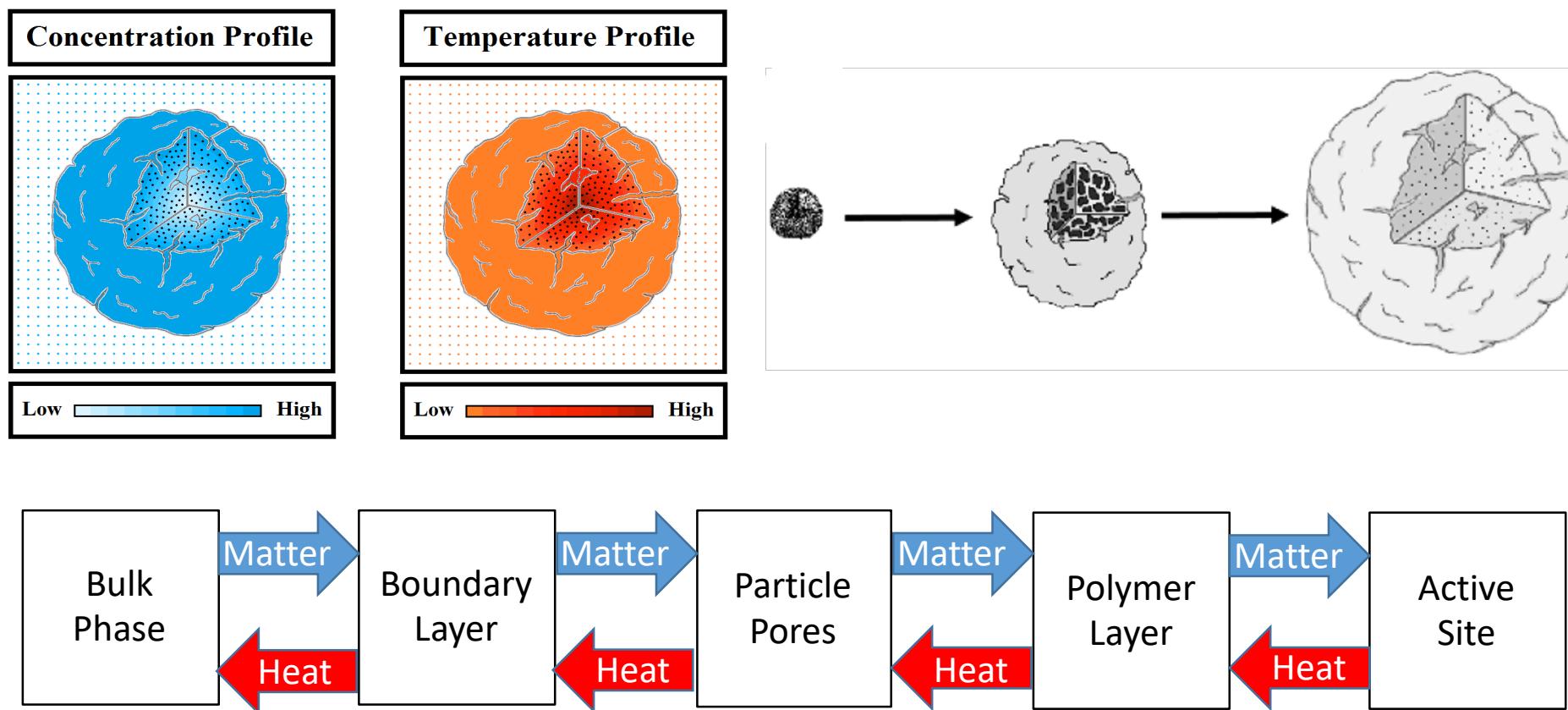
(Or, How I learned to stop worrying and find thermodynamics interesting!)

"It was the catalyst!" – Process engineers everywhere (1968 – present)
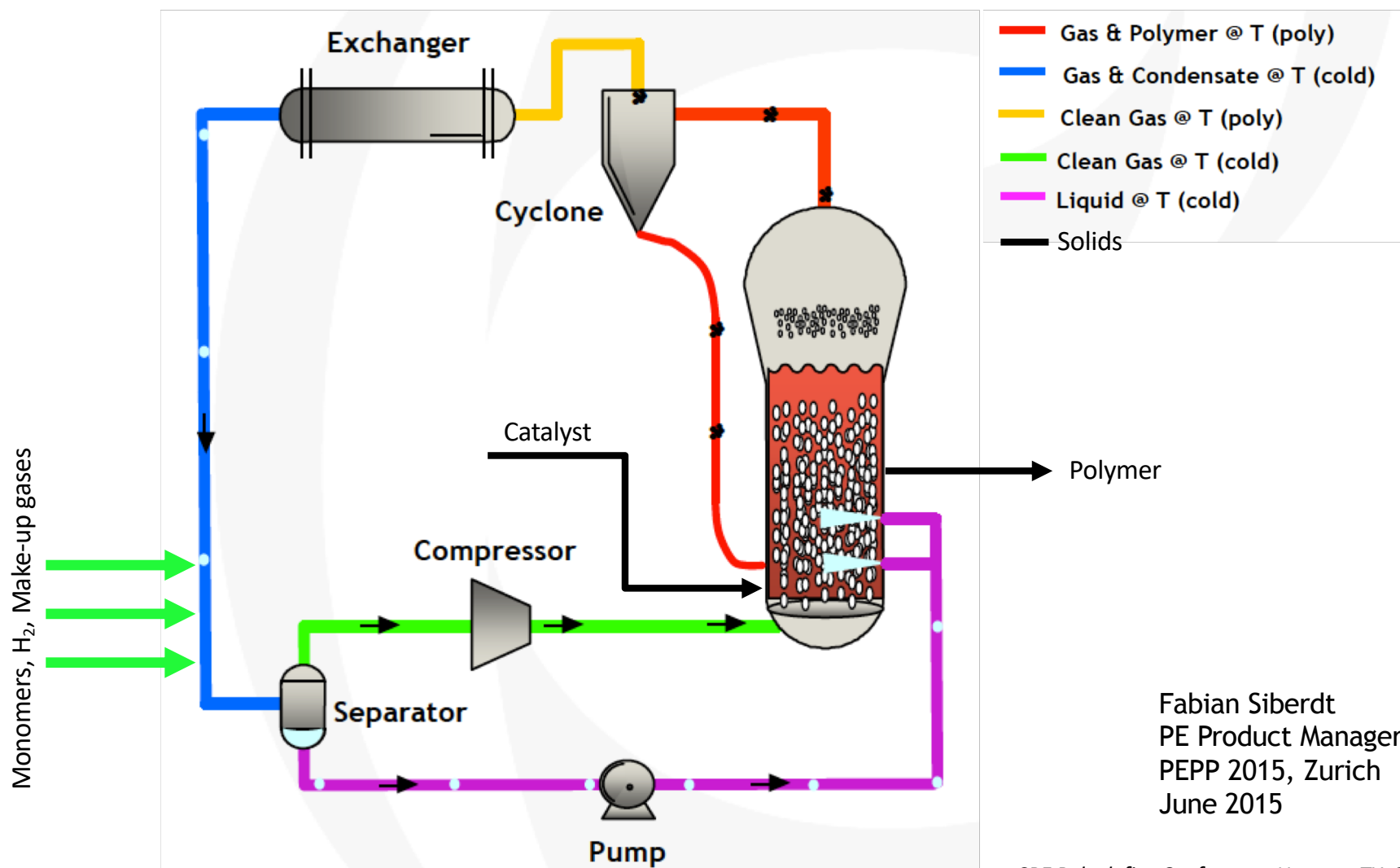
Context and Motivation

- Quick reminder - this type of polymer is made on supported catalysts.

- Polymer forms on the active sites deposited in the pores of the catalyst.

- Initial structure breaks up, and remains dispersed in the polymer as it accumulations.

| Bulk Phase | → Matter → ← Heat ← | Boundary Layer | → Matter → ← Heat ← | Particle Pores | → Matter → ← Heat ← | Polymer Layer | → Matter → ← Heat ← | Active Site |

Context and Motivation

- Why is condensed mode cooling important?

  ➢ Polyethylene (PE) is the mostly widely produced polymer on the planet in terms of volume.

  ➢ At least 50-60 MM tonnes of PE made in gas phase, and this will grow faster than average GDP.

  ❯ **NEED TO MAKE MORE STUFF!**

  ❯ **Typical plant generates 50-80 MEGAWATTS**

  ❯ **To make more stuff, need to get out more heat**

- One of the most significant constraints in terms of reactor design and operation is heat removal.

  ➢ Overcome via operating protocols, but:

    ❯ Cannot change gas flow rate significantly (carry-over/defluidisation)

    ❯ Limited range of possibilities through reactor wall (S/V small anyway)

3

Context and Motivation

- Schema of an FBR for PE production (Innovene G)

Fabian Siberdt
PE Product Manager
PEPP 2015, Zurich
June 2015

Context and Motivation

Condensed and Super Dry

Condensed

$$PRODUCTIVITY = R_p V_R = \frac{\dot{m}_{g,in} c_{pg,in} \left(T_R - T_{g,in} \right) + UA(T_R - T_W) + Q_{vap}}{(-\Delta H_p)}$$
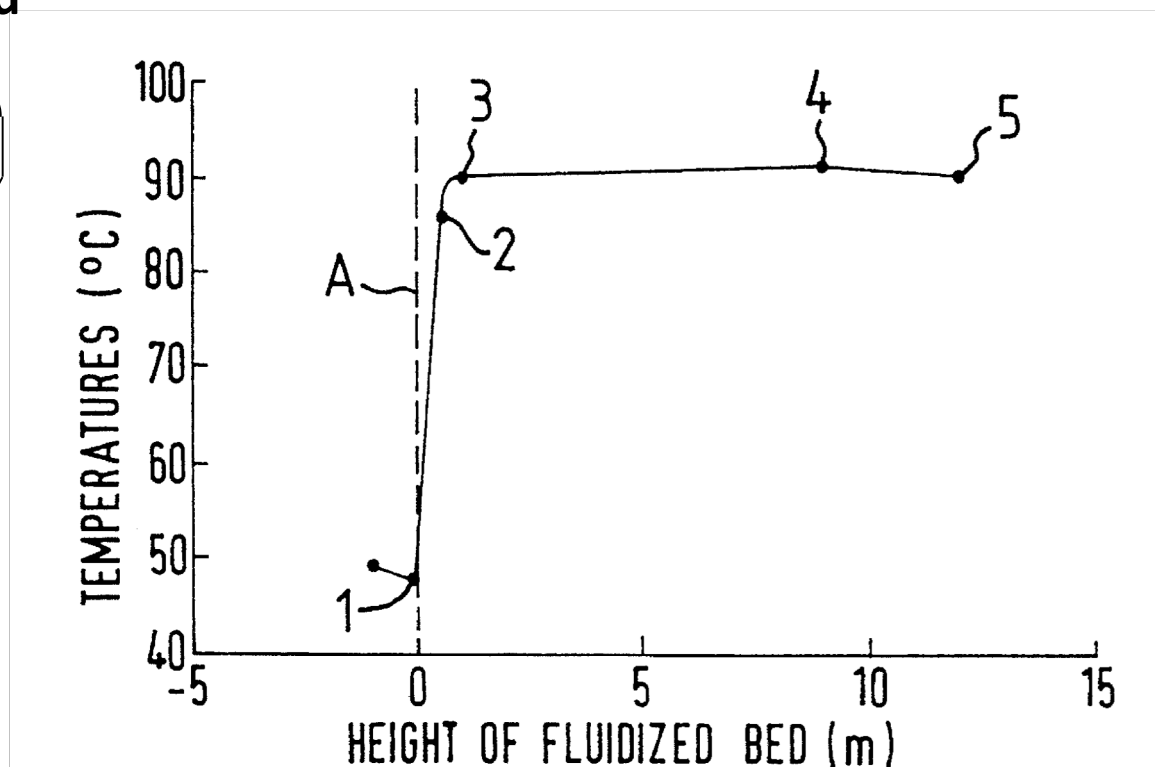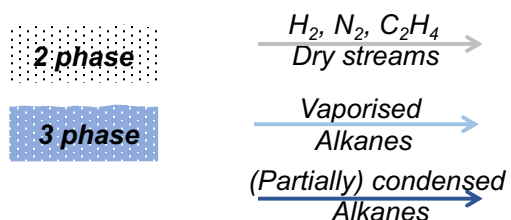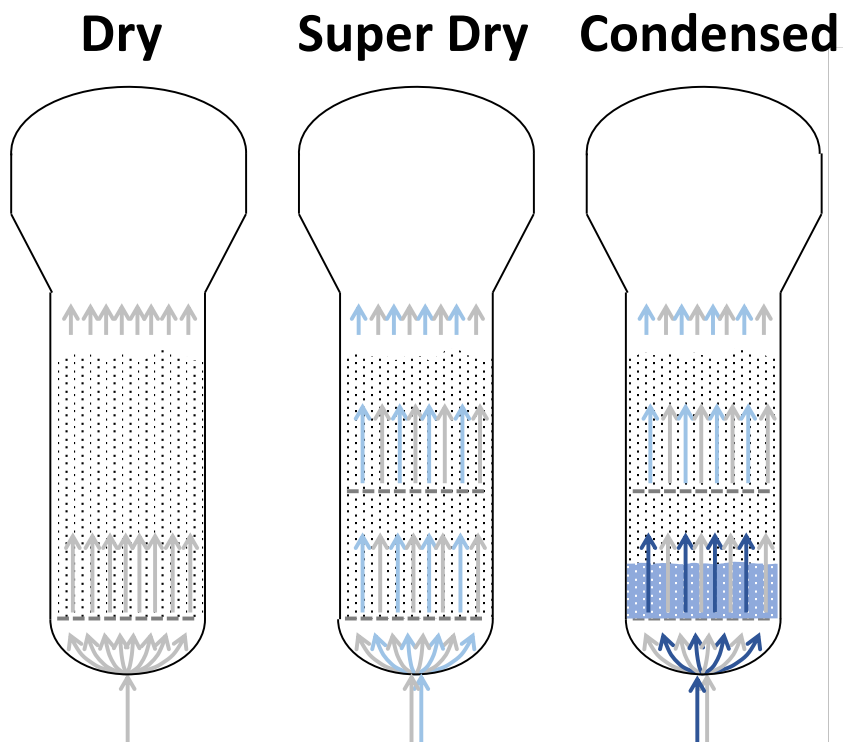
2 Solutions to increase Productivity

Latent heat of vaporisation of ICA

$$Q_{Vap} = E(-\Delta \dot{H}_{Vap})$$

▶ DRY = C_2H_6 and C_2H_4, N_2, H_2 (reactor contains very low swelling materials)

▶ SUPER DRY = DRY + ICA + higher alkenes *in vapour phase*

▶ (SUPER) CONDENSED = SUPER DRY + (partially) condensed C4 and higher

Use induced condensing agents (ICA)

Context and Motivation

Dry **Super Dry** **Condensed**

- 2 phase
- 3 phase

H_2, N_2, C_2H_4
Dry streams

Vaporised
Alkanes

(Partially) condensed
Alkanes

➤ Vaporised alkanes (ICA) can vaporise quickly – most of the reactor is filled with vapour/solid mixture (unless super condensed!).

➤ *Examine the impact of vaporised ICAs*

Impact of ICA
What else does the ICA do?

- Can increase space-time yield by adding inert components to an FBR.

- **In many processes only a small fraction of bed volume actually contains liquid**

- What else does the ICA if it is not liquid?

Swells Polymer
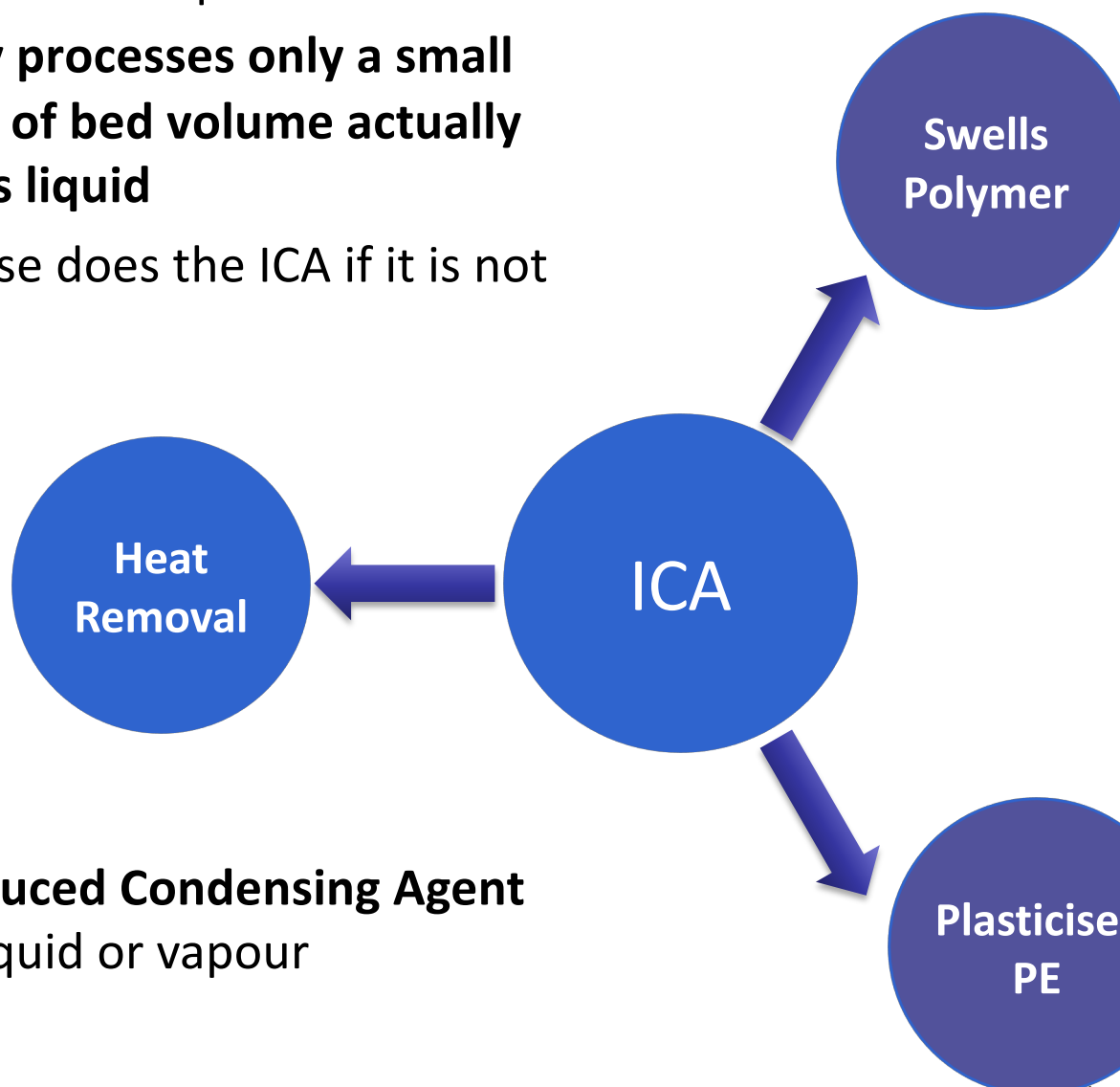
- Sorption influences *solubilities*
- Changes ratio of concentrations at the active sites

Heat Removal ← **ICA**

Plasticises PE

- Changes mass transfer
- Changes physical properties *in situ* – change in PE structure!

- **ICA = Induced Condensing Agent**
- Can be liquid or vapour

Role of ICA

- Experimental Analysis under Reactive Conditions

  ➢ Effect of presence of n-hexane as ICA on rate of polymerisation
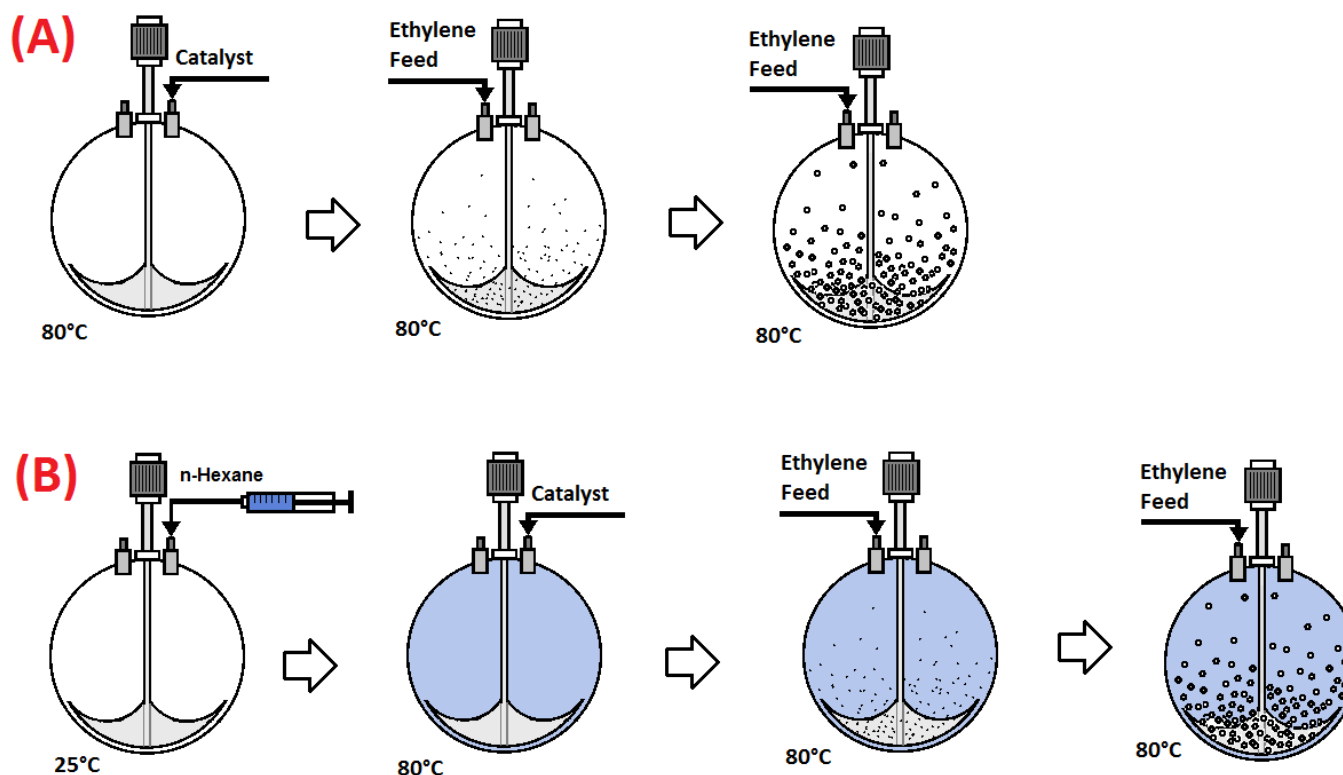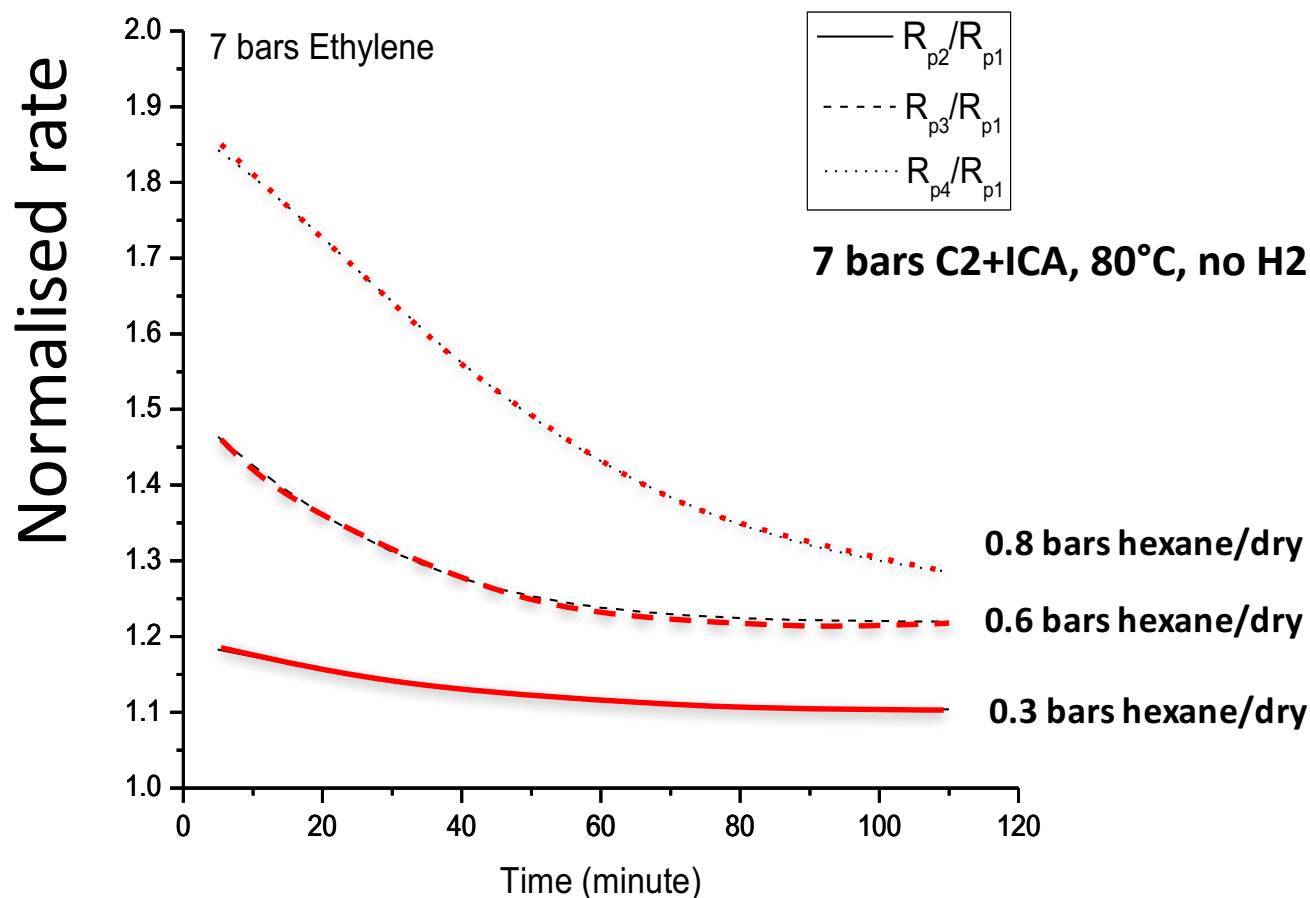

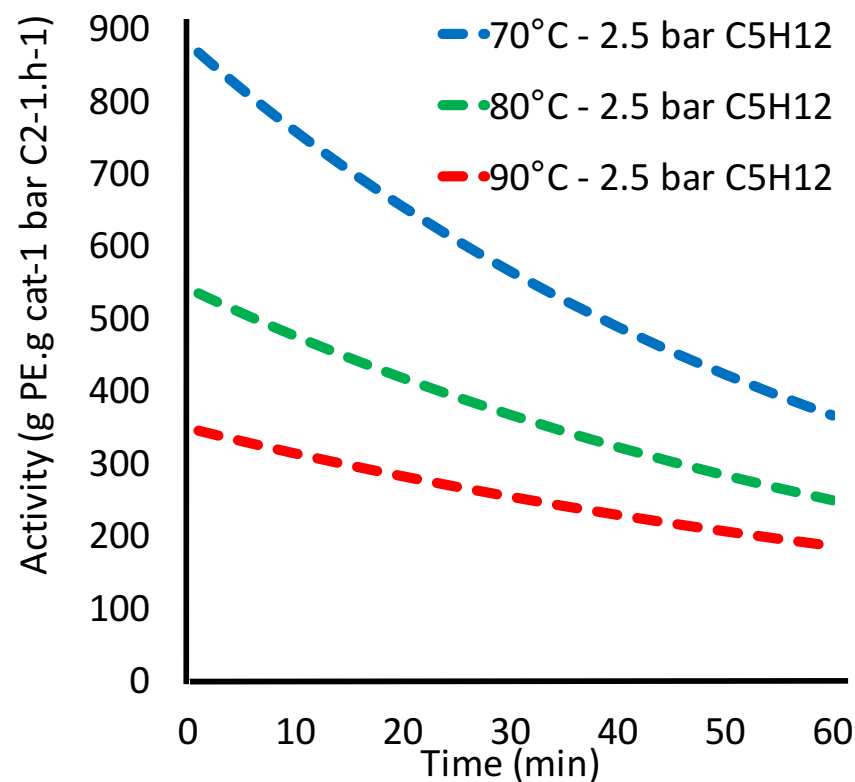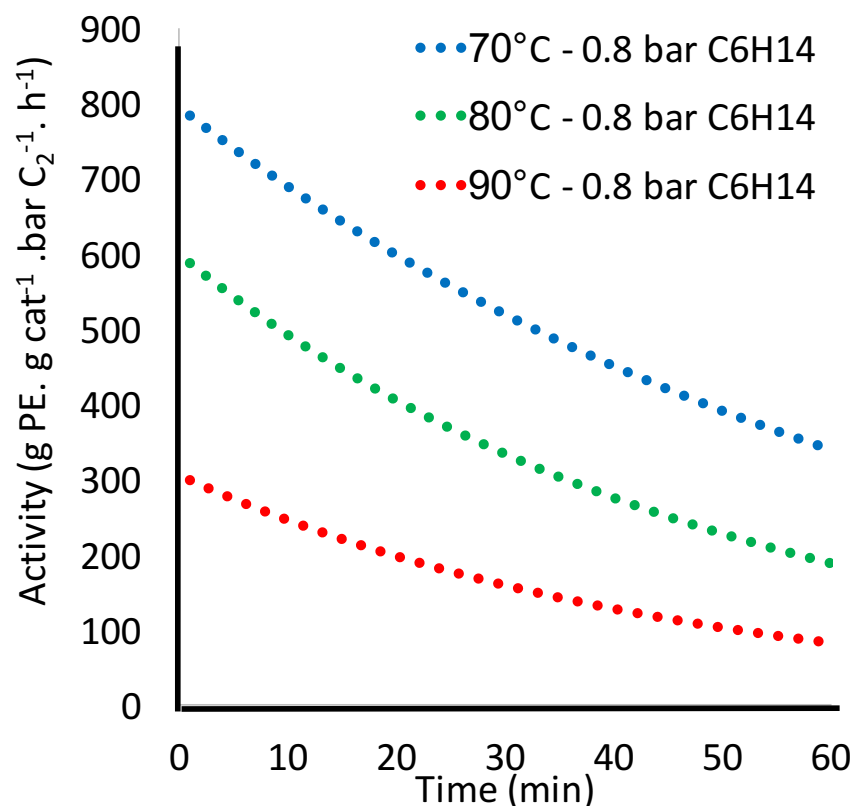 ➢ Comparison of instantaneous and overall polymerisation rate between mode (A) and (B)

Role of ICA – Effect on reaction rate

- Adding vaporised ICAs can have unintended effects. E.g. the reaction goes faster in the presence of ICA
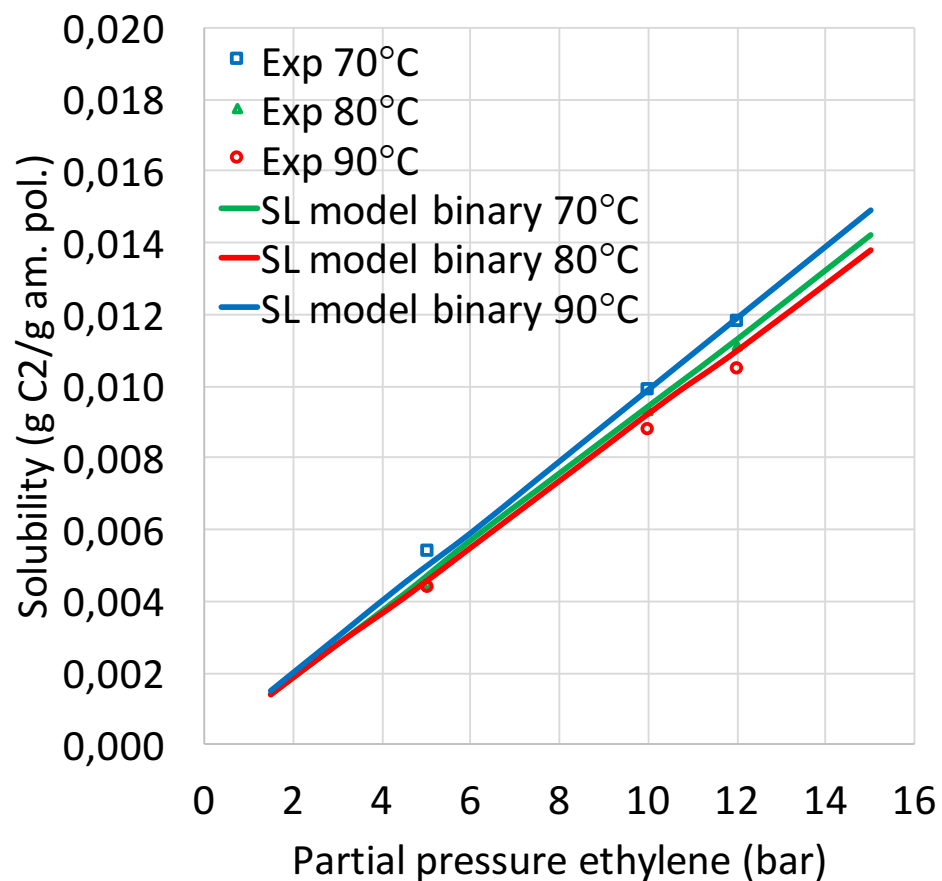
« Over-Enhancement » not due to temperature

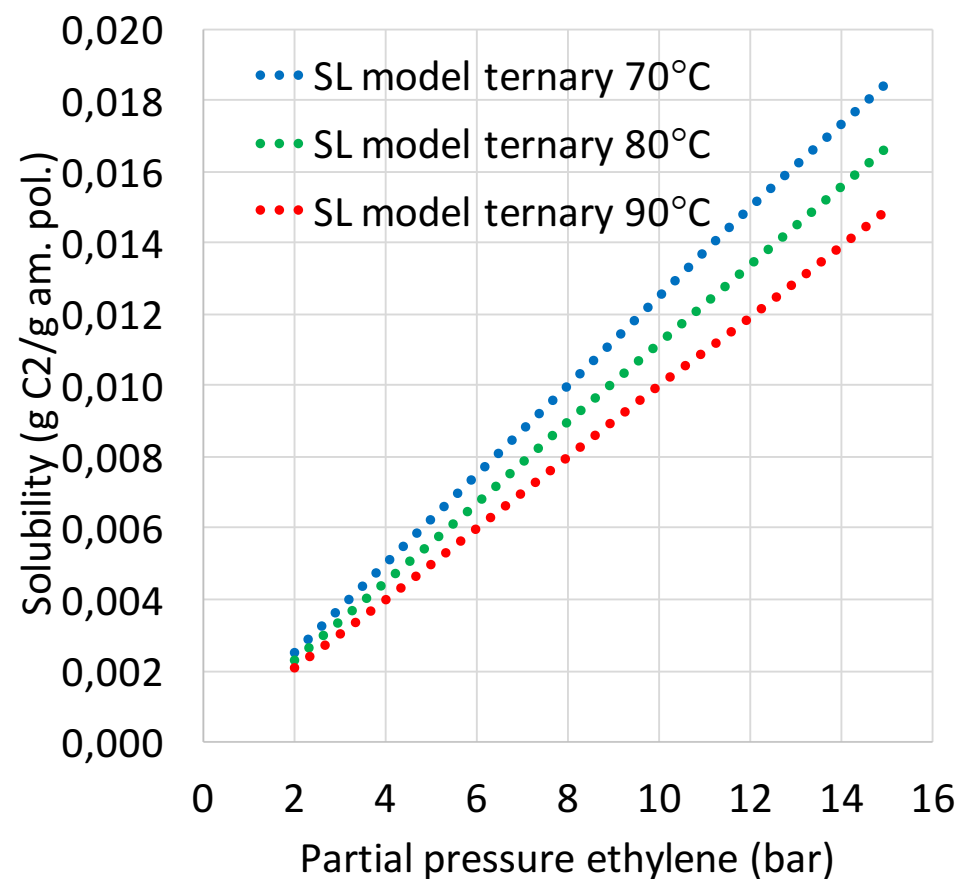- Competing effects means effect of T changes might not be what we expect in presence of ICA

« Over-Enhancement » not due to temperature

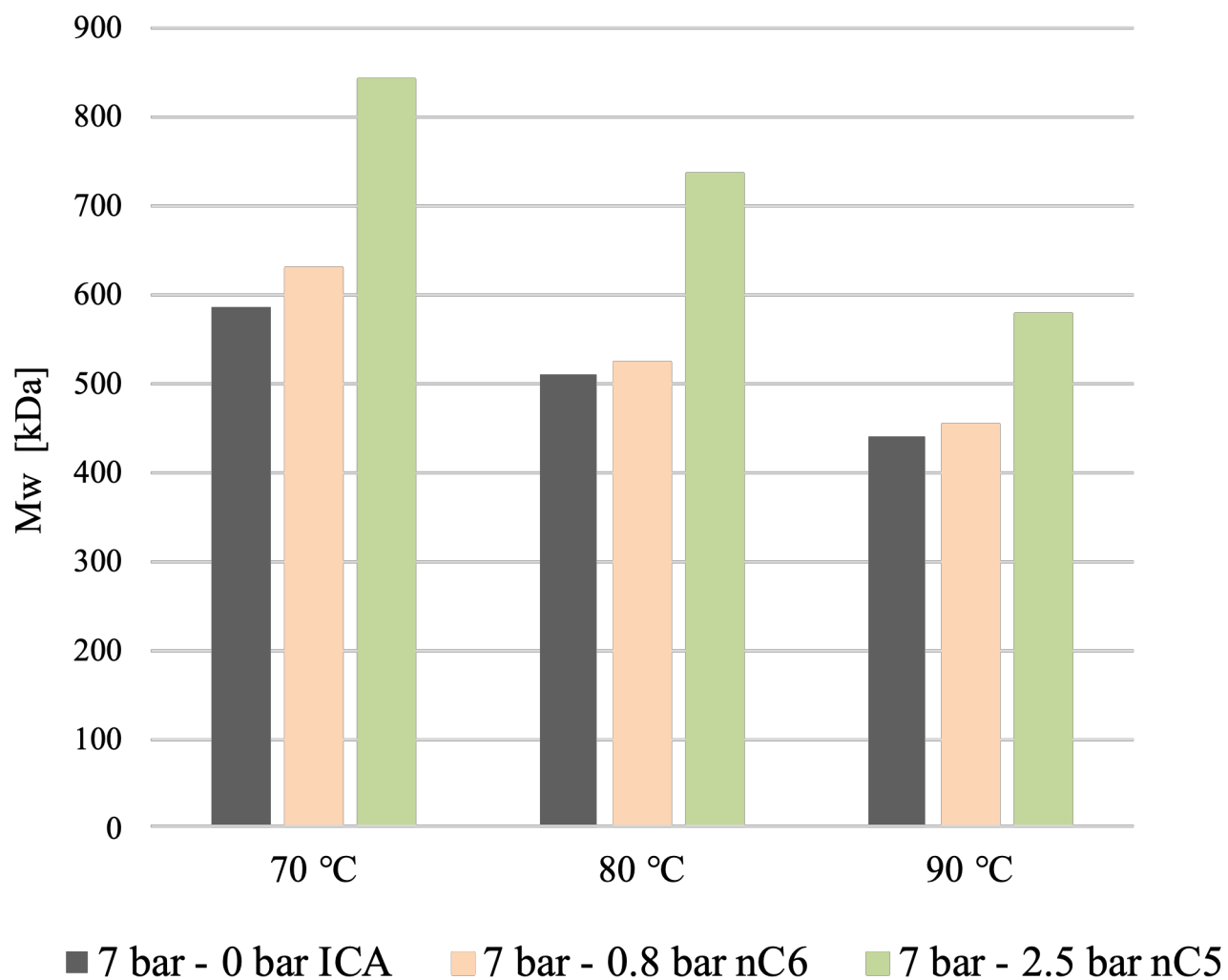- Essentially due to T sensitivity of ICA solubility

Binary system – Polyethylene / Ethylene

Ternary system – Polyethylene / n-Hexane / Ethylene
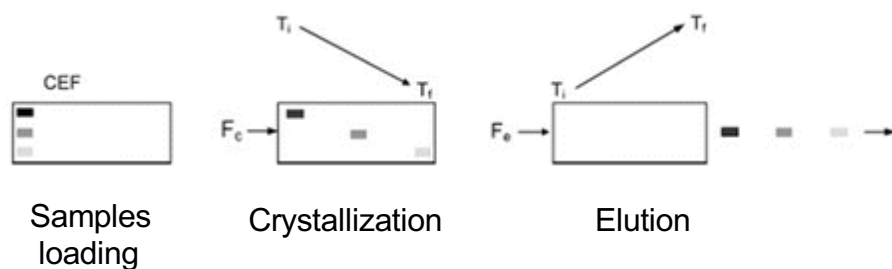
Role of ICA – Effect on polymer properties

Role of ICA – Effect on polymer properties

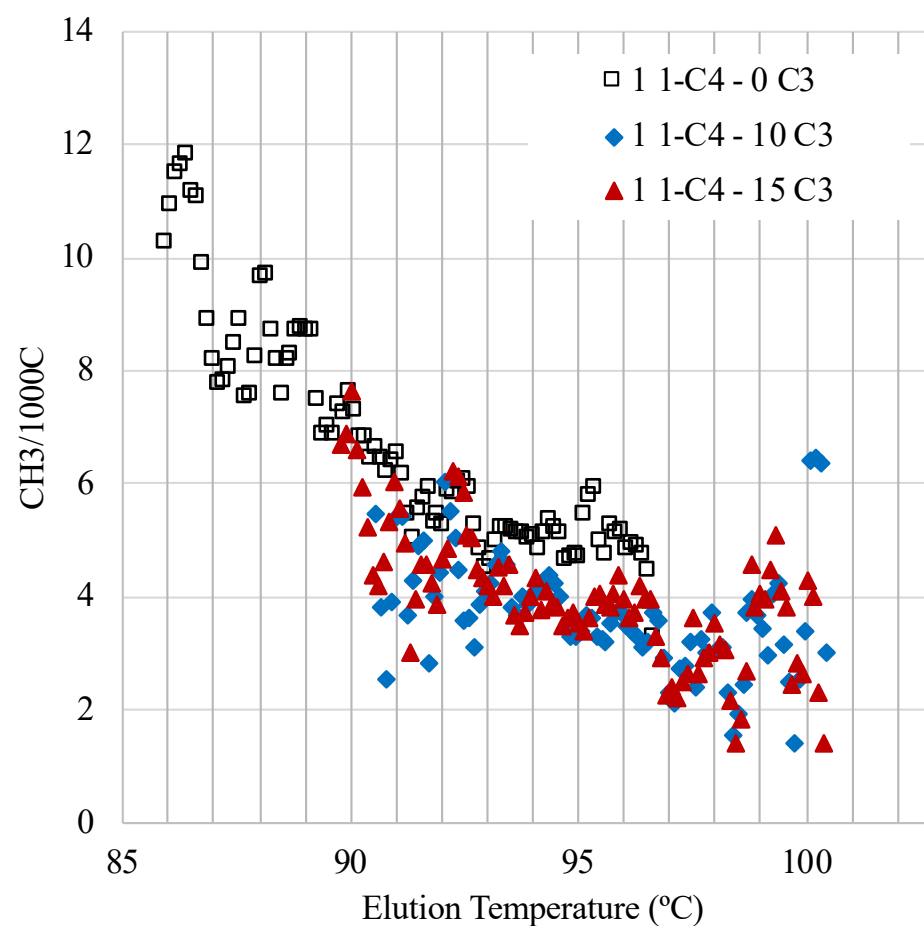## Poly(ethylene-co-1-butene) + propane

CEF - Crystallization Elution Fractionation

CH_3 / 1000 C

CEF

Samples loading   Crystallization   Elution

Pasch, H. and Malik, M. (2014). *Advanced Separation Techniques for Polyolefins*. Cham: Springer.
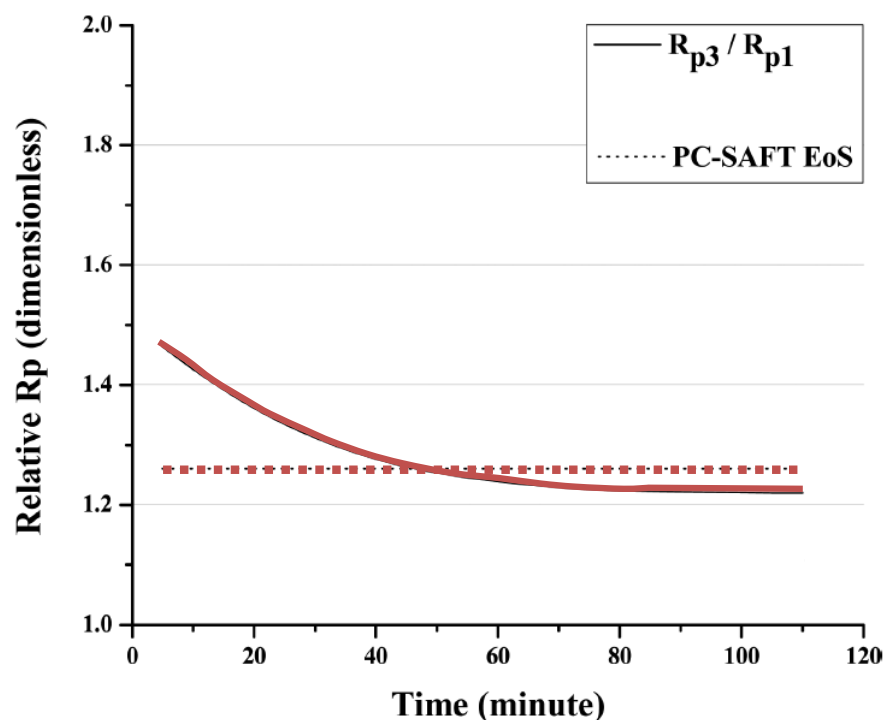
Role of ICA – Effect on reaction rate

Magnitude of enhancement due to cosolubility $= \dfrac{R_{p_{ICA}}}{R_{p_{Dry}}}$

Reactor temperature - 80 °C
Ethylene pressure - 7 bar
N-Hexane pressure – 0.6 bar

> **Reactor temperature**
>   70 – 80 – 90 °C

> **Reactor pressure**
>   7 – 15 bar

> **ICA**
>   2.5 bar n-Pentane
>   0.8 bar n-Hexane

A. Alizadeh, J. Chmelař, F. Sharif, M. Ebrahimi, J. Kosek, and T. F. L. McKenna,
"Modeling Condensed Mode Operation for Ethylene Polymerization: Part I.
Thermodynamics of Sorption," Ind. Eng. Chem. Res., vol. 56, no. 5, pp. 1168–1185, 2017.

Role of ICA – Single Particle Modelling

- Mass balance for SPM

$$\frac{\partial [M_1]_{ov}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r}\left(D_{1,ov} r^2 \frac{\partial [M_1]_{ov}}{\partial r} \right) - R_v$$

- Use RPPFM of Kiparissides[2]

$$D_{i,ov} = \frac{\varepsilon}{\tau_f^2} D_{i,g} + (1-\varepsilon)(1+3\varepsilon)D_{i,pol}$$

- Modified free-volume approach to capture impact of ICA on ethylene diffusion[3] (similar exp for ICA diffusion):

$$D_{1,am.pol}^{ternary} = D_{01} \exp\left(\frac{-(\omega_1 \hat{V}_1^* + \omega_2 \hat{V}_2^* \xi_{13}/\xi_{23} + \omega_3 \hat{V}_3^* \xi_{13})}{\omega_1\left(\frac{K_{11}}{\gamma}\right)(K_{21}+T-T_{g1})+\omega_2\left(\frac{K_{12}}{\gamma}\right)(K_{22}+T-T_{g2})+\omega_3\left(\frac{K_{13}}{\gamma}\right)(K_{23}+T-T_{g3})} \right)$$
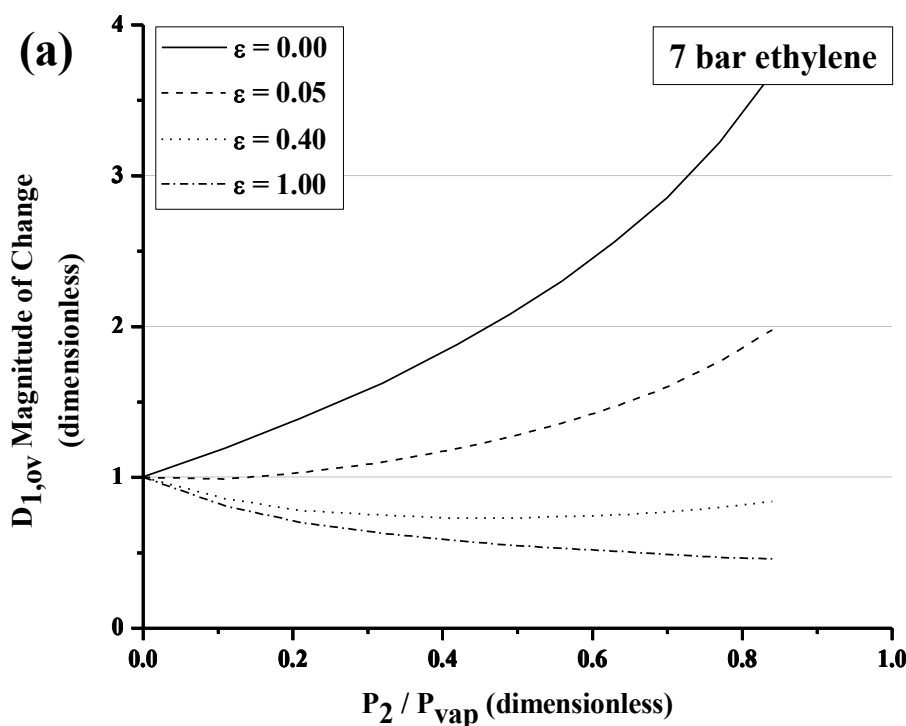
[2] Kanellopoulos et al., Ind. Eng. Chem. Res. 2004, 43, 5166
[3] Alizadeh et al., Ind. Eng. Chem. Res., 2018, 57, pp 6097

Role of ICA – Effect on reaction rate

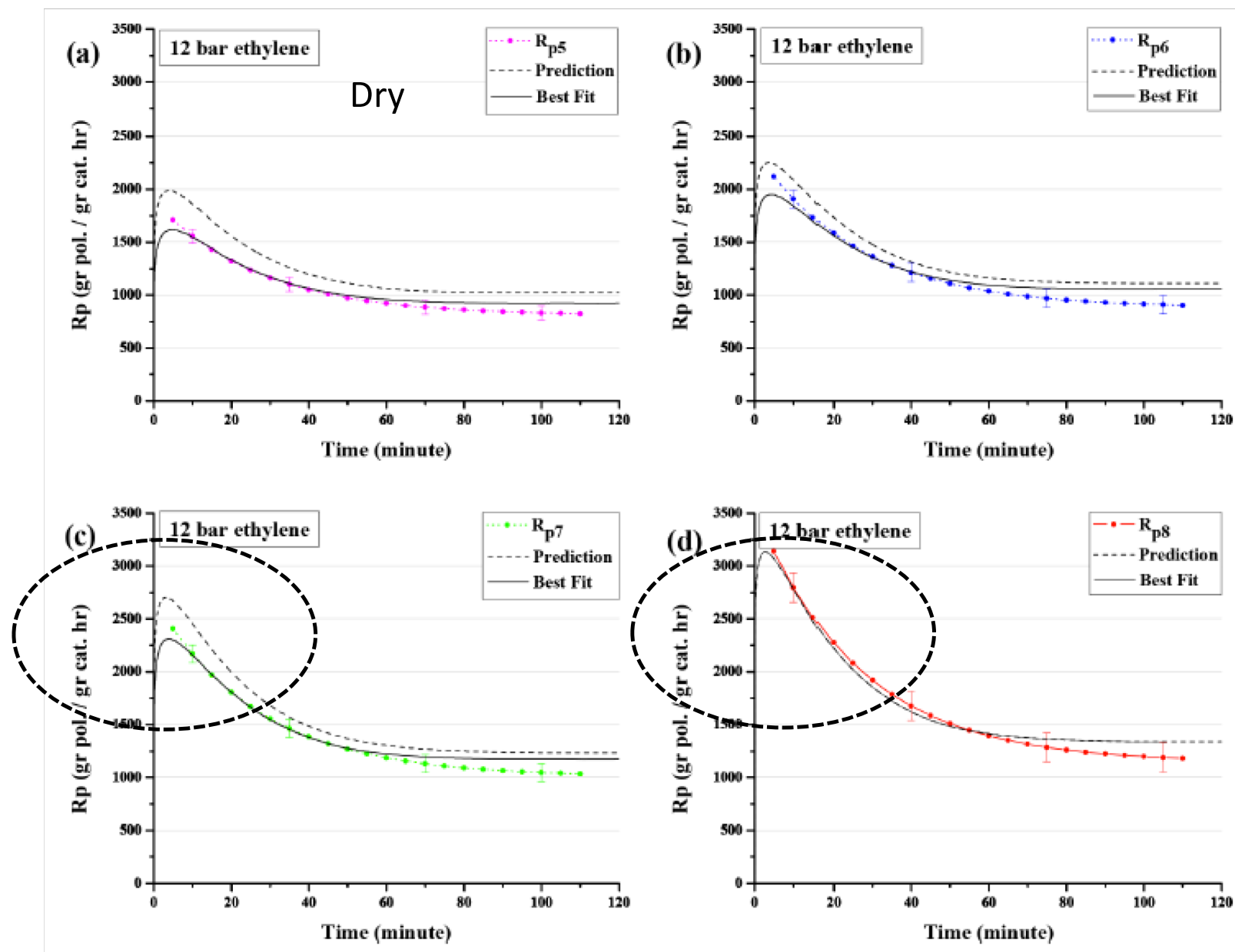- Need to account for impact of ICA on penetrant diffusivity:

$$D_{i,ov} = \frac{\varepsilon}{\tau_f^2} D_{i,g} + (1-\varepsilon)(1+3\varepsilon)D_{i,pol}$$

The magnitude of change in the overall diffusion coefficient of ethylene *P* of *n*-hexane normalized with its vapor pressure at 80 °C and partial pressure of ethylene equal to 7 bars
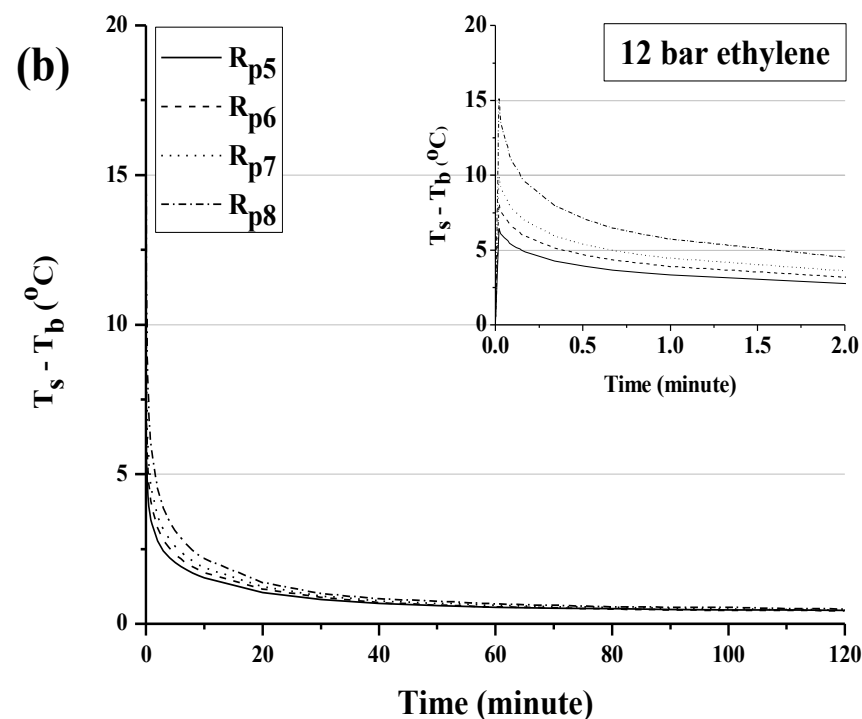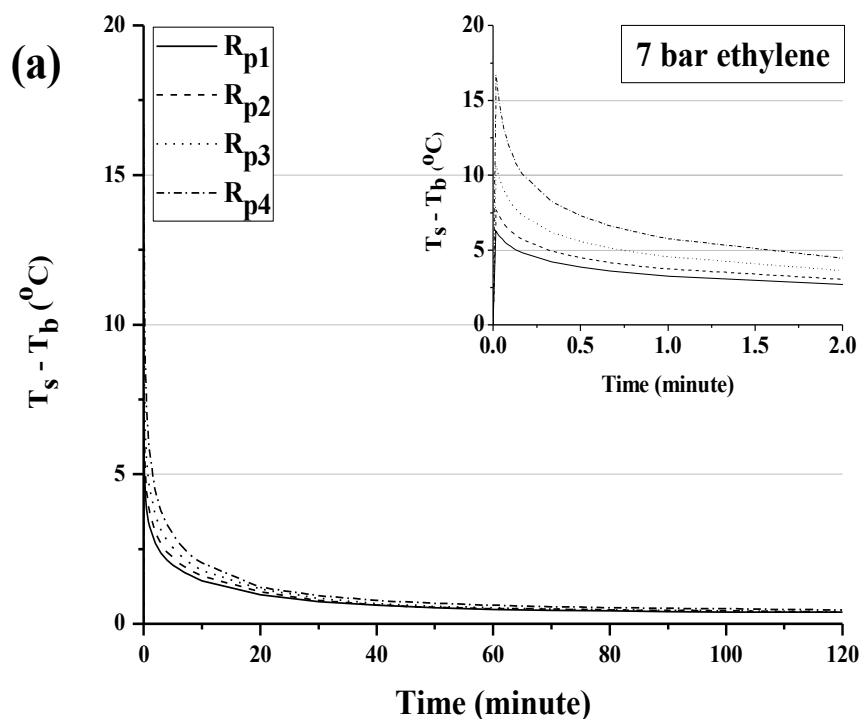
Role of ICA – Single Particle Modelling

Role of ICA – Single Particle Modelling

- Interestingly, presence of ICA does not seem to have a major impact on predicted surface-bulk temperature gradients

Role of ICA – Single Particle Modelling

- Assumptions:
  - ➢ Know porosity (very low from some experimental work)
  - ➢ Constant crystallinity
  - ➢ Interaction parameters of the Sanchez-Lacombe equation of state account for crystallinity.

- Big question:
  - ➢ How does the crystallinity evolve? In particular, how does it evolve during the early stages of polymerisation?
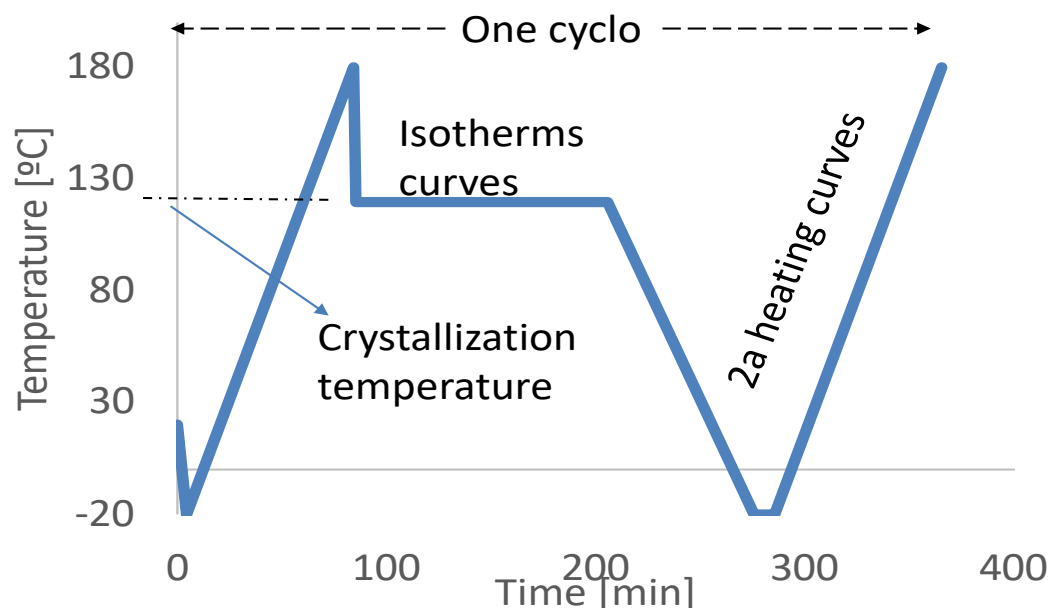
Role of ICA – Crystallisation vs polymerisation
Interpretation of lab scale kinetics

- ✓ Blends HDPE+ICA in the capsule medium pressure 120 µL

HDPE mass   ICA mass
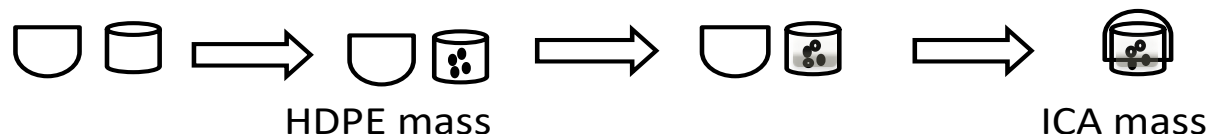
Samples	ICA concentration blends (y_{ICA})
HDPE70 and HDPE90	99.8 - 85 - 17 - 0 %

- ✓ The method in DSC consist in cycles for each crystallization temperature (Tc)

- Isotherms curves: time of crystallization;

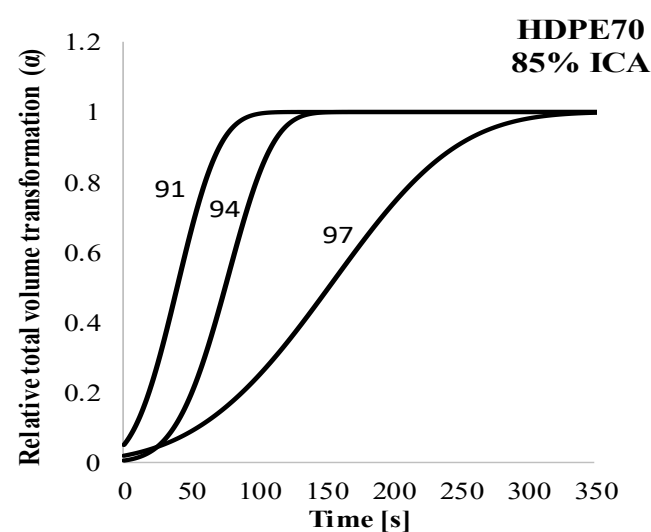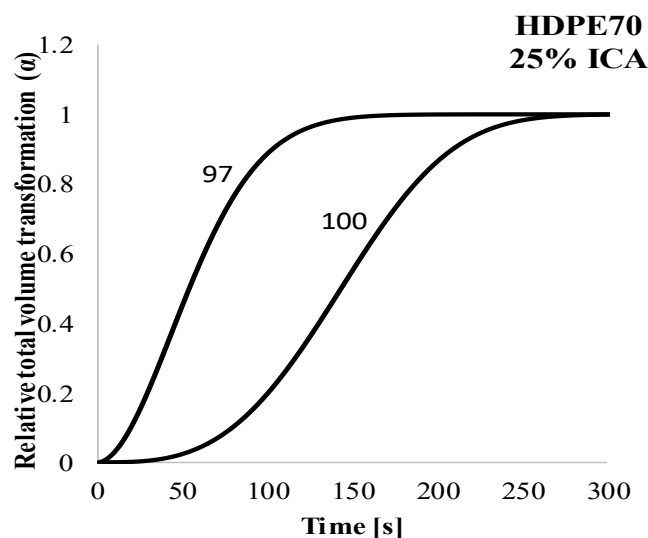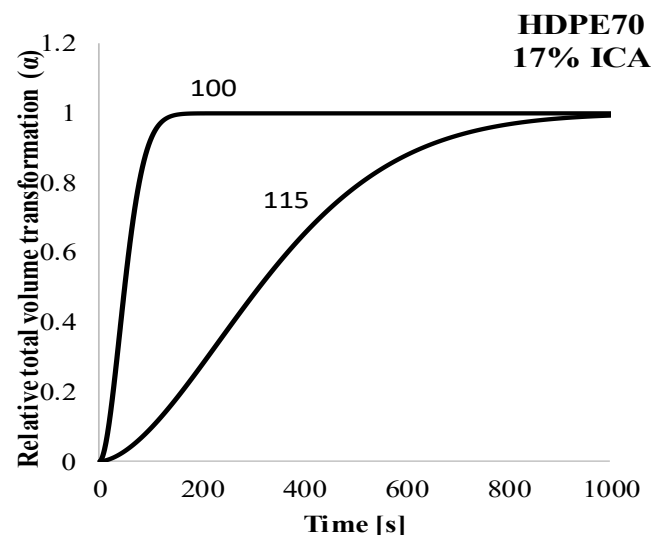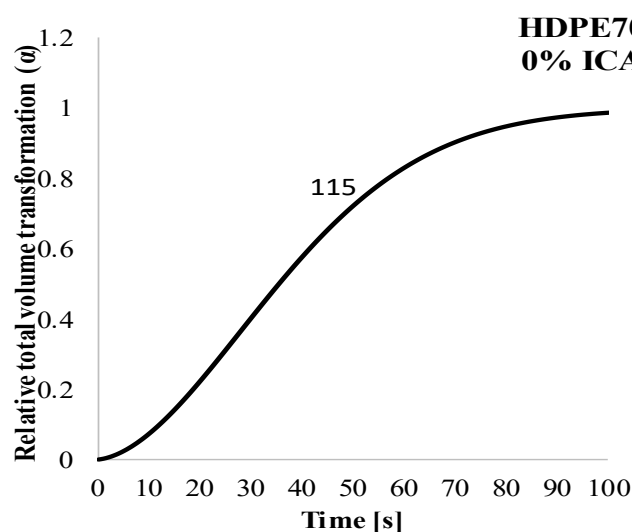- 2a heating curves: melting temperature and rate crystallization.

Role of ICA – Crystallisation vs polymerisation

- Obviously adding ICA changes important temperatures (implications for FBR operation!!)
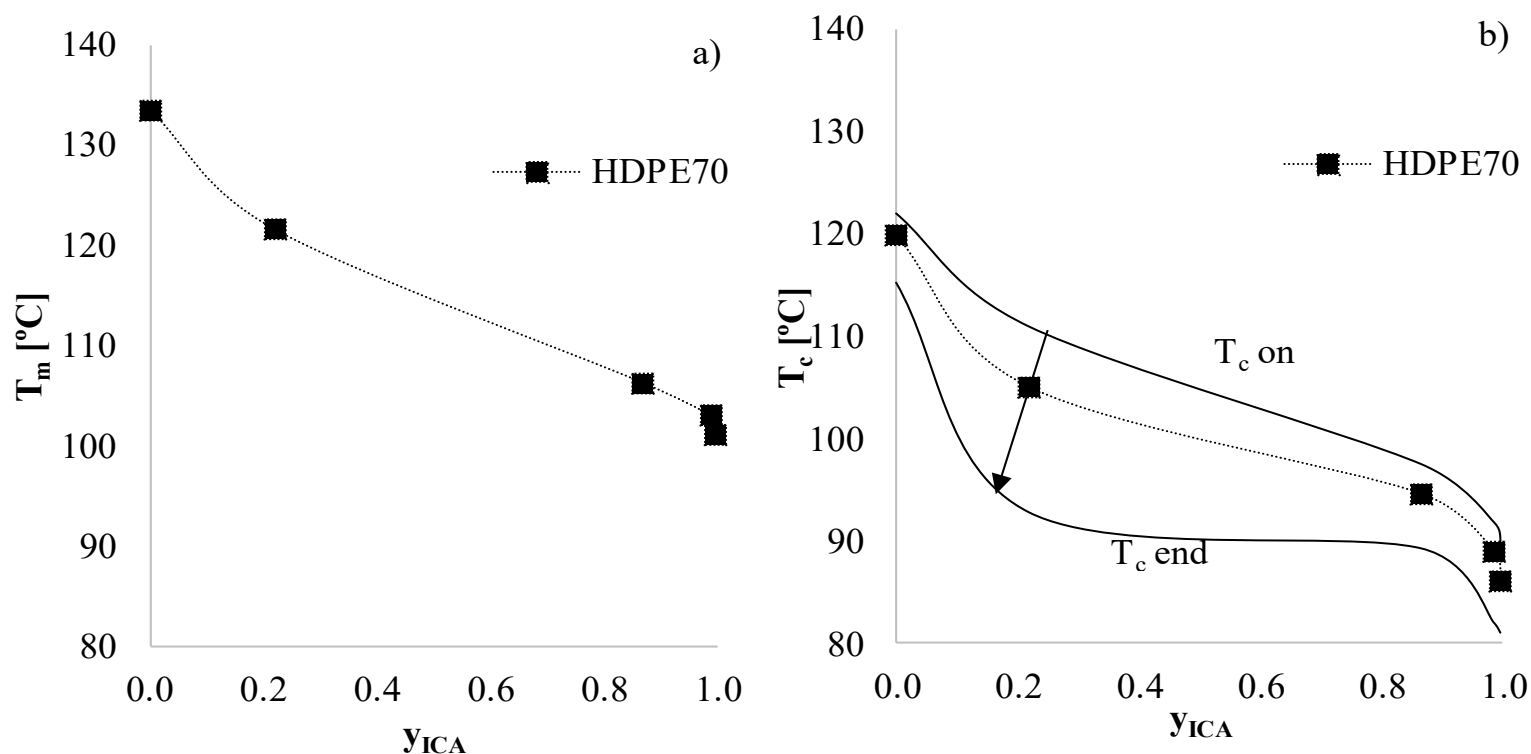
Role of ICA – Crystallisation vs polymerisation

- Time of crystallization can be quite long, even for low ICA levels

Role of ICA – Crystallisation vs polymerisation
Interpretation of lab scale kinetics

Parameters from second phase the thermograms for samples of HDPE70.

Tc	y_{ICA}	t	w_{c-iso}	ΔH_{iso}	T_m	w_{c-m}	ΔH_m
°C	%	min	%	J/g	°C	%	J/g
91	99.8	3.4	48.0	140.6	100.6	61.6	-180.5
	99	1.6	*	*	101.3	74.0	-216.7
	85	1.0	69.2	202.8	105.1	68.1	-199.5
	17						
	0						
94	99.8	13.4	25.9	75.8	102.2	69.4	-203.3
	99	4.5	*	*	103.1	72.9	-213.7
	85	1.7	69.4	203.3	105.5	67.9	-199.0
	17						
	0						
97	99.8	67.0	45.6	133.6	103.6	60.4	-176.9
	99	60.3	44.0	128.9	102.9	73.2	-214.6
	85	3.6	97.0	195.4	106.2	67.2	-196.9
	17						
	0						

# *Role of ICA – Crystallisation vs polymerisation*
Interpretation of lab scale kinetics

- HDPE / ICA blends form blends, and an equilibrium melt temperature depression and an increase in the crystallinity of HDPE were observed with the presence of ICA;

- The presence of ICA at high concentrations (99.8, 99 and 85%) significantly delayed the crystallization rate of HDPE.

- However much lower concentrations of ICA still impeded crystallization.

- Clearly the presence of ICA will have a significant impact on the initial rate.

- NEED TO BE VERY CAREFUL WHEN WE ATTEMPT TO ESTIMATE RATE CONSTANTS FROM LAB SCALE DATA!!!!

General Conclusions
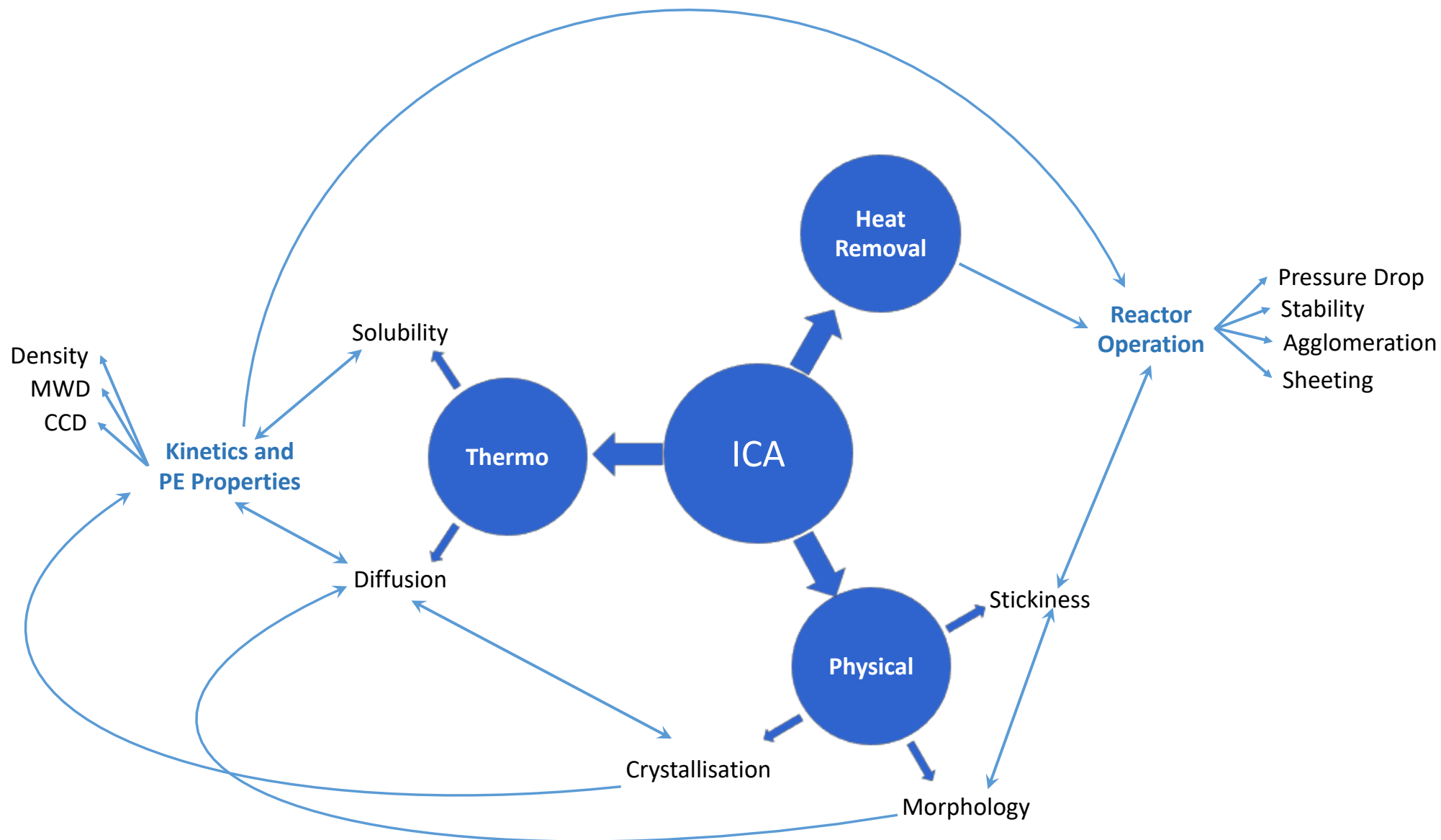
General Conclusions

- Reliable reactor and particle models NEED a good representation of solubility and diffusivity.

  - ➢ Assuming binary/additive solubilities will cause no end of problems

  - ➢ Will be more complicated in the case of 3 or more penentrants

    - ◗ Did not show here, but if one has hexane PLUS hexene, solubility of ethylene is not the same as with just hexane

  - ➢ Even interpreting copolymerisation data will be incorrect if we do not account for cosolubility.

- Major Problem is a LACK OF DATA (reliable or otherwise!) for systems of 2 or more penetrants under reaction conditions.

  - ➢ Moving forward with an experimental campaign to resolve this… hopefully will talk to about this next time.
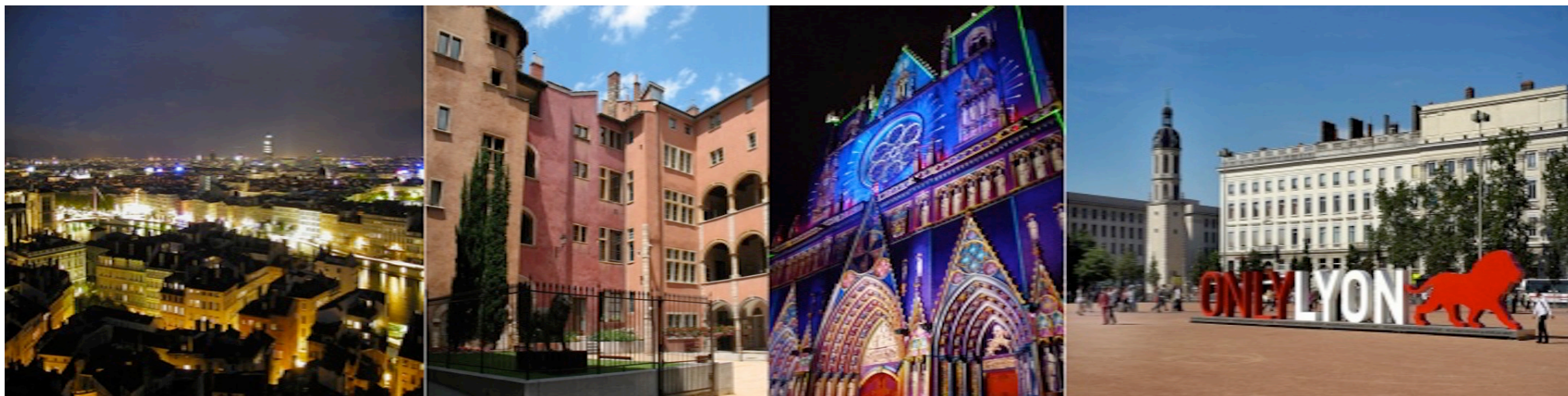
Contributors

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Dr. Muhammad BASHIR,Ms. Rita ALVES, Dr. Montree Namkajorn

THANK YOU FOR YOUR ATTENTION

Role of ICA – Single Particle Modelling