



“Accelerating New Petrochemical Product Development using Integral Modeling Technique”

Presenters

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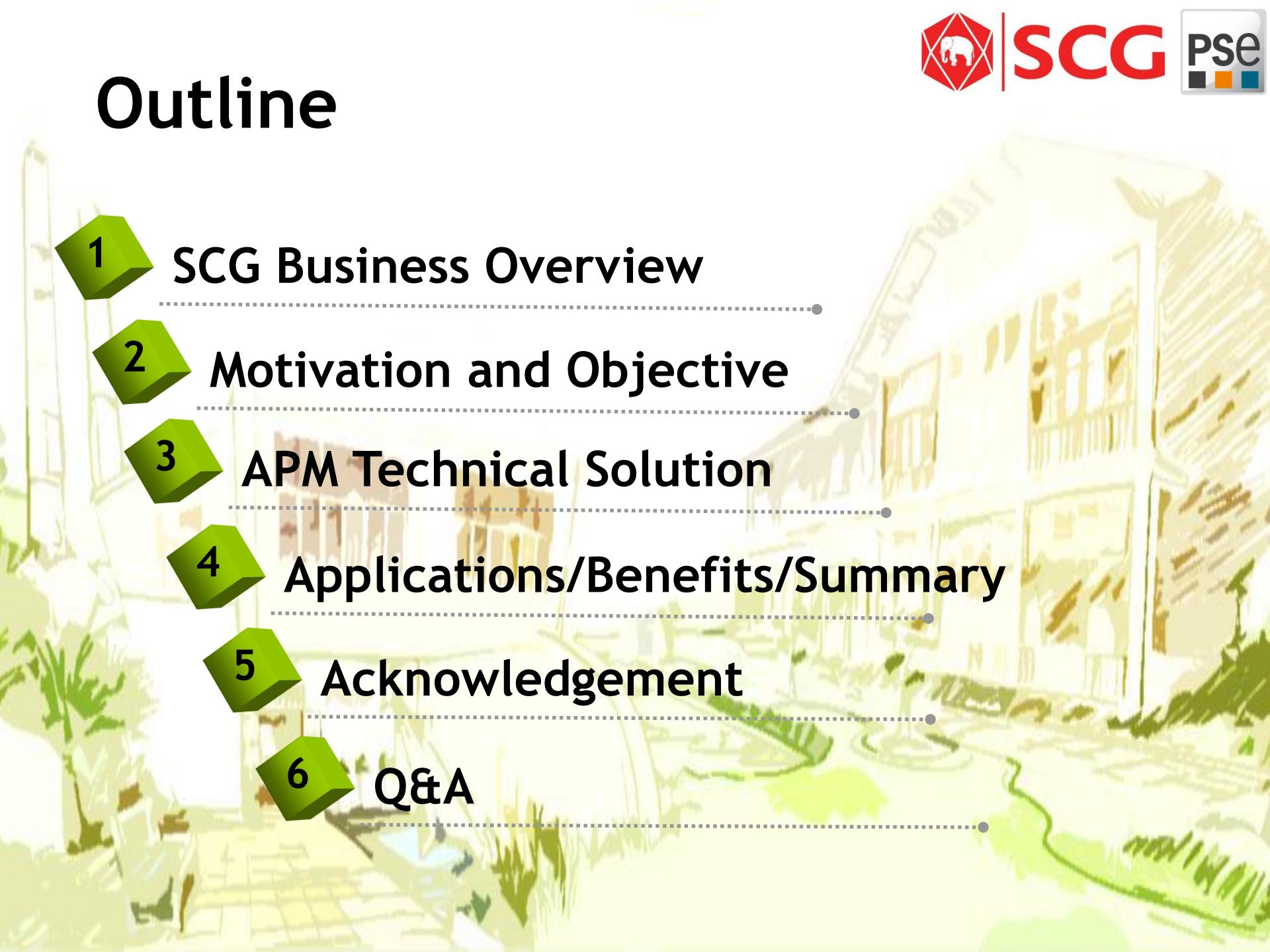
Mr.Choosak Kiwjaroen

Lead Engineer-Process Innovation, SCG Chemicals, Thailand

Dr.Alejandro Cano

Head of Consulting, Process System Enterprise, USA

Outline

- 
- 1 SCG Business Overview
 - 2 Motivation and Objective
 - 3 APM Technical Solution
 - 4 Applications/Benefits/Summary
 - 5 Acknowledgement
 - 6 Q&A



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SCG Business Overview



Siam Cement Group (SCG) Overview

One of Thailand's largest conglomerate ... 100 years old in 2013

- Siam Cement Public Co., Ltd. (SCC) founded in 1913
- \$18.4 billion in market cap. (Top 5 in Thailand's stock market)
- 3 Business Groups: Historic roots in **Cement and Building Materials** , with diversification into **Paper**, and **Chemicals**.



Chemicals



Paper



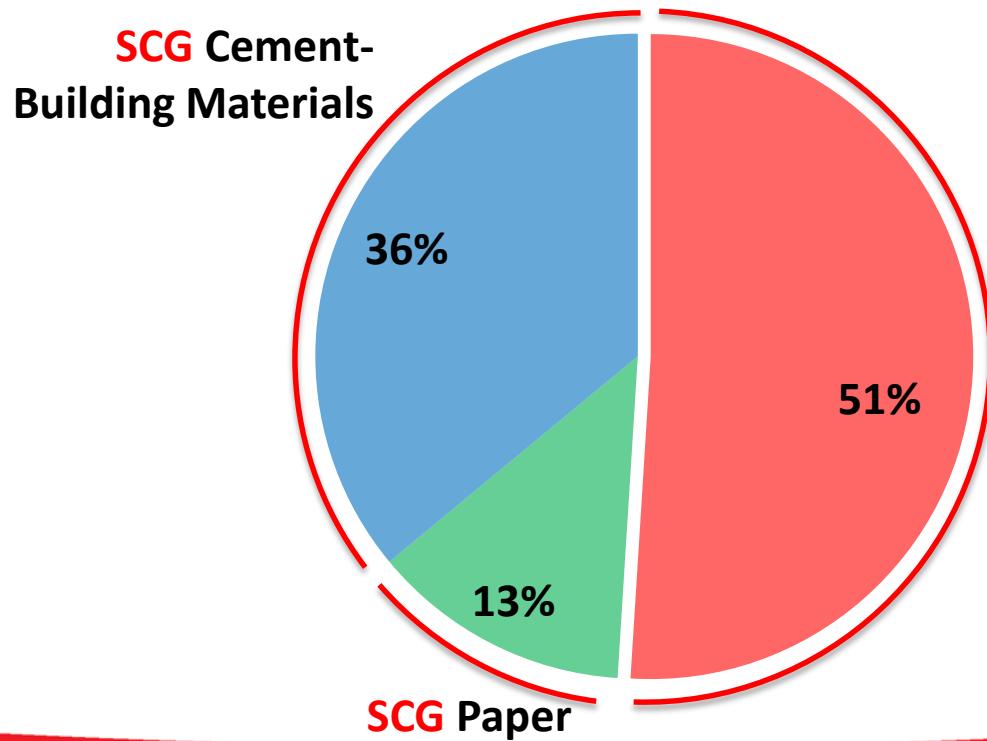
Cement



Building Materials

SCG has consistently grown into a strong Regional company

SCG Revenues Y2014



<i>Companies :</i>	Over 200
<i>Products :</i>	Over 60,000
<i>Assets Size :</i>	US\$ 14.5 billions
<i>Employees :</i>	Over 48,000

SCG Chemicals contributes about half of the whole SCG's performance

SCG Chemicals

- **SCG Chemicals Co., Ltd.** is the holding company for SCG's chemicals businesses, established in 1986
- One of ASEAN's largest integrated producers of upstream and downstream petrochemical products
- Successful partnership with world-class leaders such as



Mitsui Chemicals



MITSUBISHI RAYON CO., LTD.



Worldwide market coverage thru overseas offices

- Offices in Vietnam, Indonesia, Philippines, China, Dubai, Singapore, Japan
- Investment in Vietnam, Indonesia, Iran, China



Oil & Gas

Petrochemicals

Fabrication

Feedstock

Upstream

Intermediate

Downstream

Converter



- Naphtha
- LPG

- Ethylene (C2)
- Propylene(C3)
- Mixed C4
- Benzene

- PTA
- MMA
- EDC/VCM
- Styrene

- Polyethylene
- Polypropylene
- PVC
- PET
- Polystyrene
- PP compound
- PE compound
- Formulation products

- Pipe & Profile
- Acrylic cast sheet

"A complete chemical solution to fulfill your everyday needs"





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Motivation & Objective



Product Development Cycle



Market
Trend/Custo
mer Need



Pilot Plant
Prototyping



R&D
Lab scale
prototyping

5
4
3
2
1

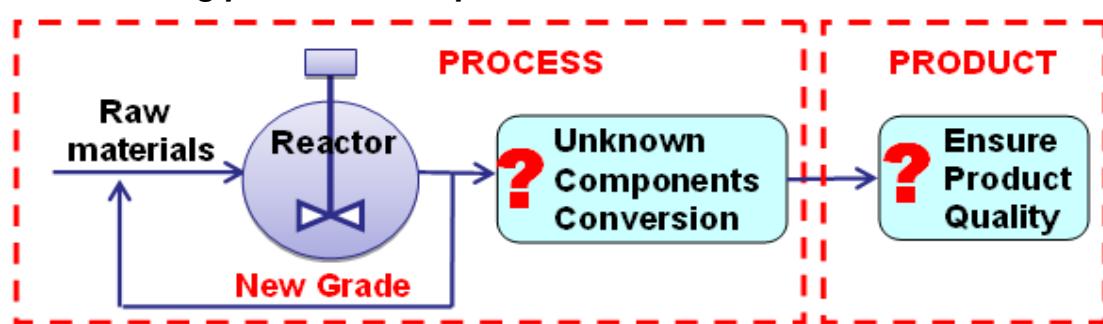
Why do we need “Advance Modeling”?

For New Petrochemicals Product Development (NPPD)



Business Problem faced

- High plant trial cost
- Long product development time



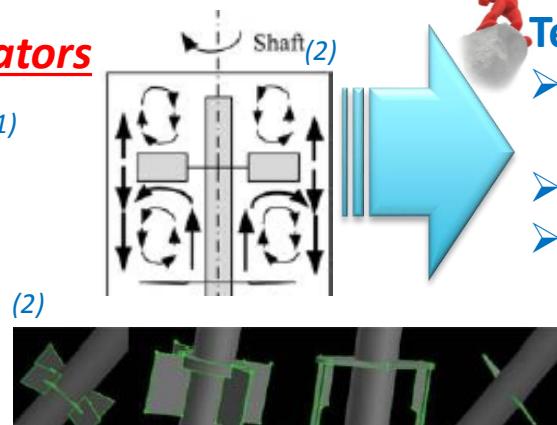
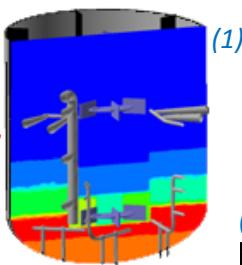
- Reduce plant trials
- Reduce losses
- Reduce risks
- Speed up development time

Technical Problem faced

Limitations of general Process simulators

- Highly non-ideal mixing
- Mass Transfer Limitation
- Complex system i.e. Reactions, catalysts
- Accuracy

$$\frac{\partial x_i}{\partial z} = \sum_{j=1}^3 \frac{[x_i N_j - x_j N_i]}{c_i D_{ij}}$$

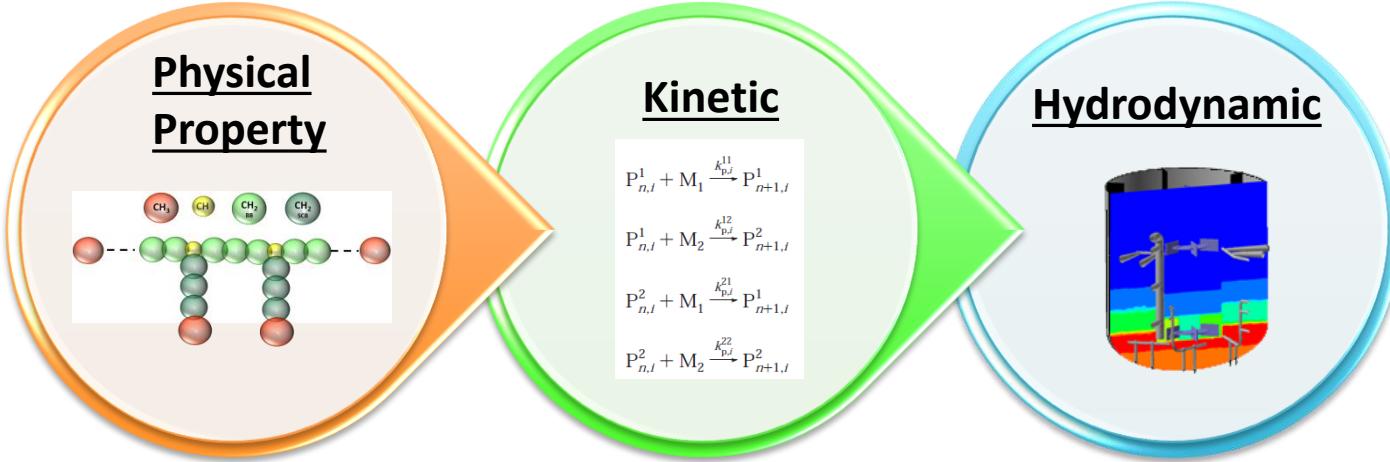


Technical Solved...

- gPROMS Custom modeling
- gSAFT
- Multizonal CFD

Objectives & Scopes of work

The project objective is to develop the prototype of polyolefin model with integration of



TO accelerate '**NPPD**' using *High fidelity Integral Modeling*

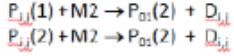
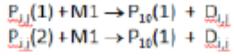
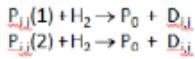
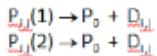
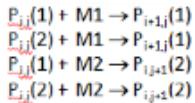
Scopes of work

- Phase 1: Physical properties research and model
- Phase 2: Prototype kinetic model research and model
- Phase 3: Multizonal CFD (*Integral Modeling Technique*)
- Phase 4: Kinetic Adjustment (*Future work*)

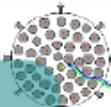
Key elements of PE polymerization model & Challenges

Challenge #2: Detailed Kinetic Parameters

Homo-/Co-Polymerisation
Reaction Chemistry

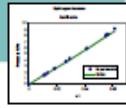


Polymer
particle
physics

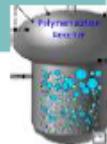


Challenge #1: Physical properties

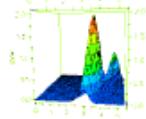
System
Thermodynamics



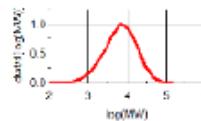
Reactor RTD/
Hydrodynamics



2D
co-monomer
distribution



1D
polymer
description



Polymer
properties

MI, ρ

Challenge #3: Hydrodynamics (mixing)

- 3 -

Advanced Process Modeling Technical Solution

Alejandro Cano – Head of Consulting

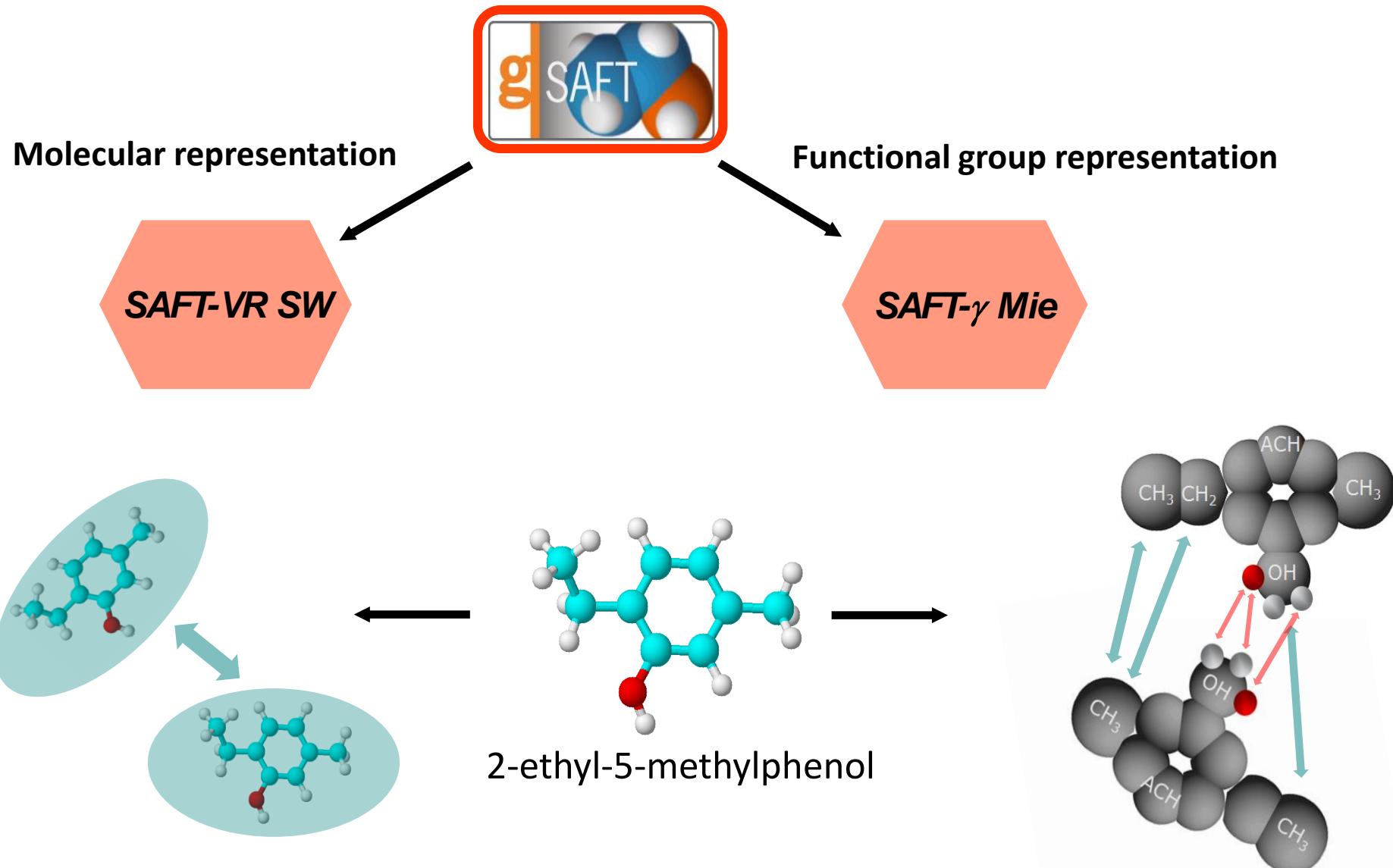


Features of a good model

- Challenge #1: Accurate physical properties:
 - Accurate prediction of heat release → temperature predictions
 - Accurate prediction of phase behavior
 - Accurate prediction of viscosity → gel effect
- Challenge #2: Detailed kinetics:
 - Predict shape of molecular weight distribution, not just M_n and M_w
 - Predict degree of long-chain and short-chain branching
- Challenge #3: Accurate hydrodynamics:
 - Account for deviations from ideal perfectly stirred reactors
 - Design details (geometry, internals, etc.) affect the residence time distribution of the various feeds.

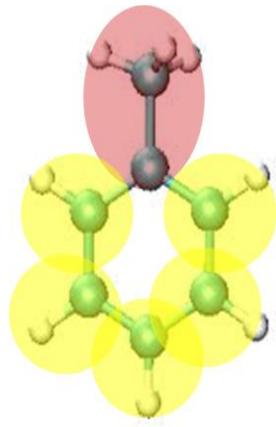
Challenge I.

Accurate physical properties

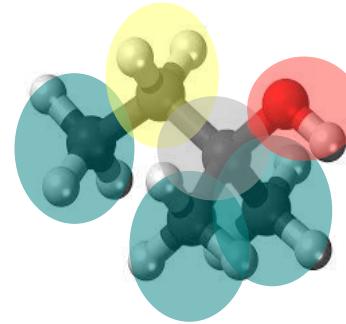


- Each molecule comprises one or more (generally non-identical) functional groups

toluene



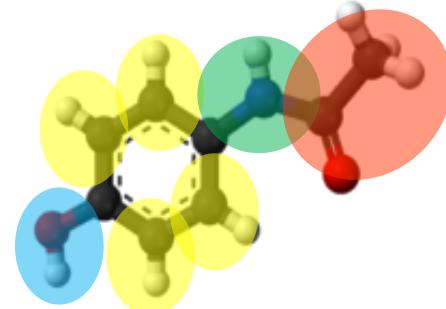
alcohols



carbonate ion

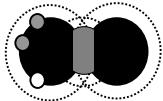


paracetamol



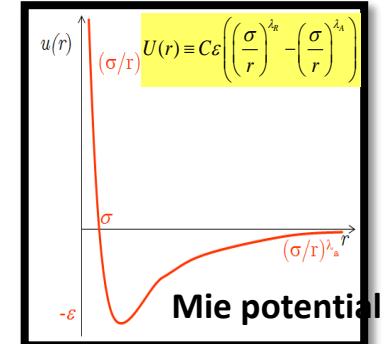
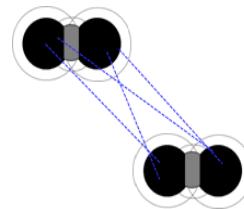
SAFT- γ Mie molecular model – II

- Each functional group comprises one or more identical segments

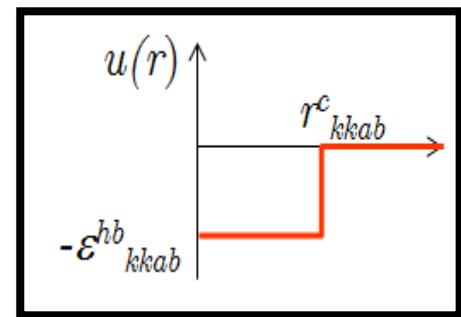
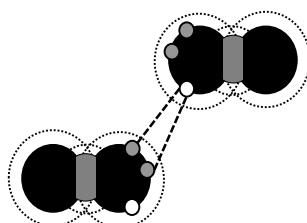


- ## ■ Interactions between segment

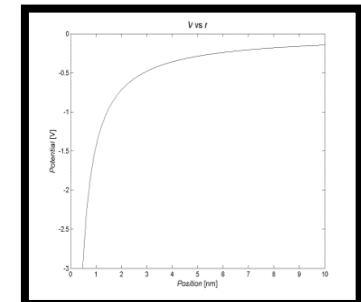
- dispersion/repulsion
(van der Waals) forces



- hydrogen bonding via off-centre electron donor/acceptor (“association”) sites



- ### – ionic (coulombic) forces



Increasing strength

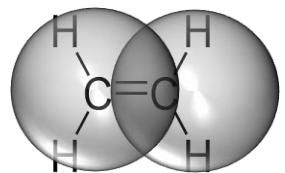
The values of the segment/segment interaction parameters
are (assumed to be) constant across
different molecules and mixtures
in different phases
under different temperatures, pressures and compositions

An approximation

- based on SAFT- γ Mie's fundamental molecular basis
- supported by considerable (& increasing) practical evidence

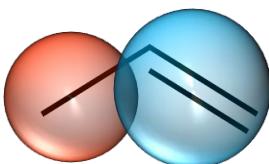
Group decomposition for the relevant species

ethylene



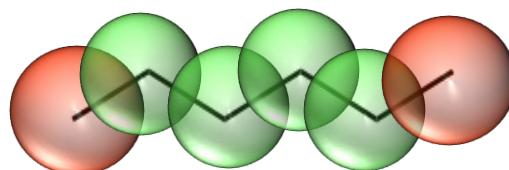
Modeled as a single group
 C_2H_4

propylene



Modeled with CH_3 , $\text{CH}_2=$ and
 $\text{CH}=$

n-alkanes



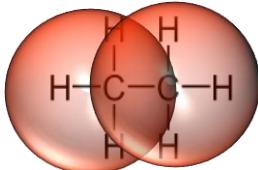
Modeled with CH_3 and CH_2
groups

methane



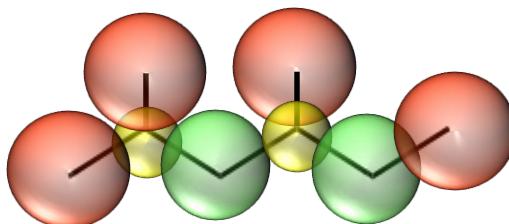
Modeled as a single group
 CH_4

ethane



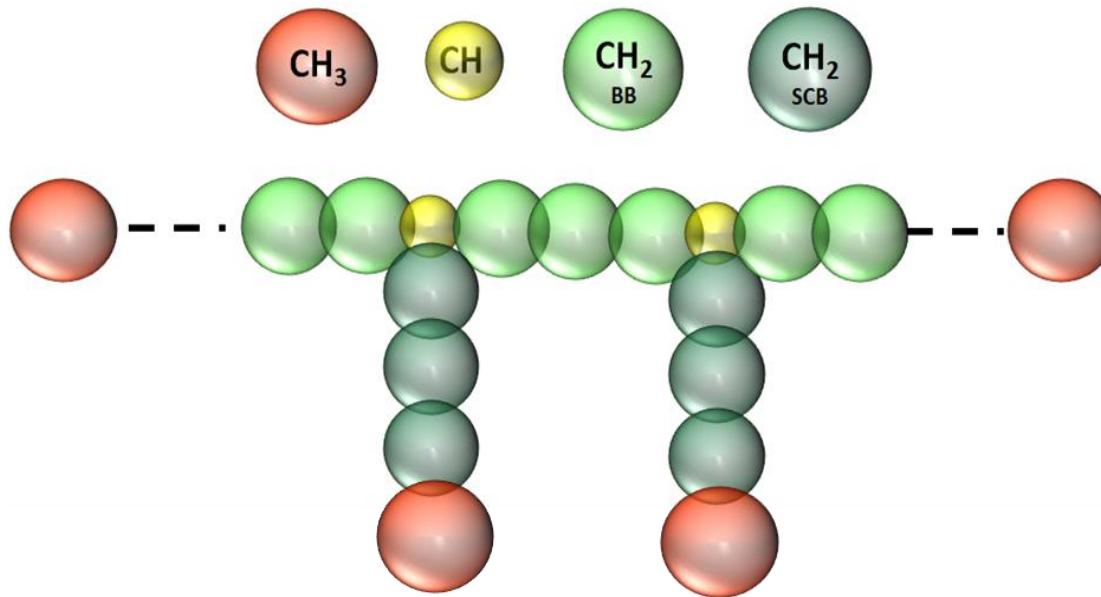
Modeled with two CH_3 groups

Branched alkanes



Modeled by introducing the CH group

gSAFT model for polyethylene



- A detailed group contribution model was developed for PE to account for the effect of branching, which is known to significantly impact cloud curves.
- Two new groups are introduced CH2_bb (CH_2 in the backbone) and CH2_scb (CH_2 in the short chain branches).
- If no branching information is provided, we assume that each branch contains 3 CH_2 groups.

gSAFT group-group interactions

All the compounds of interest can be represented by a combination of the following 9 functional groups

Groups	CH ₃	CH ₂	CH ₂ -bb	CH ₂ -scb	CH	CH ₂ =	CH=	C ₂ H ₄	CH ₄
CH ₃									
CH ₂									
CH ₂ -bb									
CH ₂ -scb									
CH									
CH ₂ =									
CH=									
C ₂ H ₄									
CH ₄									



group-group interactions in PSE's gSAFT databank prior to this project

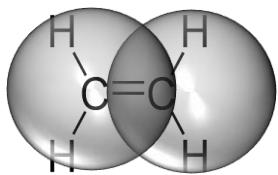


group-group interactions added to PSE's gSAFT databank during this project

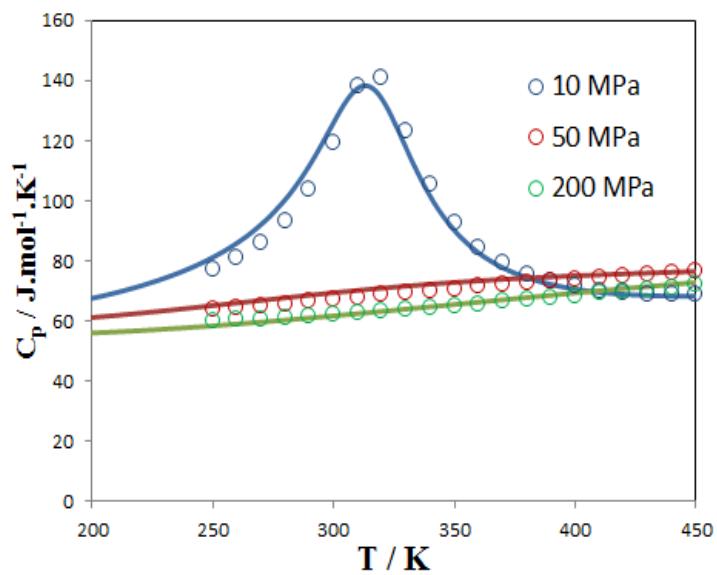
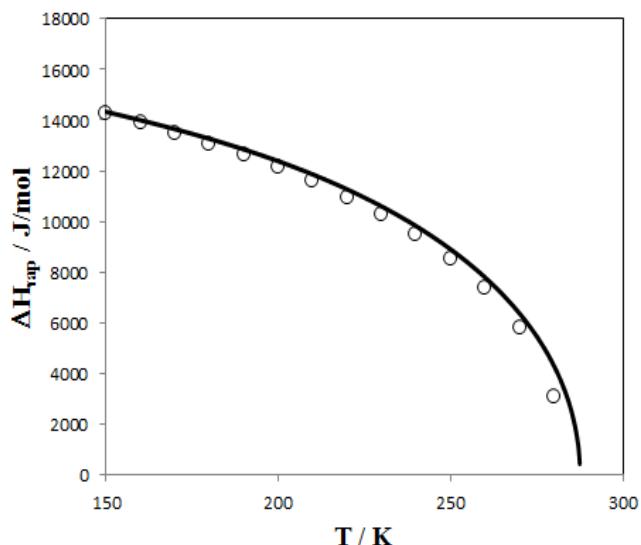
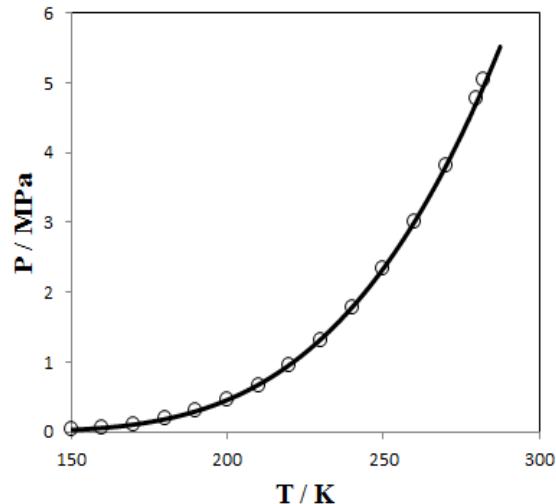
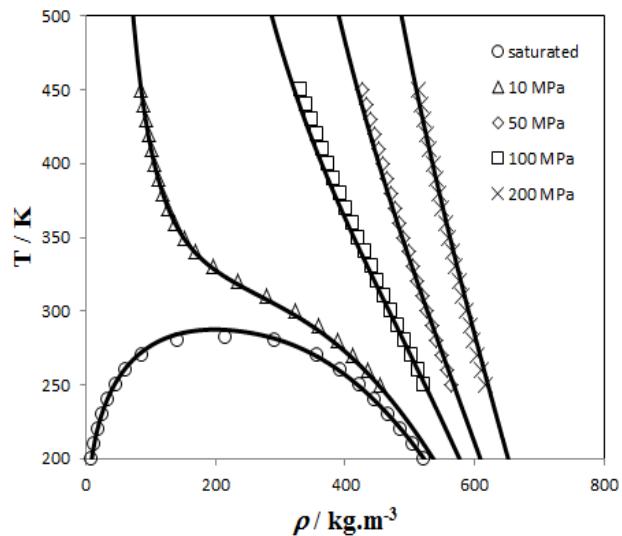


Parameters evaluated using combining rules

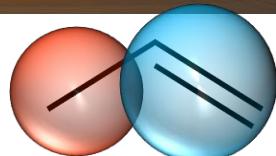
Ethylene



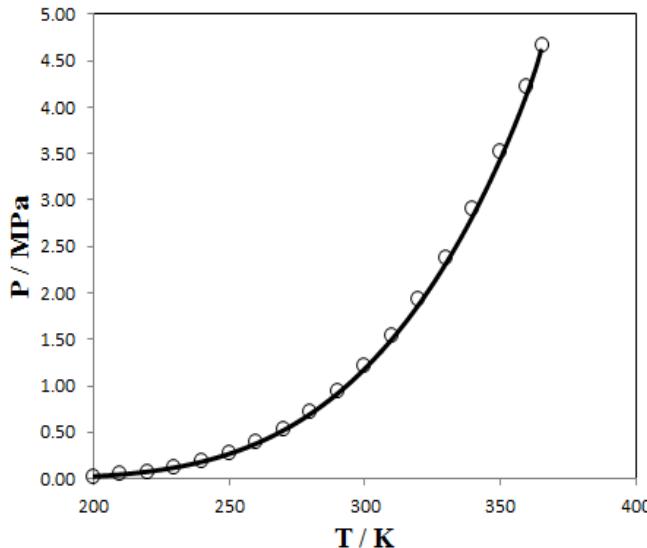
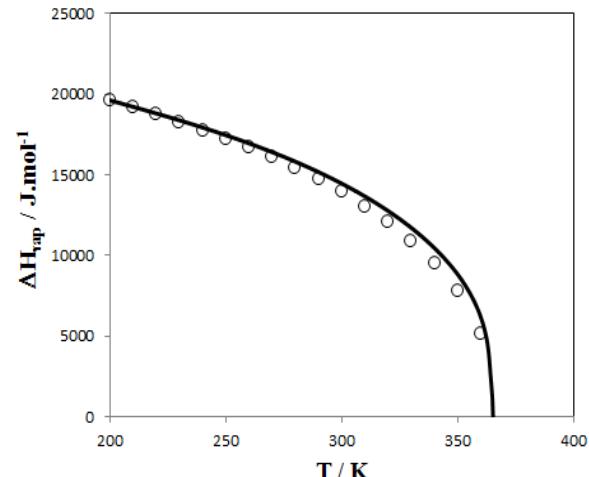
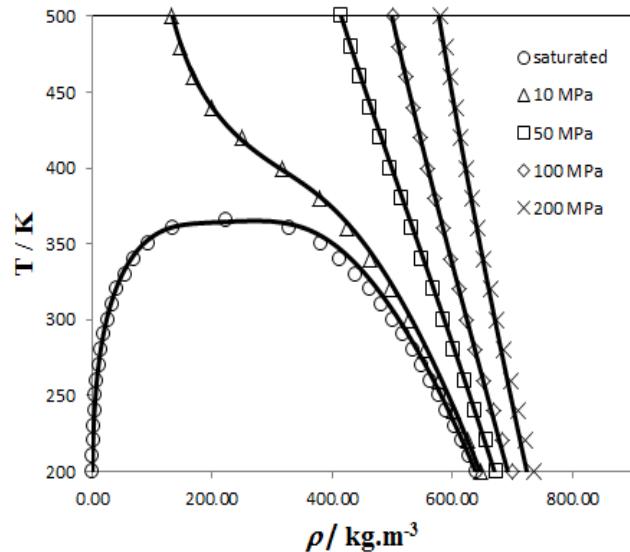
Experimental data : NIST (<http://webbook.nist.gov/chemistry>)



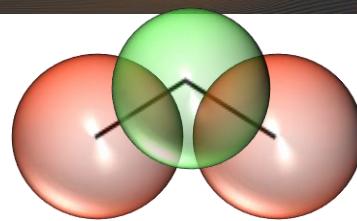
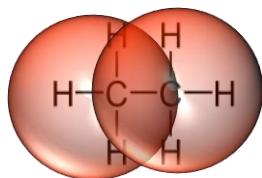
Propylene



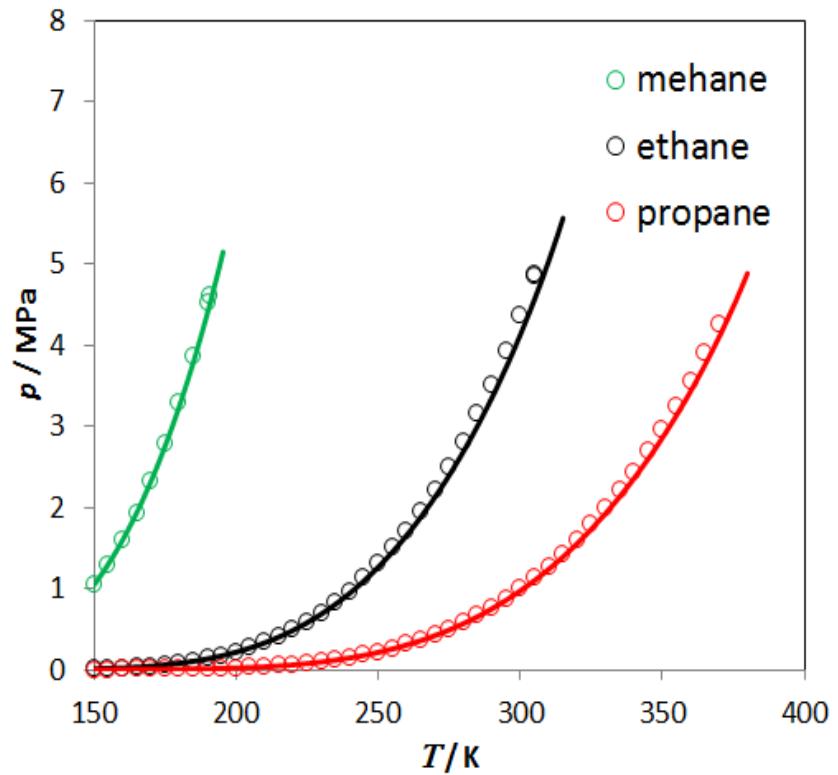
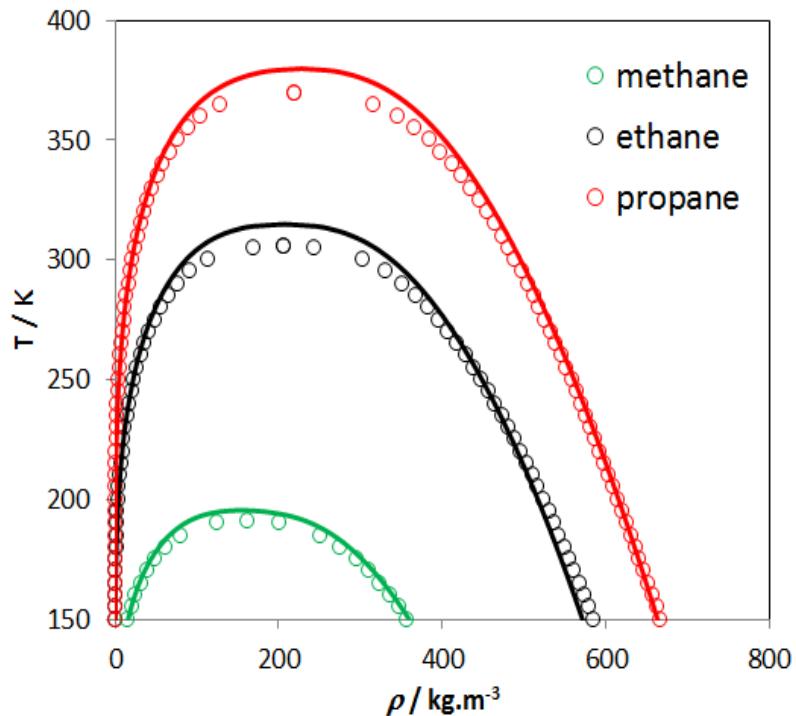
Experimental data : NIST (<http://webbook.nist.gov/chemistry>)



Methane / ethane / propane



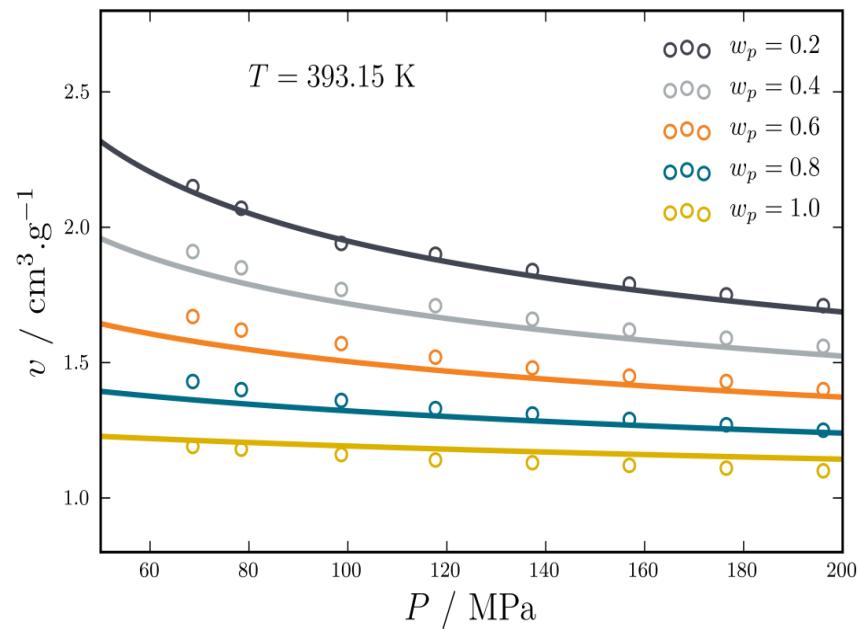
Experimental data : NIST (<http://webbook.nist.gov/chemistry>)



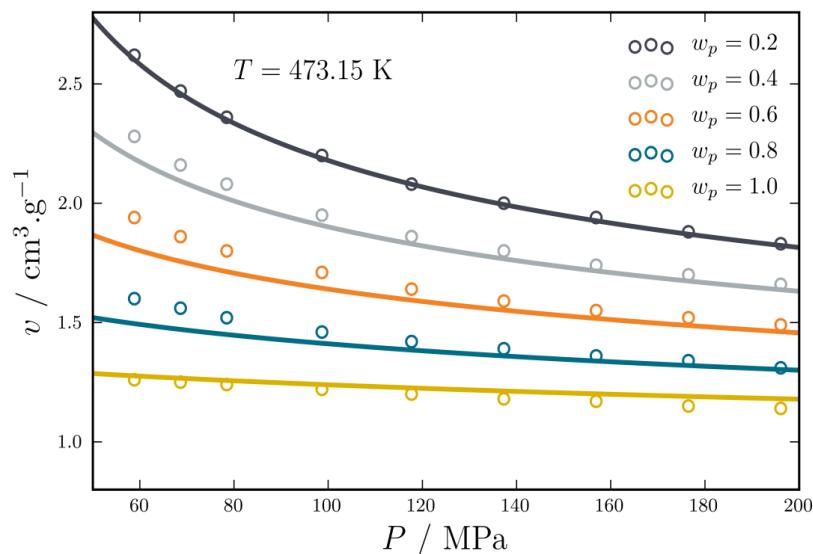
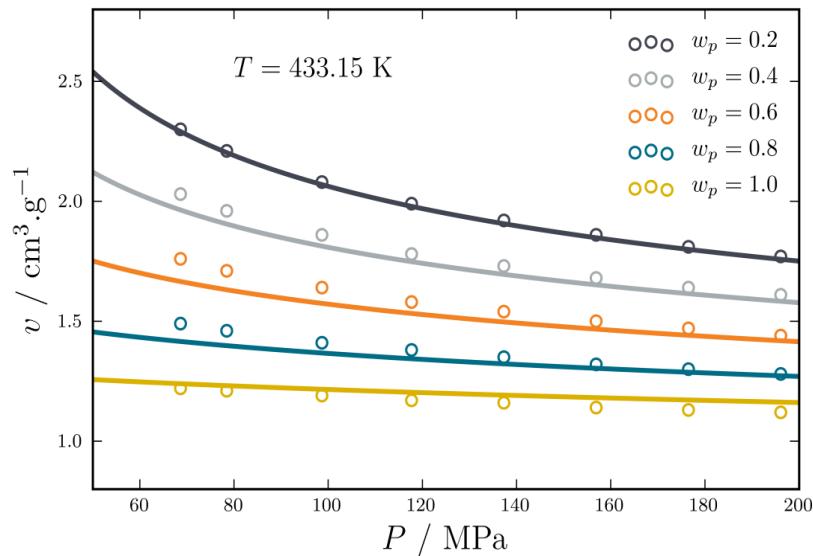
Ethylene + PE ($M_n=0.74 \text{ kg.mol}^{-1}$)

Pseudo components for PE ($M_w=1.6 \text{ kg.mol}^{-1}$, $M_n=0.74 \text{ kg.mol}^{-1}$)

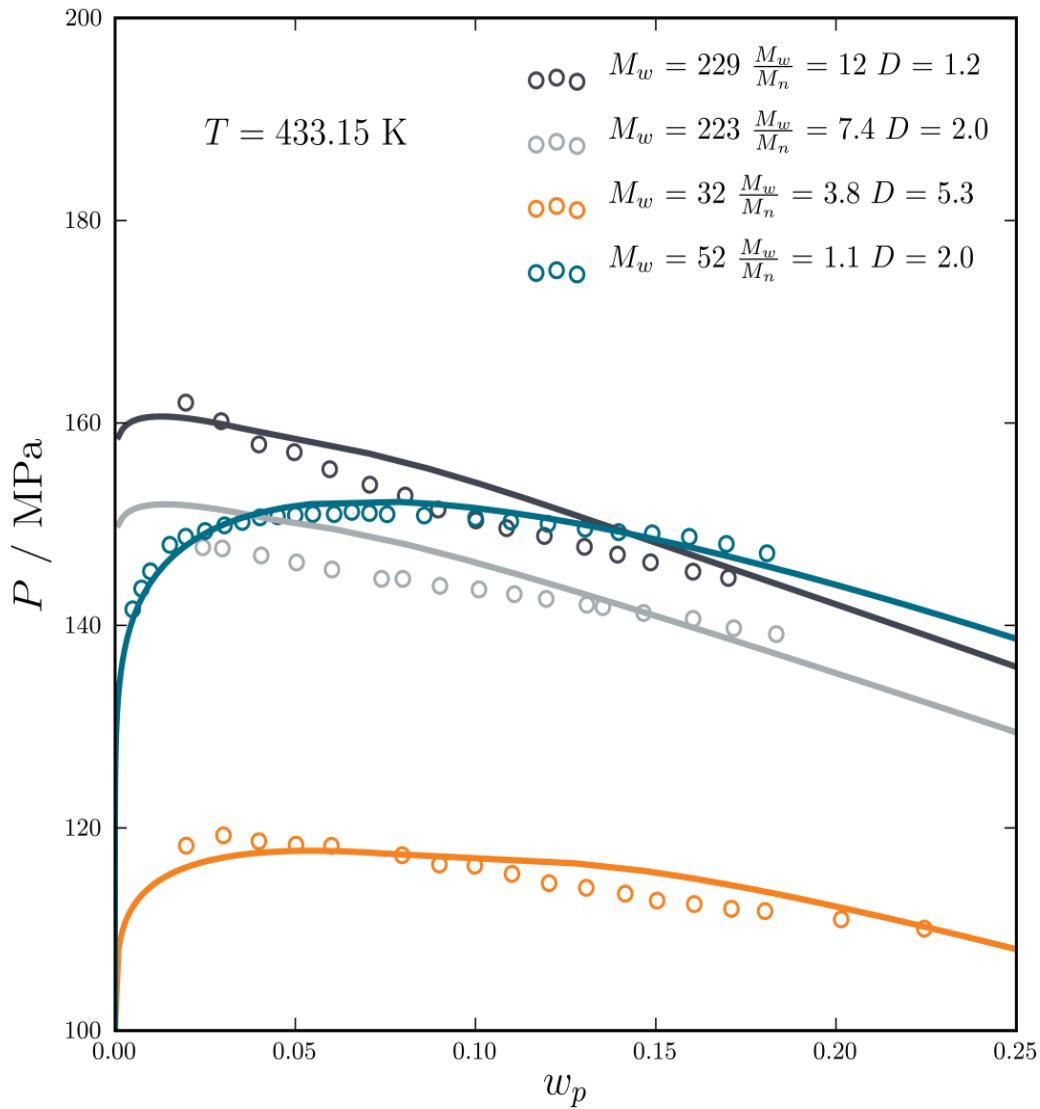
Index	w_i	$M_i (\text{g.mol}^{-1})$
1	0.230769	255
2	0.538462	1460
3	0.230769	3369



Single-phase densities comparing SAFT- γ Mie calculations and experimental data (Kobyakov, 1979)



LLE Ethylene-PE: Cloud curves

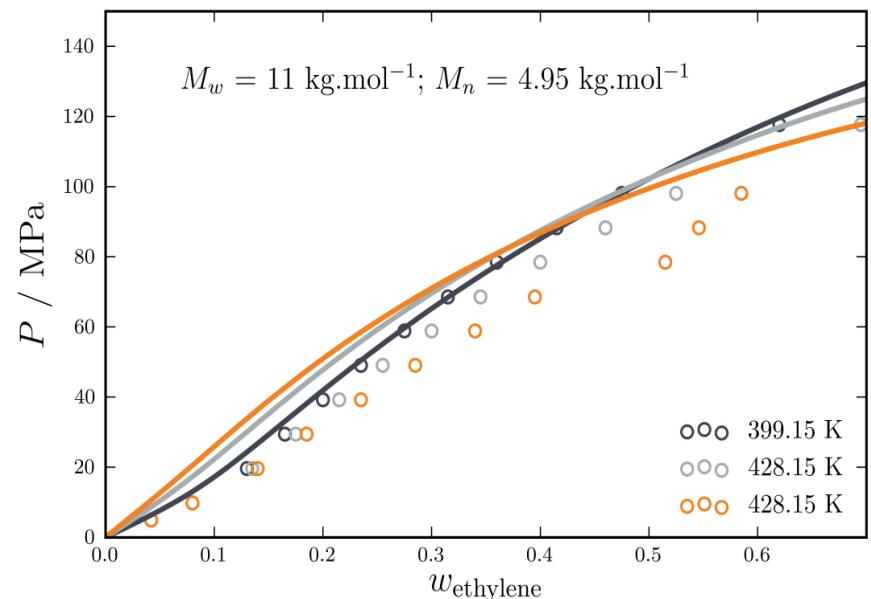


Cloud curves of ethylene + PE of various molecular weights and degree of branching (D, mol%), comparing SAFT-g Mie calculations and experimental data (**De Loos, 1995**)

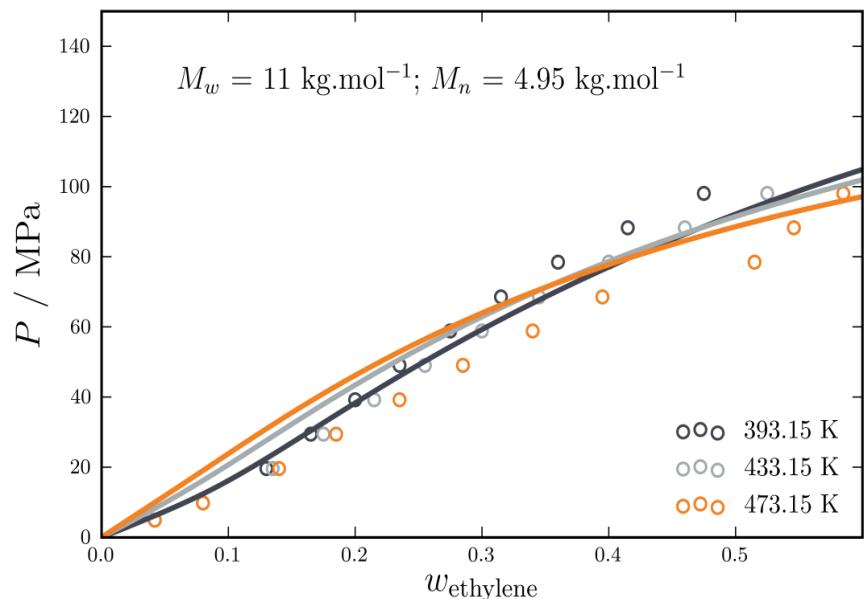
Model predicts impact of M_w , M_n , and degree of branching on the formation of a second phase

VLE, Ethylene+PE, $M_w=11\text{kg mol}^{-1}$ (Kobyakov, 1979)

Degree of branching=0%

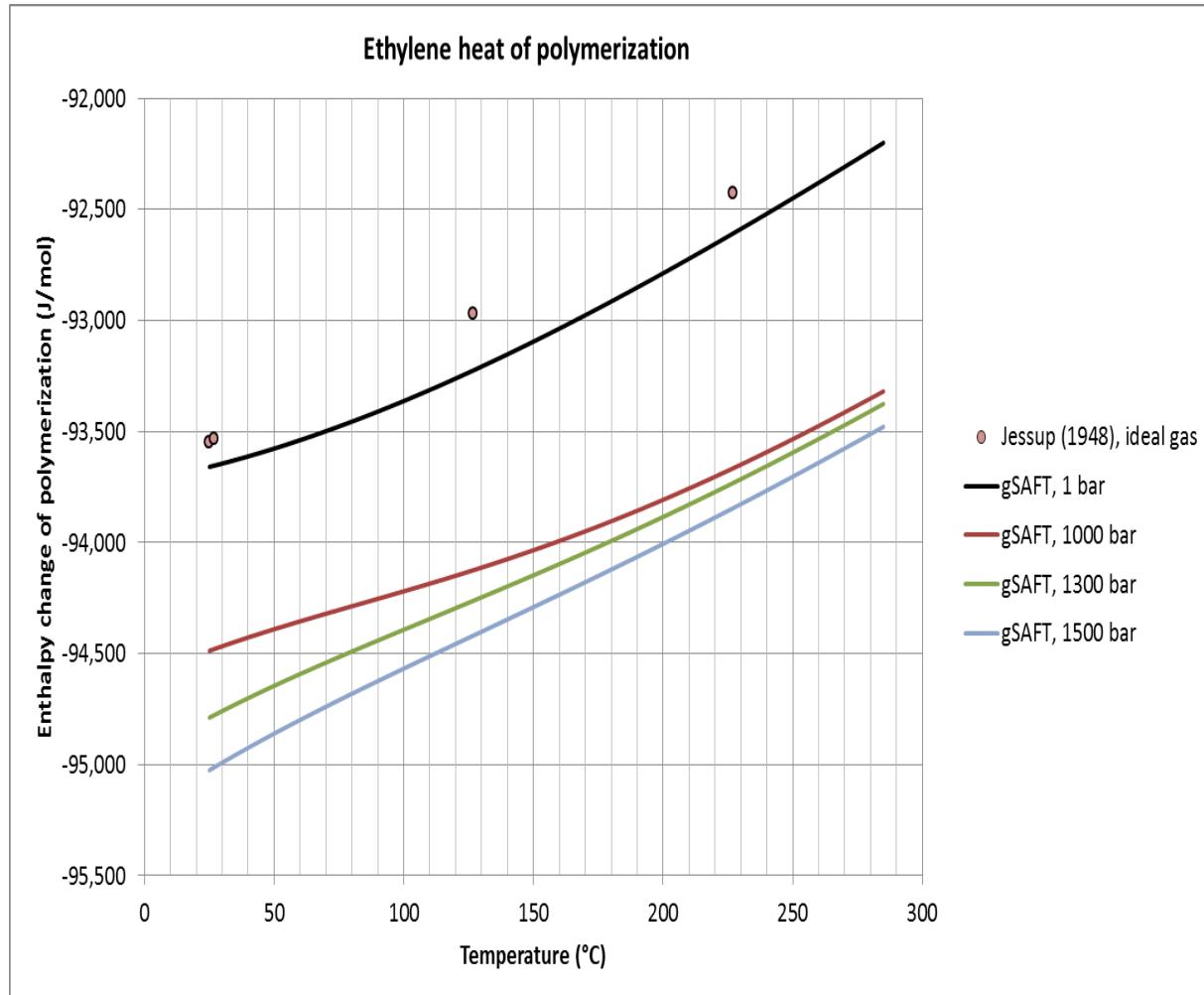


Degree of branching=2%



Prediction of VLE important for the modeling of downstream separation processes

Enthalpy of polymerization



- Rigorous thermodynamic model predicts impact of pressure and temperature on the heat of polymerization

1. gSAFT is able to provide a good description of the thermodynamic properties for the components involved in the PE production process
2. The group contribution approach allows for a straightforward modelling of polymer of varying molecular weight

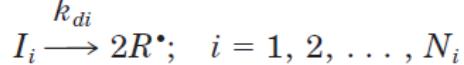
Challenge II.

Detailed kinetic modelling of PE reactions

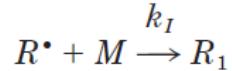
Example of a PE polymerization scheme from literature*



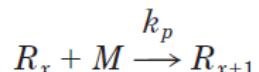
Initiation (by oxygen, peroxides, or azo compounds):



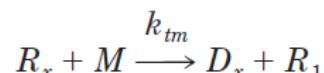
Chain initiation:



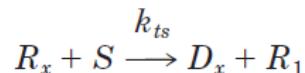
Propagation:



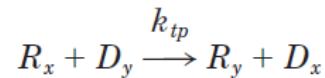
Chain transfer to monomer:



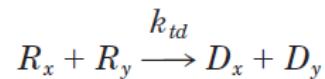
Chain transfer to solvent (chain-transfer agent):



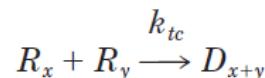
Chain transfer to polymer:



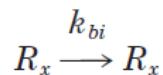
Termination by disproportionation:



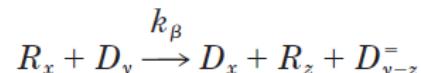
Termination by combination:



Intramolecular transfer (SCB):



β -Scission of sec- and tert-radicals:



* Pladis and Kiparissides, J. Appl. Polymer Science, 73, 2327-2348 (1999)

Features of kinetic scheme to be captured in a detailed kinetic model



- Different types of polymer chains:
 - Growing chains of various types (e.g. R_x , $R_x^=$)
 - Dead chains (e.g.)
- Reactions that add one monomer to the growing chain
$$R_x + M \xrightarrow{k_p} R_{x+1}$$
- Reactions that combine chains of different lengths
$$R_x + R_y \xrightarrow{k_{tc}} D_{x+y}$$
- Reactions that split chains into pieces of arbitrary length:
$$R_x + D_y \xrightarrow{k_\beta} D_x + R_z + D_{y-z}^=$$

Advantages of detailed kinetic model implemented over other commercial packages



- Full Molecular Weight Distribution (MWD) modeling.
 - Other packages use Method of Moments, which can only predict M_n , and M_w , but not the shape of the distribution
- Chain length distribution domain discretized using special techniques that optimize trade-off between accuracy and computational speed: Fixed Pivot Technique
- Model built on gPROMS platform
 - Allows use of powerful Parameter Estimation functionality to adjust kinetic parameters based on operating and GPC data from various PE grades
 - Allows use pf powerful Optimization functionality to adjust operating parameters to obtain polymer with desired MWD.

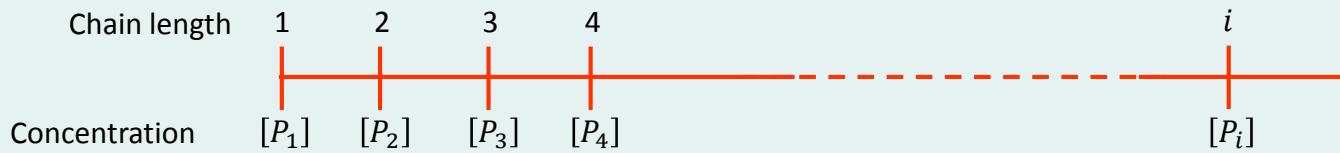
Molecular Weight Distribution, Average MW

- To find polymer concentration profiles, MWD, or the average MW, the kinetic rate expressions need to be integrated simultaneously in time.

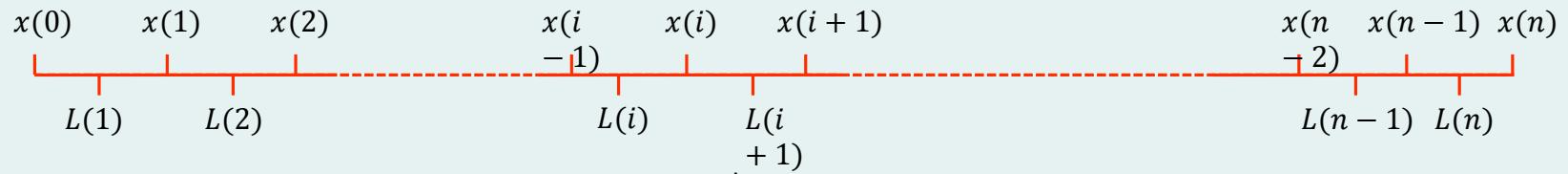
$$\frac{d\mathbf{D}}{dt} = f(\mathbf{D}; \mathbf{K})$$

- Generally maximum possible chain length of polymers can be of the order 10^7 which would generate about 10^7 differential equations. To solve these many DEs is not practical.
- The problem size must be reduced by
 - Chain length discretization (Number of DE \sim number of discretization points)
 - Solving the moments equations instead (Number of DE \sim number of moments considered)
- Note: The method of moments can be used to find only the average MW and not the MWD.

Method of Discretization, Method of Moments



$[P_i]$: concentration of polymers with chain length i



$L(i)$: Characteristic chain length of i^{th} grid with domain $[x(i-1) \ x(i)]$

$$P_i = \int_{x(i-1)}^{x(i)} [P_L] dL$$

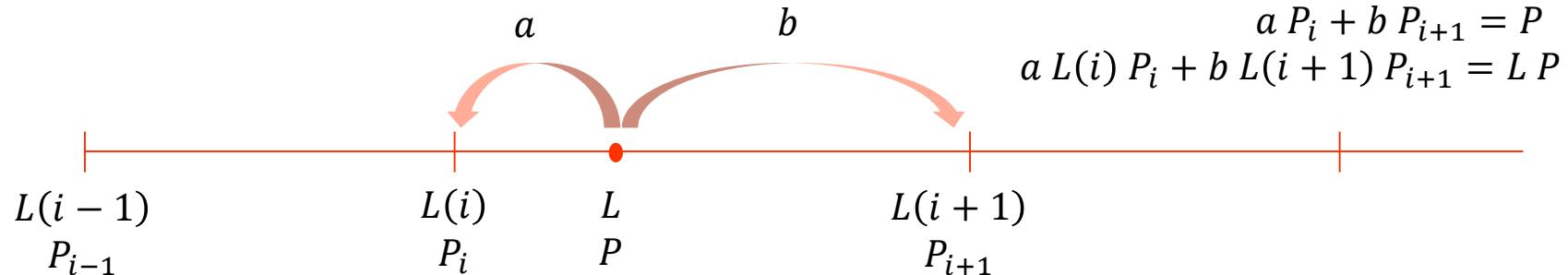
P_i : Lumped polymer concentration of all polymers in i^{th} element

kth moment of polymers: $\lambda_k = \sum_{i=1}^{\infty} i^k [P_i]$

0th moment: $\lambda_0 = \sum_{i=1}^{\infty} [P_i]$: Total number of polymer units

1st moment: $\lambda_1 = \sum_{i=1}^{\infty} i [P_i]$: Total mass of polymer units

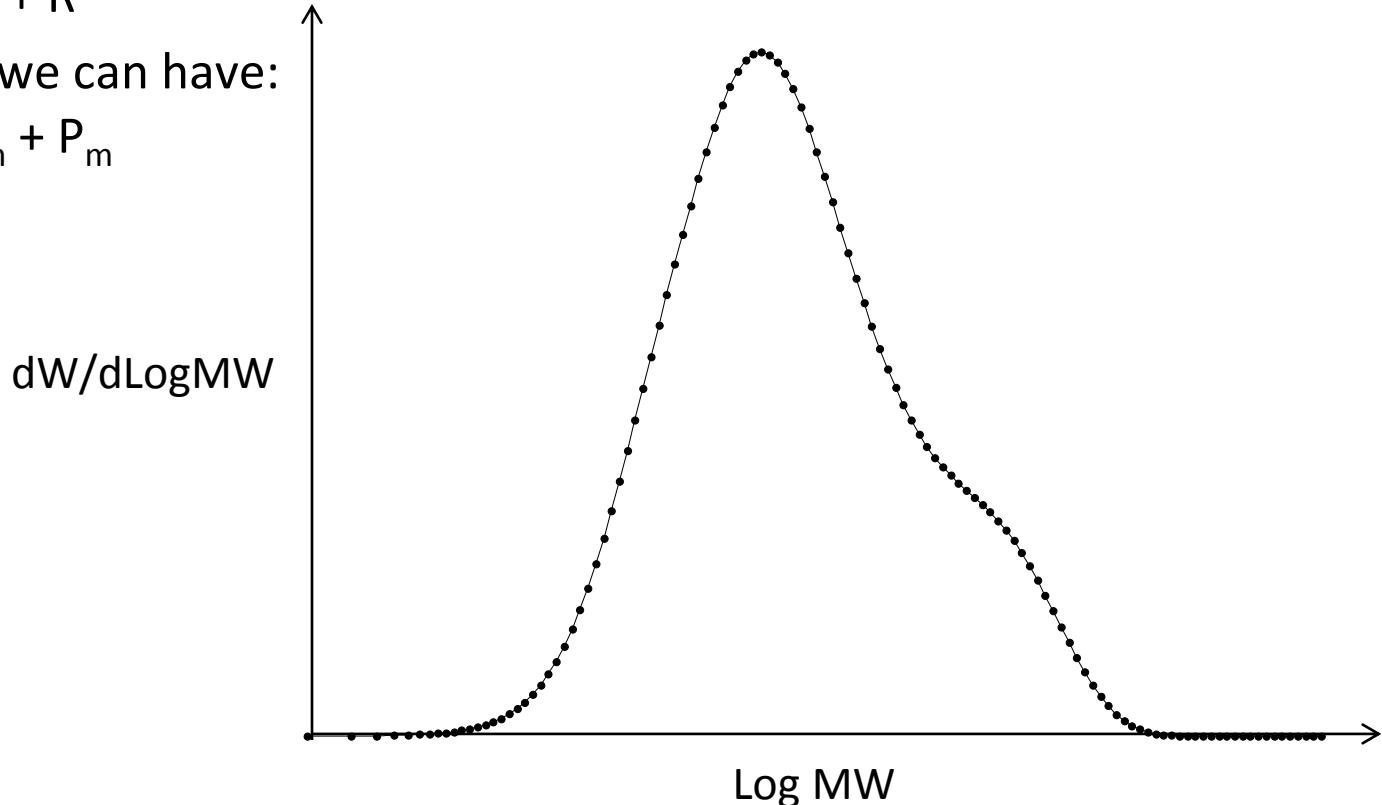
- When chains undergo propagation, combination, or scission, the resulting polymer may not lie exactly on the grid points.
- The concentration of the resultant polymer needs to be split between the neighboring grid points in such a way that two selected properties of distribution (generally number and mass) are conserved.
- This leads to matrices that quantify the fraction of a reaction product that is allocated to each grid point



Detailed kinetic model allows MWD prediction

- Example: beta scission reaction important for predicting high MW shoulder shape

- Most software use simplified mechanism that only considers $P_n \rightarrow D_{n-1} + R$
 - In reality we can have: $P_n \rightarrow D_{n-m} + P_m$

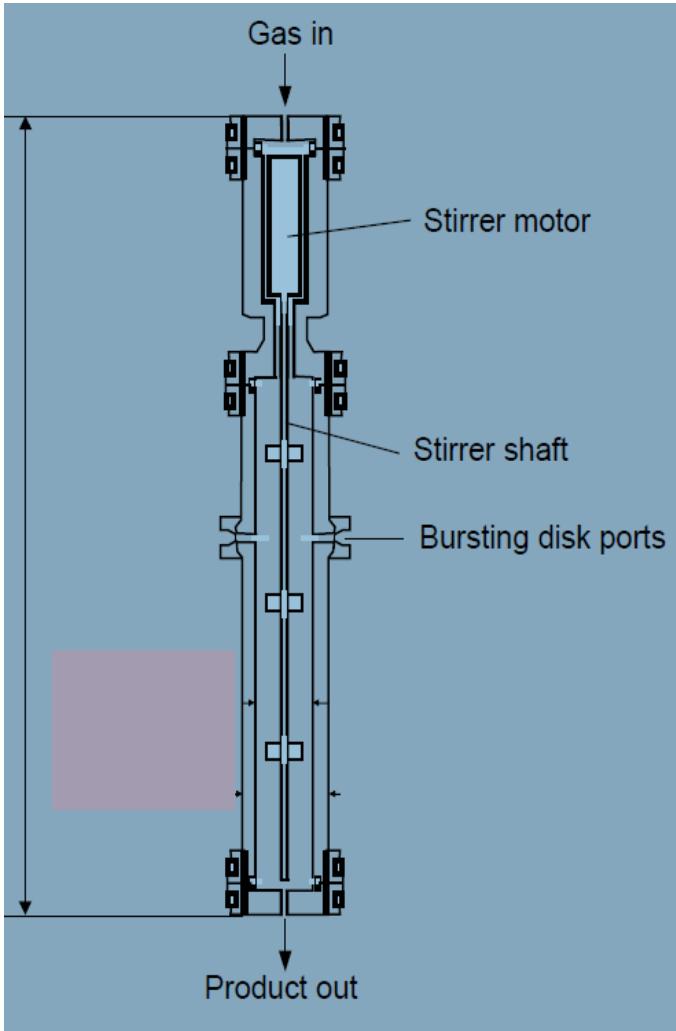


Challenge III.

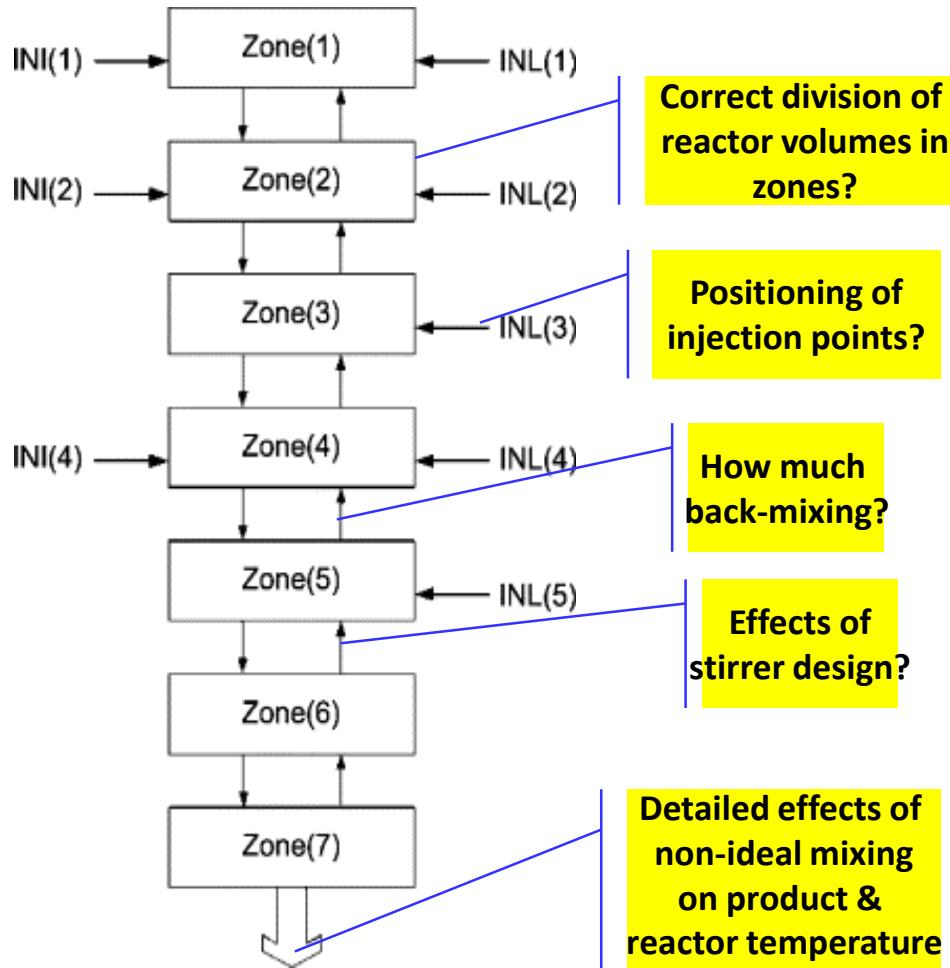
Accurate modelling of mixing imperfections in polymerization reactors

Hydrodynamic modeling of autoclave reactors (e.g. EVA)

Typical EVA autoclave reactor

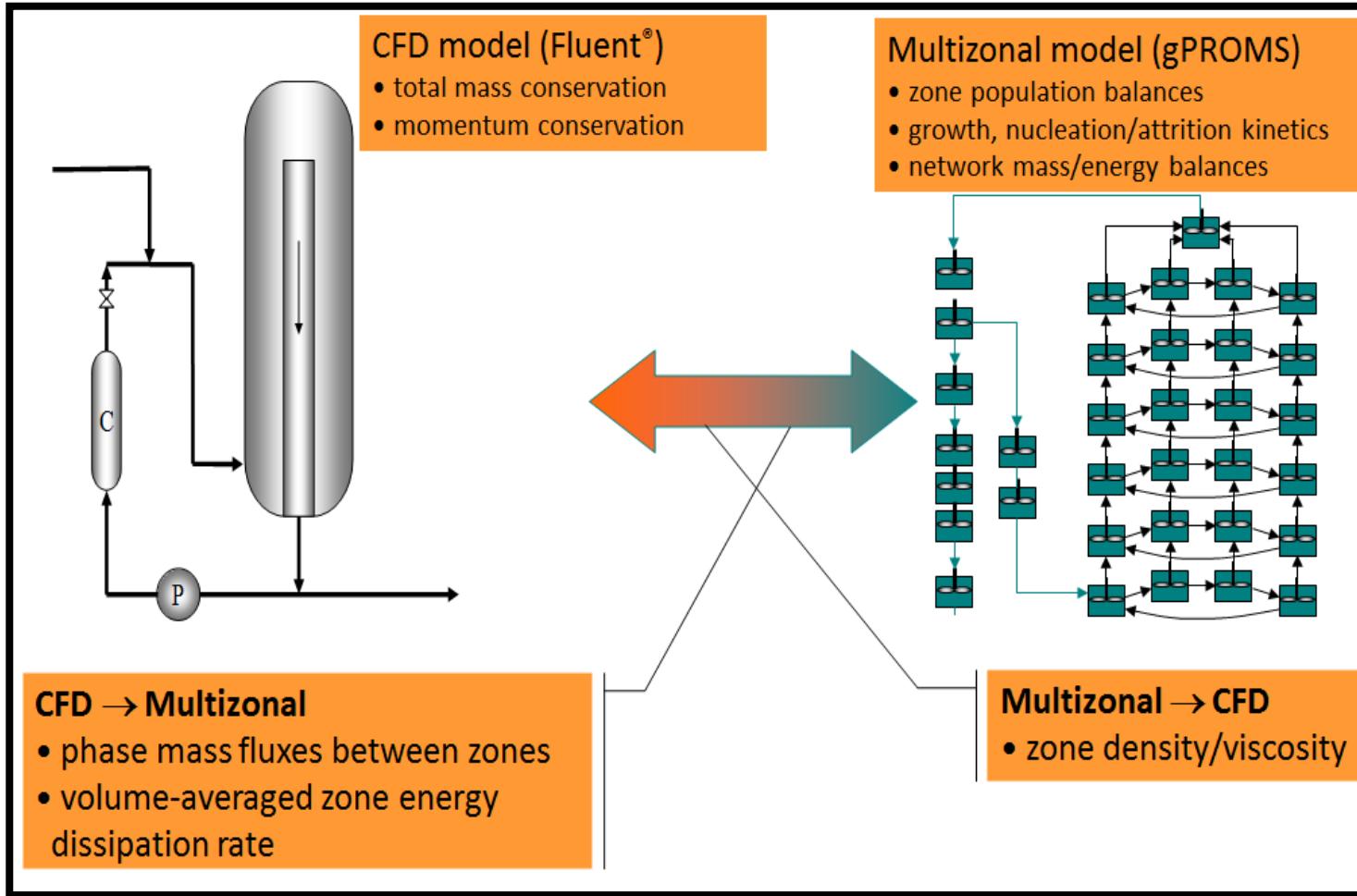


Typical model structure for EVA autoclave reactor



Some important questions

Hybrid Multizonal gPROMS/CFD modelling for agitated tank equipment



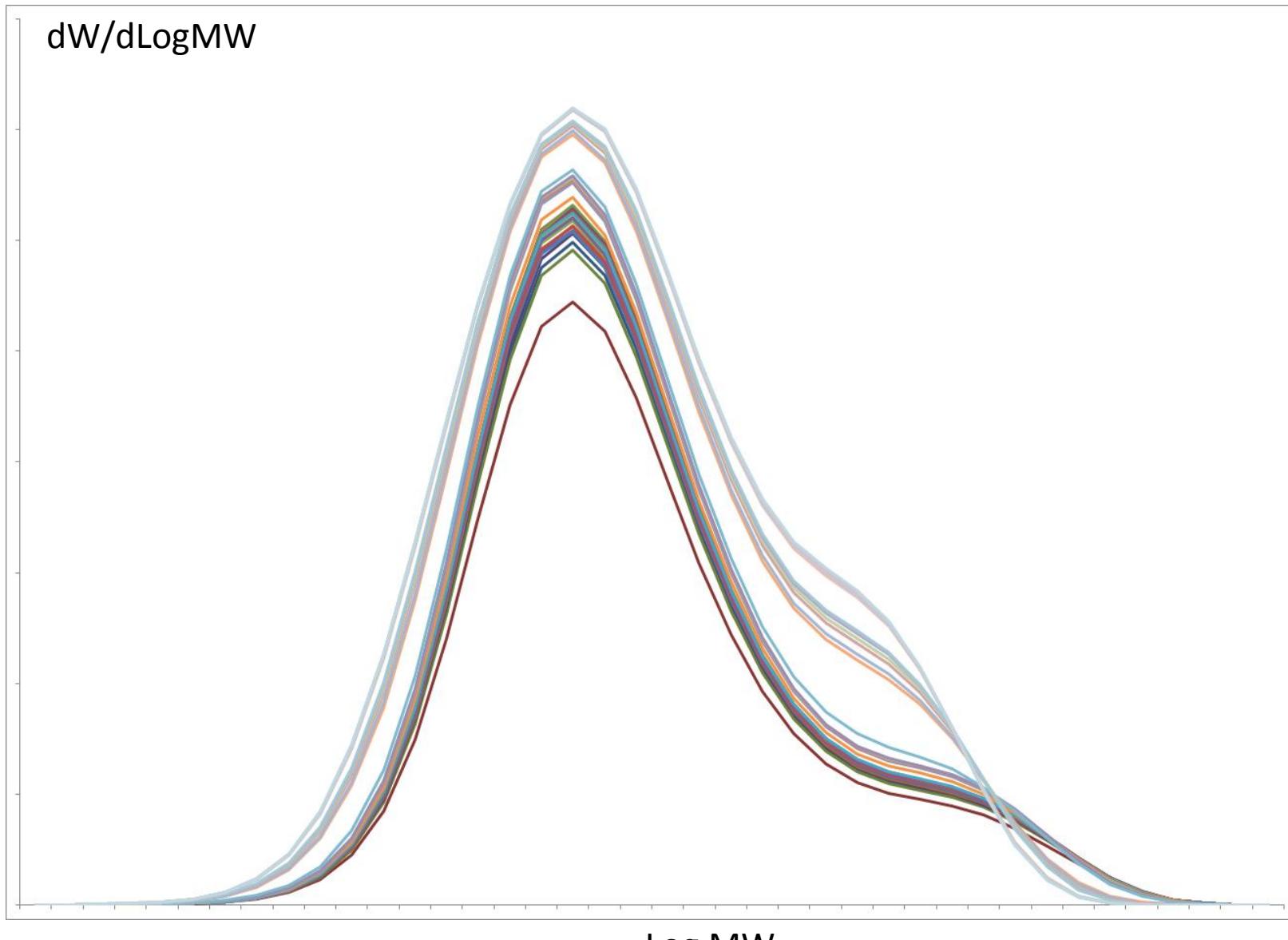
PSE Proprietary Technology

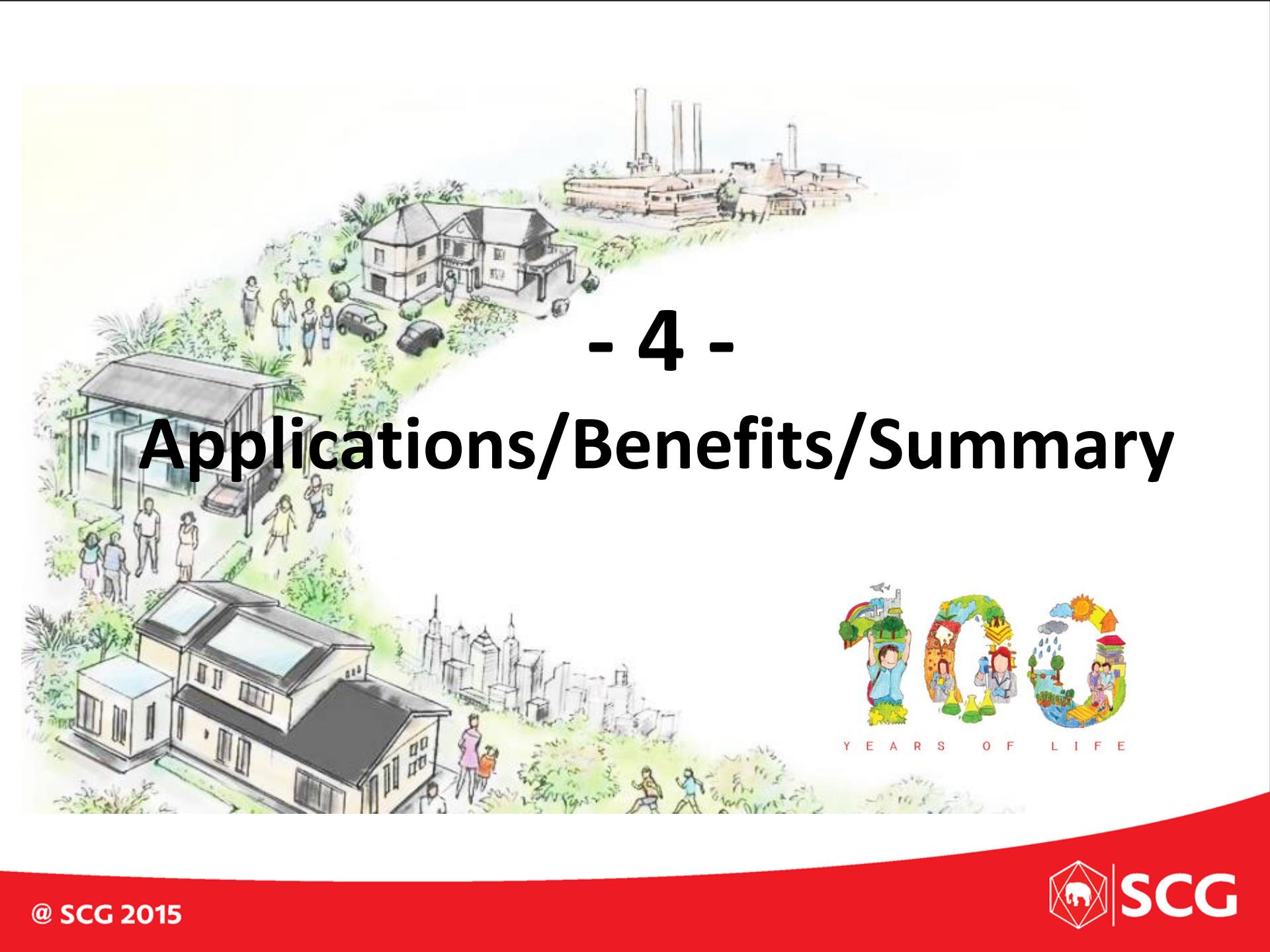
Building Multizonal Models



1. Build CFD model of reactor using Ansys Fluent®
 - Reactor drawings required
 - Accurate physical properties (density, viscosity) of reacting mixture calculated using PSE models
2. Obtain converged solution of mixing problem (CFD)
3. Analyze CFD results to design a zoning approach
4. Use PSE Multizonal to extract zone information from the converged CFD solution
5. Combine Multizonal network model with detailed reaction kinetics into final gPROMS model:
 - Dynamic or steady state
 - Access to gPROMS parameter estimation and optimization capabilities
 - Combine with upstream/downstream unit operations in ProcessBuilder

Example: Evolution of MWD in 41-zone model



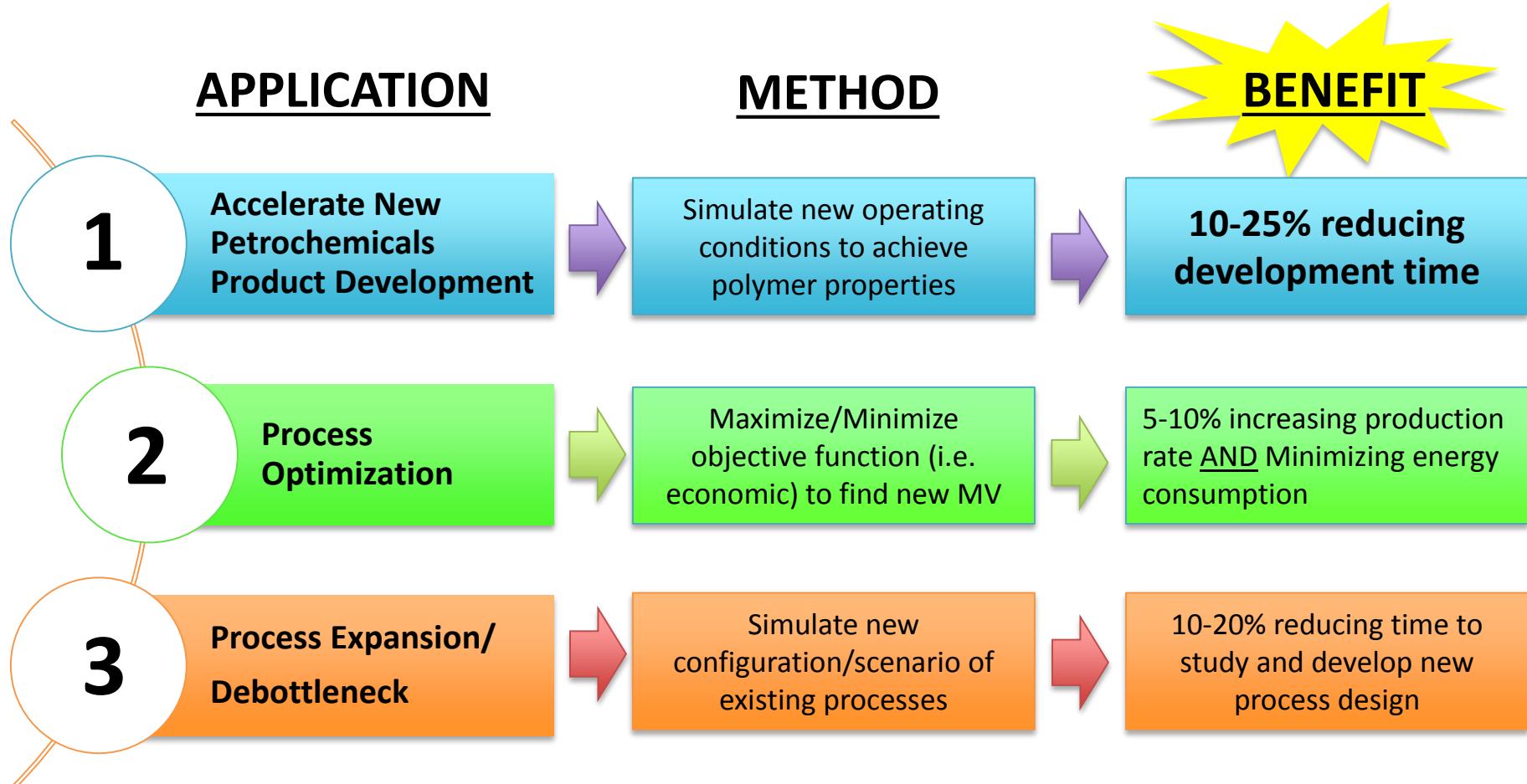


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Applications/Benefits/Summary

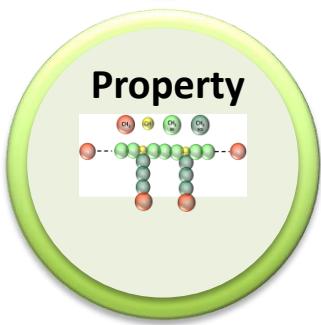
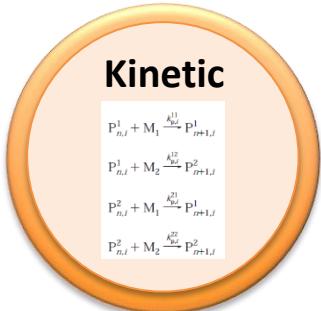


Model Applications and Benefits



Summary

"Key elements of Integral Modeling"



"Scenario Simulation"



Virtual simulation

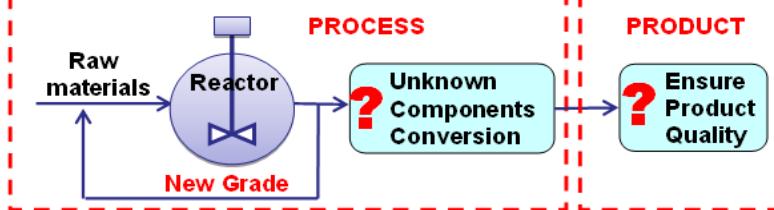
- ✓ New recipes for NPPD
- ✓ Process Optimization
- ✓ Process Synthesis
- ✓ etc

Modeling Driver

Recipe Guidance

Conversion Prediction

Product Property Prediction



"Reduce plant trials"



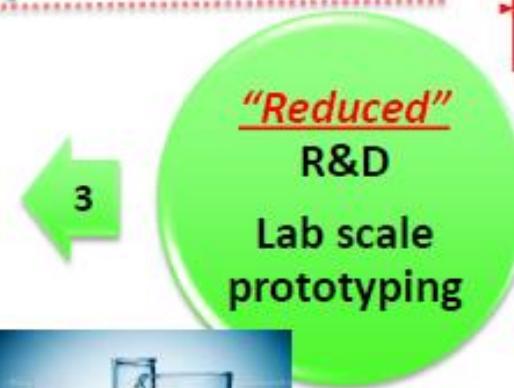
"Reduce losses"



"Reduce risks"

"Reduce times"

Product Development Cycle "With Adv. Modeling"



Acknowledgement



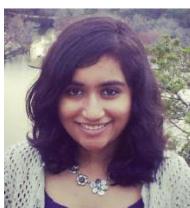
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Thermodynamic property

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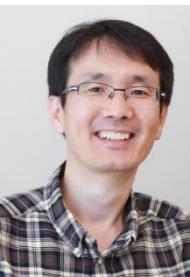
Transport property

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Kinetic Modeling

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CFD Modeling

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