CFD: Perspectives of a Commodity Chemical Company

Glenn Price & Eric Clavelle
NOVA Chemicals Research & Technology Centre
NOVA Chemicals Corporation
Calgary, Canada

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NOVA Chemicals

- NOVA Chemicals is a focused commodity chemical company
- Main businesses: Olefins/Polyolefins
- Produce billions of pounds of ethylene (6.4) & polyethylene (3.4) each year

Ethylene Capacity

Global	North America
Dow	Dow
ExxonMobil	Equistar
Shell	ExxonMobil
SABIC	Chevron Phillips
Equistar	Shell
#12 **NOVA Chemicals**	#6 **NOVA Chemicals**

Polyethylene Capacity

Global	North America
Dow	Dow
ExxonMobil	ExxonMobil
SABIC	Equistar
Sinopecl	Chevron Phillips
Equistar	#5 **NOVA Chemicals**
#13 **NOVA Chemicals**	Formosa

NOVA Chemicals

- NOVA Chemicals is a focused commodity chemical company
- Main businesses: Styrene/Polystyrene
- Produce billions of pounds of styrene (2.6) & polystyrene (3.6) each year

Styrene Capacity

Global

- Shell
- Dow
- BASF
- Lyondell
- ATOFINA

#6 NOVA Chemicals

North America

#1 NOVA Chemicals

- Chevron Phillips
- Lyondell
- Sterling
- Dow
- ATOFINA/Gen Elec

Polystyrene Capacity

Global

- Dow
- BASF
- ATOFINA

#4 NOVA Chemicals

- Chi Mei
- Chevron Phillips

North America

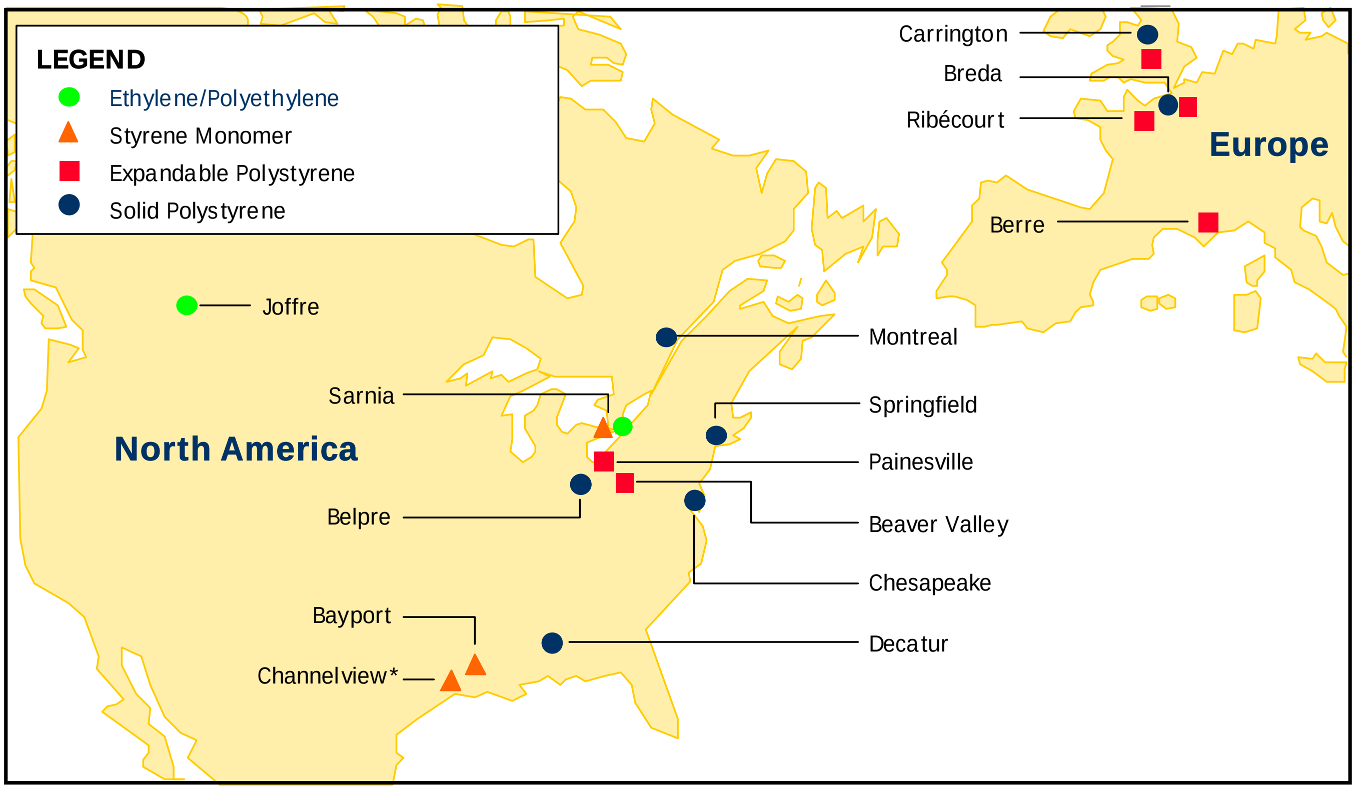
- Dow
- ATOFINA

#3 NOVA Chemicals

- BASF
- Chevron Phillips
- Resirene

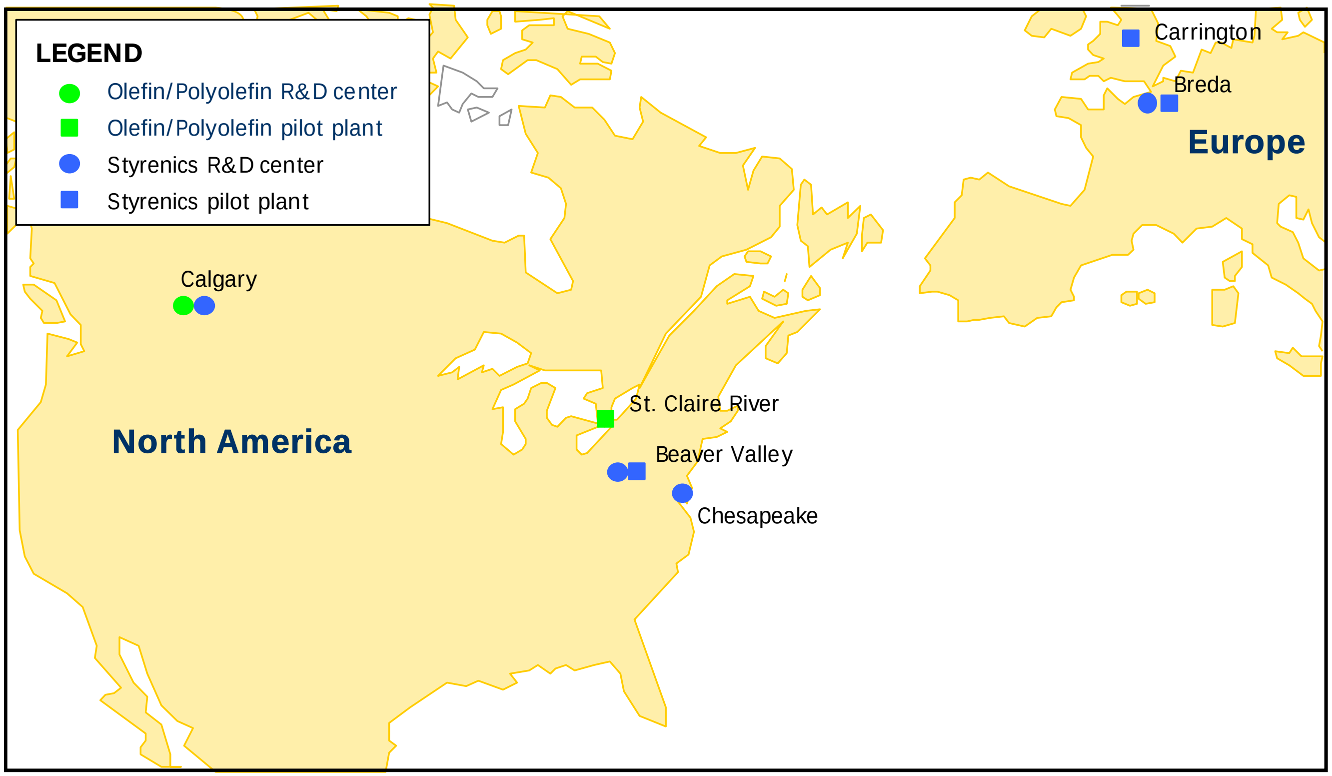
Manufacturing Sites

- 4000+ employees worldwide
- 18 plants in the United States, Canada, France, the Netherlands, and the United Kingdom



Research & Technology

- Commodity chemicals is a technology intensive industry
  - Need to develop new technology to remain competitive
  - e.g. Emerald catalyst, Advanced SCLAIRTECH™, anti-coking tubes for ethylene furnaces (ANK®)



Polyethylene – End Products

Polyethylene Resins

SURPASS®, SCLAIR®, NOVAPOL®

Linear Low-Density Polyethylene (LLDPE)

e.g., ice bags, shrink wrap, stretch film

Low-Density Polyethylene (LDPE)

e.g., grocery bags, squeezable bottles, cable insulation

High-Density Polyethylene (HDPE)

e.g., industrial drums, children's toys, pressure pipe

Very Low-Density Polyethylene (VLDPE)

e.g., "boil-in" packaging for rice, soup and pasta products

Styrenic Polymers – End Products

Solid and crystal polystyrene

e.g., CD cases, food containers

DYLARK® resin

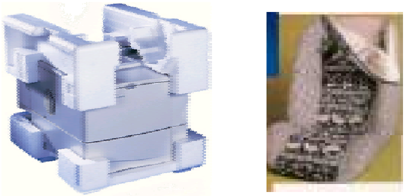
e.g., automobile panels, consoles

DYLITE® expandable polystyrene

e.g., cups, containers

ARCEL® resin

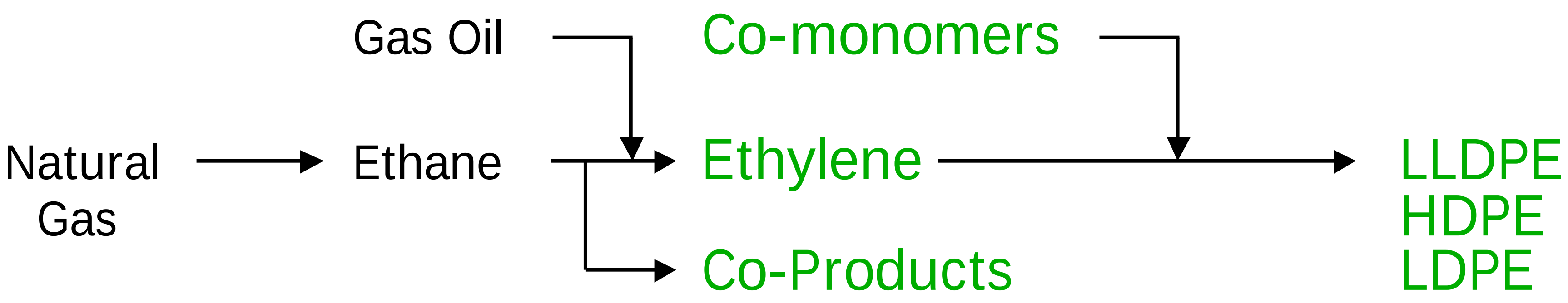
e.g., moldable protective packaging



NAS® resin and ZYLAR® resin

e.g., consumer products, medical supplies, office furniture

Olefin/Polyolefin Technology



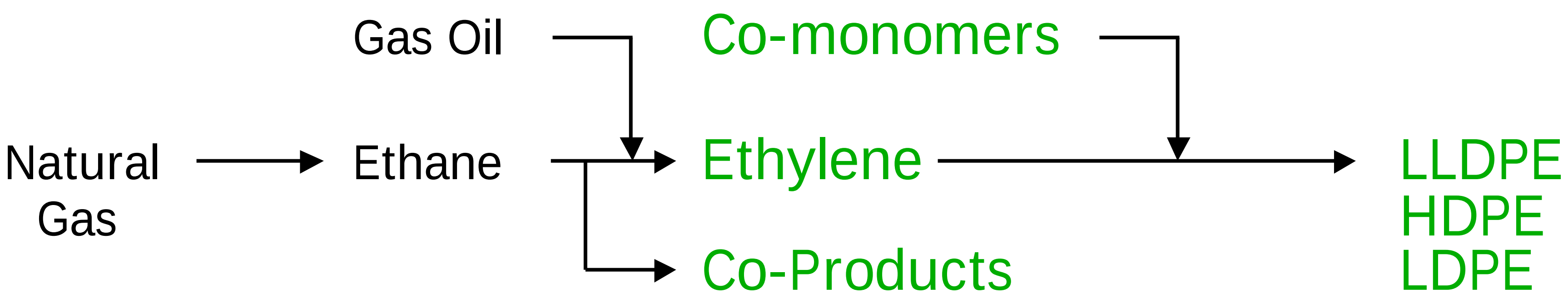
Olefin Technology

- Cracking furnace
- Heat exchangers/chillers
- Compression
- Distillation/separation
- Extrusion
- Flaring

Polyethylene Technology

- Gas Phase
- SCLAIR®
- Advanced SCLAIRTECH™
- LDPE

Olefin/Polyolefin Technology



Olefin Technology

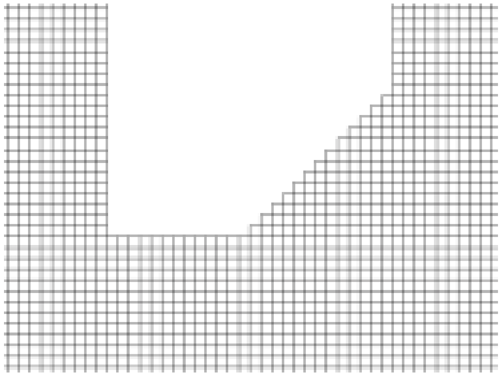
- Cracking furnaces
- Heat exchangers/chillers
- Compression
- **Distillation/separation**
- Extrusion
- **Flaring**

Polyethylene Technology

- **Gas Phase**
- SCLAIR®
- **Advanced SCLAIRTECH™**
- LDPE

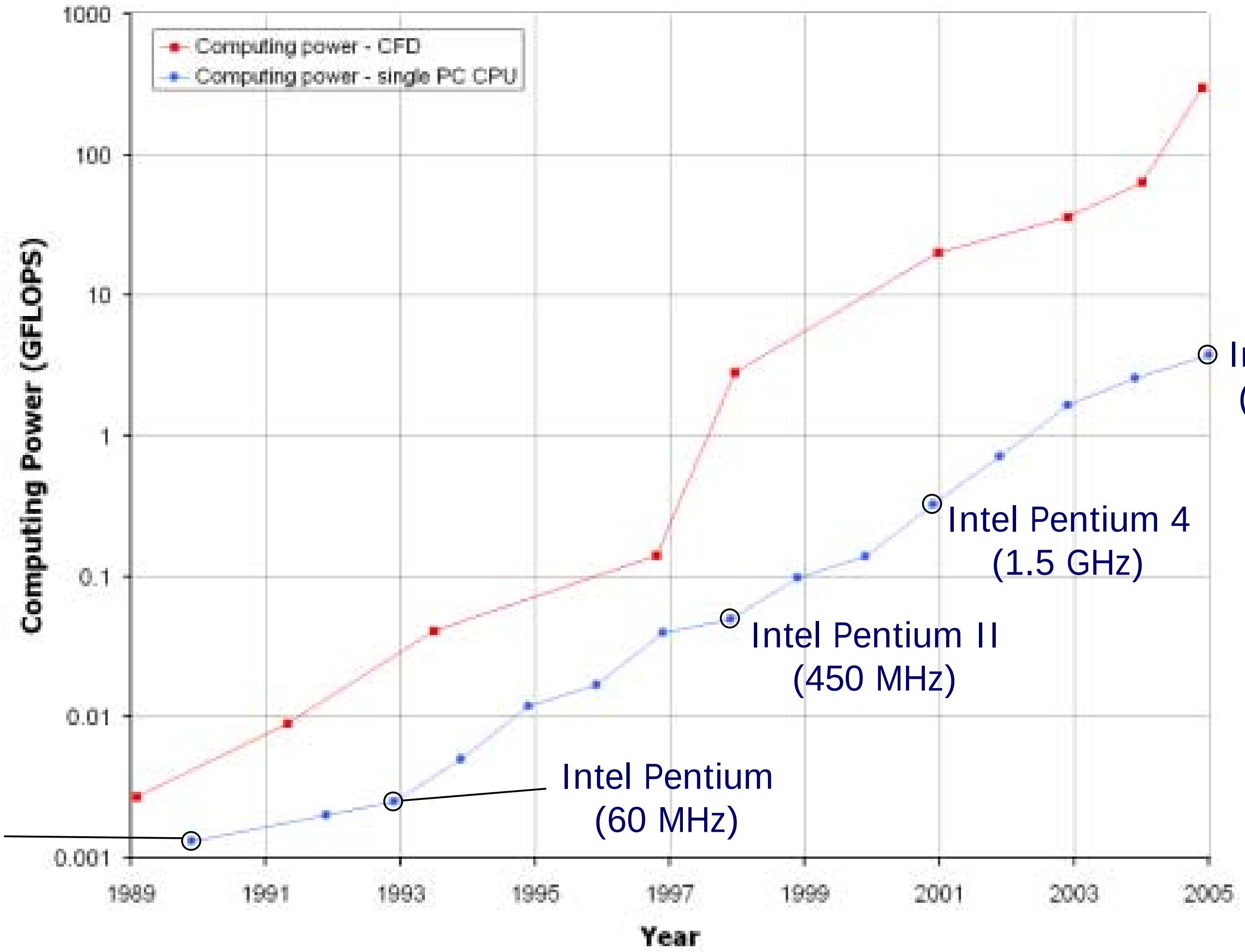
CFD at NOVA Chemicals: A Look Back

- CFD was first used in 1988
- Single-phase flows on very coarse, 2-D meshes (~5k cells)
  - e.g. transient, pulsating flow of a gas through an orifice plate



- Part-time user running Phoenics (CHAM) on a Sun 4/330 Unix workstation (33 MHz, 72 MB)
  - Fastest PC at the time was an Intel 486DX (25 MHz, 640 kB)

Computing Power



Intel P4 EE
(3.8 GHz)

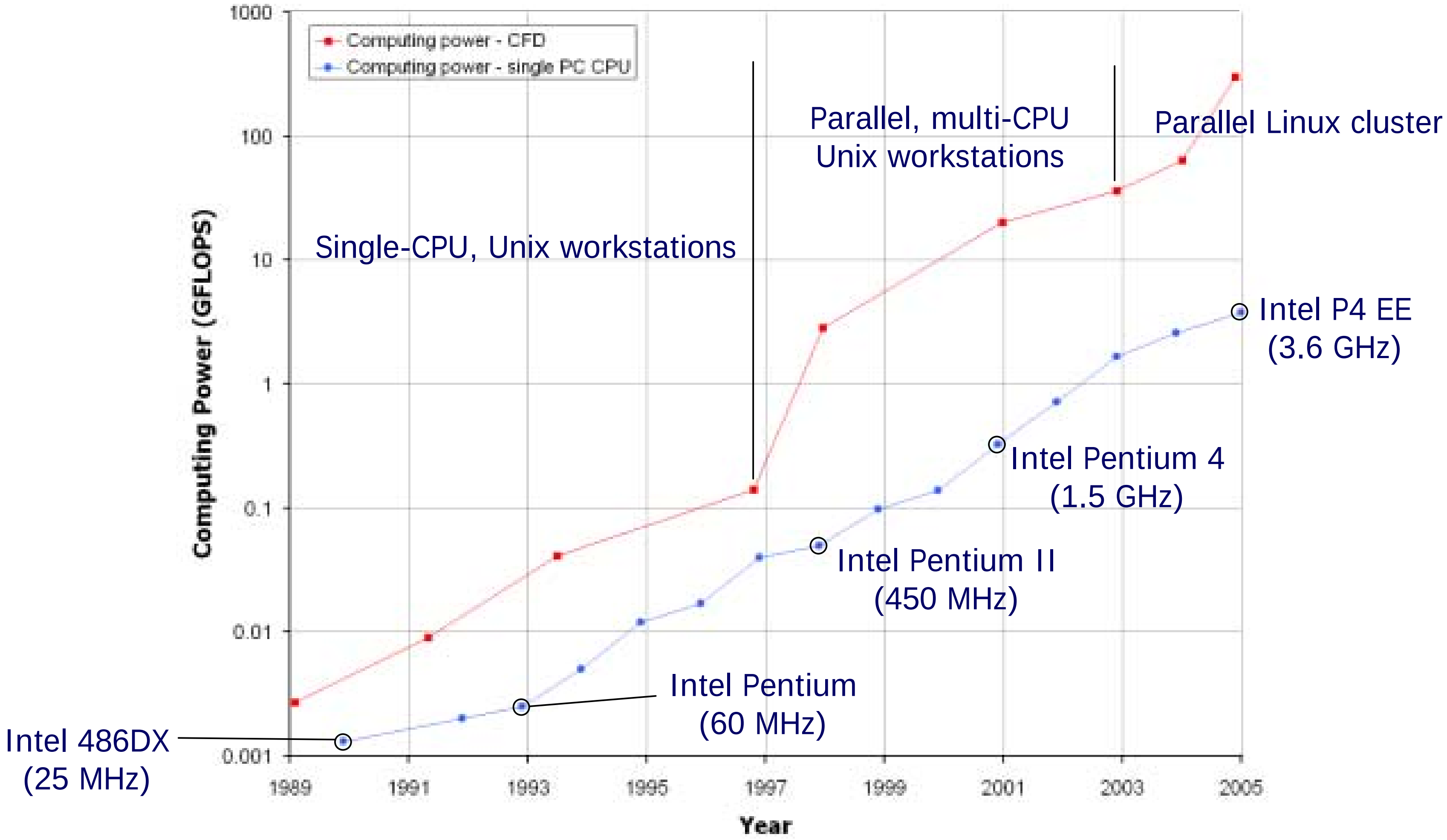
Intel Pentium 4
(1.5 GHz)

Intel Pentium II
(450 MHz)

Intel Pentium
(60 MHz)

Intel 486DX
(25 MHz)

Computing Power



Single-CPU, Unix workstations

Parallel, multi-CPU
Unix workstations

Parallel Linux cluster

Intel P4 EE
(3.6 GHz)

Intel Pentium 4
(1.5 GHz)

Intel Pentium II
(450 MHz)

Intel Pentium
(60 MHz)

Intel 486DX
(25 MHz)

CFD at NOVA Chemicals: 2005

- CFD is now generally accepted as a useful engineering tool:
    - Provide plant support by troubleshooting unit operations
    - Design new equipment and evaluate vendor designs
    - Consider different operating scenarios
    - Root-cause failure analysis
    - Address safety concerns
    - Understanding reactor scale-up
- Multiple users using Fluent v6.2 on a large, parallel Linux cluster of low-cost CPUs (PC based)
    - Balance of long-term and short-term simulations
- Apply CFD using commercial CFD packages rather than developing our own code and new algorithms
    - User subroutines to add custom models when necessary

CFD Applications

Long-Term Technology Development

- Reactors for Advanced SCLAIRTECH™ Technology
- Commercial, gas phase reactors

Plant Support - Improved Unit Operability

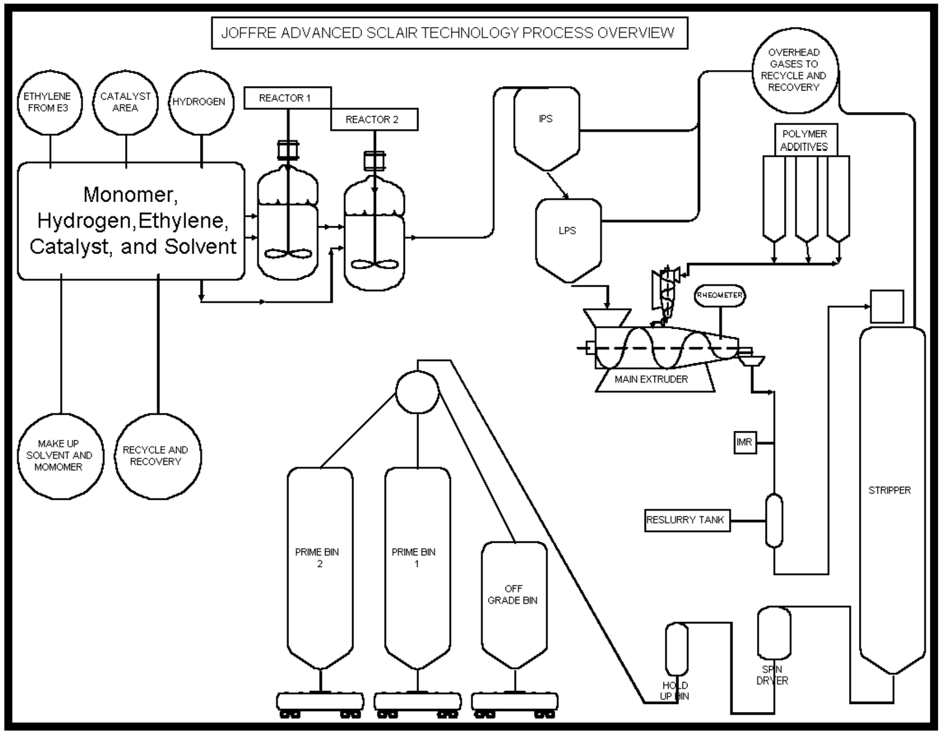
- Liquid distributor in a large gasoline fractionation tower

Plant Support - Safety

- Flare burn-back event

Advanced SCLAIRTECH™ Technology

- Advanced SCLAIRTECH™ Technology is an evolution of the classic SCLAIRTECH™ solution polyethylene process
  - Extensive product and process development on pilot plant facility
  - World's largest commercial solution polyethylene plant at Joffre



Process characteristics

– Dual reactors

– Very short residence time

– Intermediate pressures

– Operating temp. 140 to 300°C

– High ethylene conversion

– 1-Octene comonomer

– 0.905 to 0.965 resin density

– 0.3 to 150 resin melt index

– Narrow to bimodal MW distribution

Why Model with CFD?

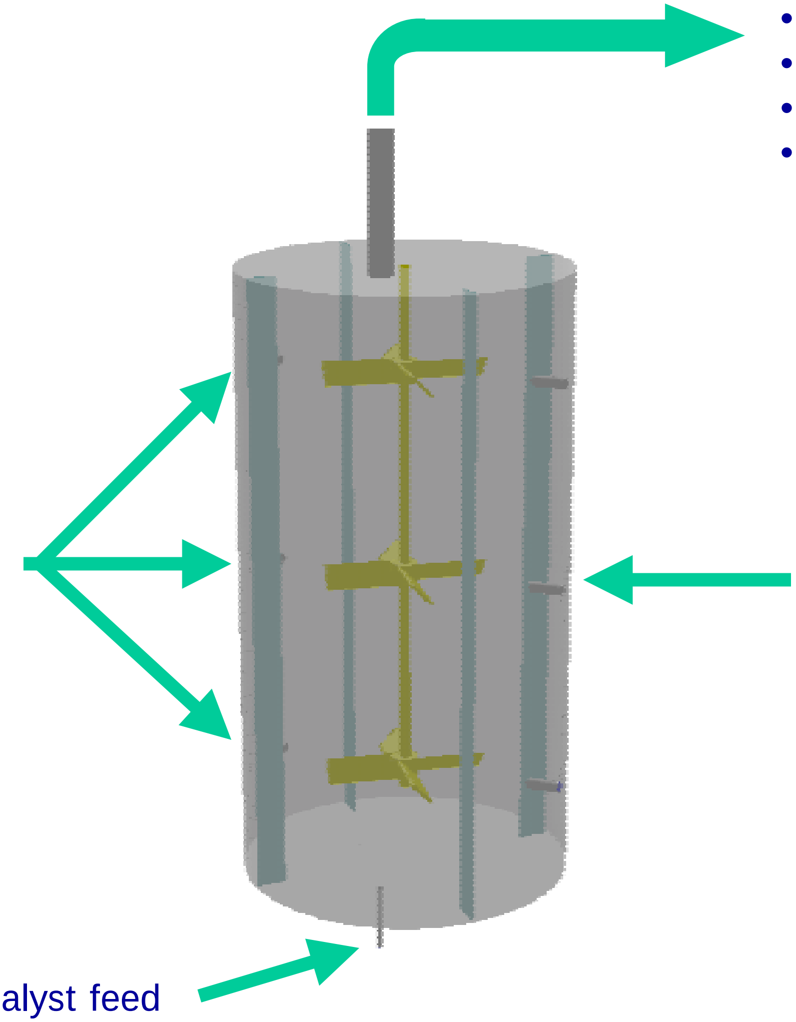
- Scale-Up
  - Need to scale-up process methods and product results across three orders of magnitude in reactor volume (bench -> pilot -> commercial)
- Potential to improve existing products and eventually aid in the development of new products
  - Identify source(s) of undesirable product characteristics such as grease or high MW tails
  - Manipulate mixing to adjust MW distribution & co-monomer incorporation
- Design & diagnostics
  - Role in design of new reactors and modification to existing reactors
  - Provide data for mechanical design: impeller forces, shaft torque, temperature distributions, etc.

The Challenges

- Complex kinetics
  - Co-polymerization with fast multi-step reactions in laminar and turbulent flow conditions
  - Require many rate constants and mechanisms
  - Need to predict product molecular weight distribution & co-monomer incorporation
- Solution physical properties
  - Reactors operate at high temperature and pressure close to critical point of the solvent & co-monomer
  - Solution viscosity:
    - Several orders of magnitude change in viscosity from monomer feed stream to bulk reactor solution
    - Non-Newtonian solution viscosity strongly dependent on polymer molecular weight
- Complex geometry
  - Multiple complex proprietary impellers; large diameter ratio
  - Multiple monomer & catalyst feed nozzles, nozzle from 1st reactor to 2nd.

Example Reactor

- Temperature
- Monomer conversion
- Co-monomer conversion
- Molecular weight distribution
- Co-monomer incorporation

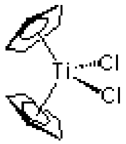


Monomer and/or co-monomer feed

Flow from 1st reactor

Catalyst feed

CFD Model – Complex Kinetics



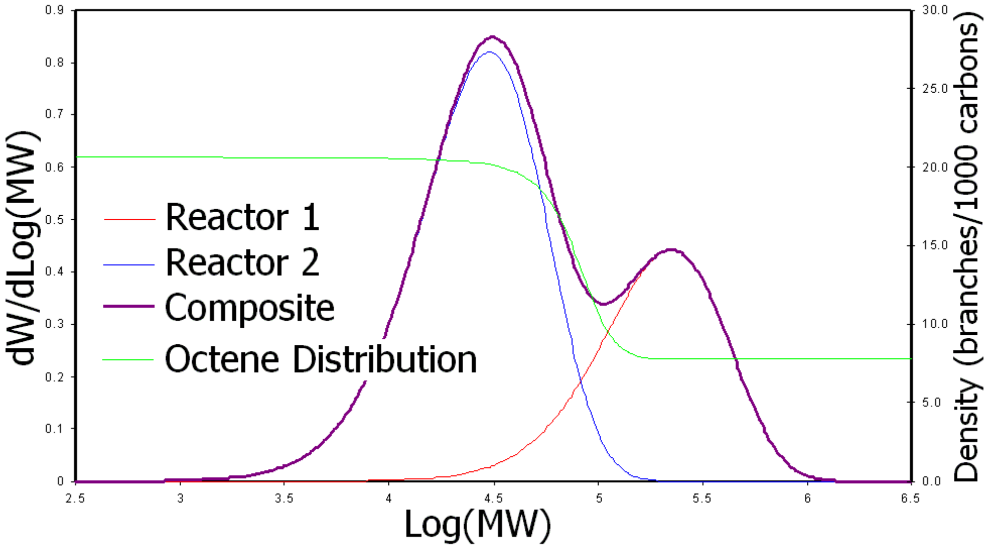
- Detailed kinetic mechanisms for co-polymerization
  - Bench scale and pilot scale experiments to determine rate constants (temperature dependent) for both single-site and multi-site (Ziegler-Natta) catalysts
  - Validation via predicted molecular weight distributions, conversion predictions, etc

Bench Scale Reactor

Sarnia Pilot Plant

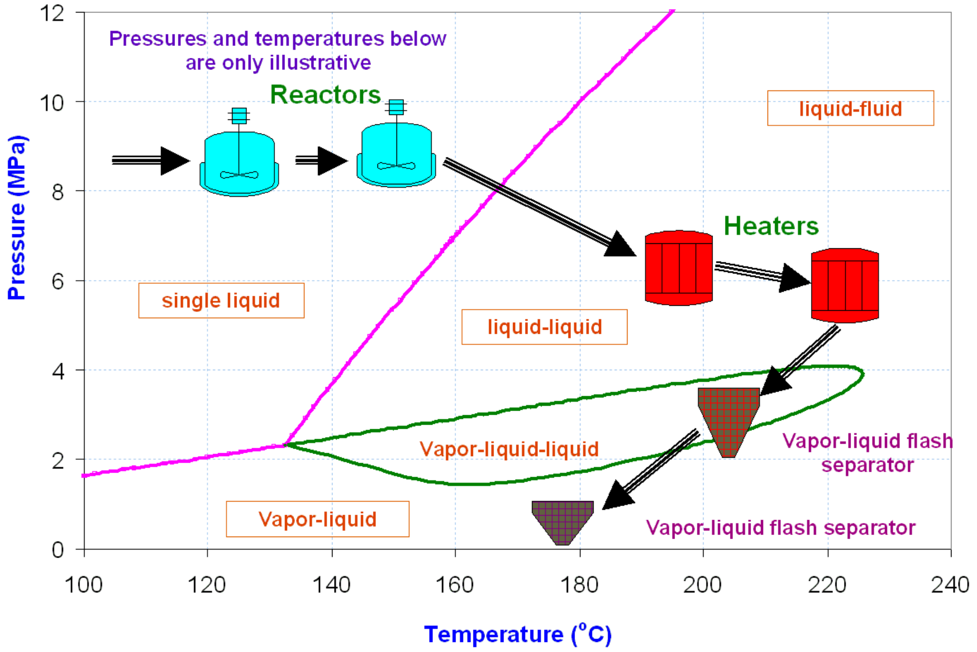
CFD Model – Complex Kinetics

- Method of moments
  - Allows prediction of catalyst, monomer & co-monomer concentrations
  - Track high enough order moments to allow prediction of number-averaged (Mn) and weight-averaged (Mw) molecular weight
  - Allows prediction of co-monomer incorporation



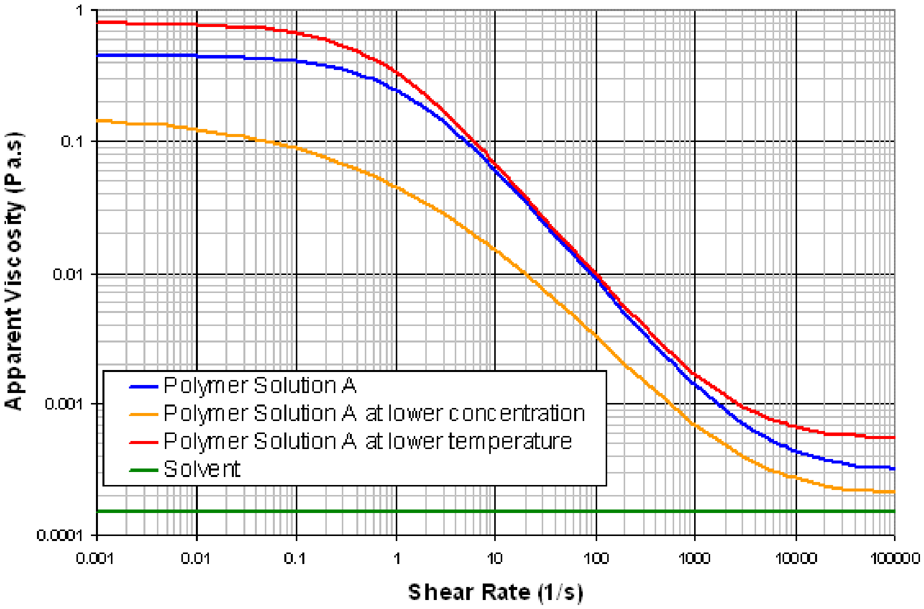
CFD Model – Physical Properties

- PC-SAFT Equation of State
  - Reasonably accurate prediction of phase envelope, pure component densities and mixture densities for polymeric systems
  - Validated in collaboration with the University of Dortmund, Rice University and University of Calgary
  - Most properties represented as polynomial fits to data to reduce computational expense



CFD Model – Physical Properties

- Viscosity
  - Solvent and pure component viscosities as a function of temperature and pressure from the University of Mainz
  - Solution viscosity determined using Multi-Pass Rheometer (MPR), which provide viscosity measurements at reactor conditions
  - Viscosity fit to a Carreau-Yasuda model wherein the coefficients are a function of polymer molecular weight (Mw and Mn)

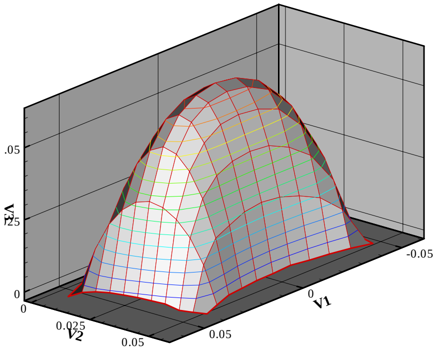


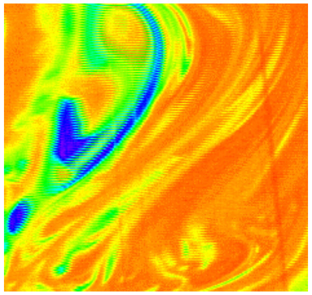
CFD Model – Complex Geometry

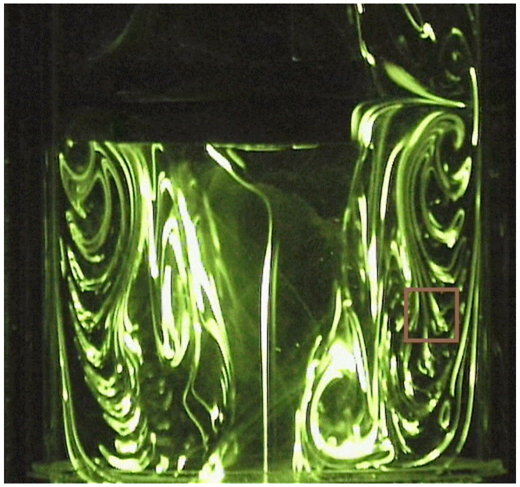
- Both reactors have complex proprietary impellers and multiple catalyst and feed nozzles
- Due to the large impeller to tank diameter ratio there is strong impeller-baffle interaction
  - Sliding mesh necessary to capture this effect accurately
  - Requires small time-steps relative to reactor hold-up times
  - Results in extreme computational requirements
- For these reasons the mesh is a fully hexahedral to minimize cell count for a given accuracy
  - Mixing experiments are extremely important to have confidence in the simulations

CFD Model – Validation

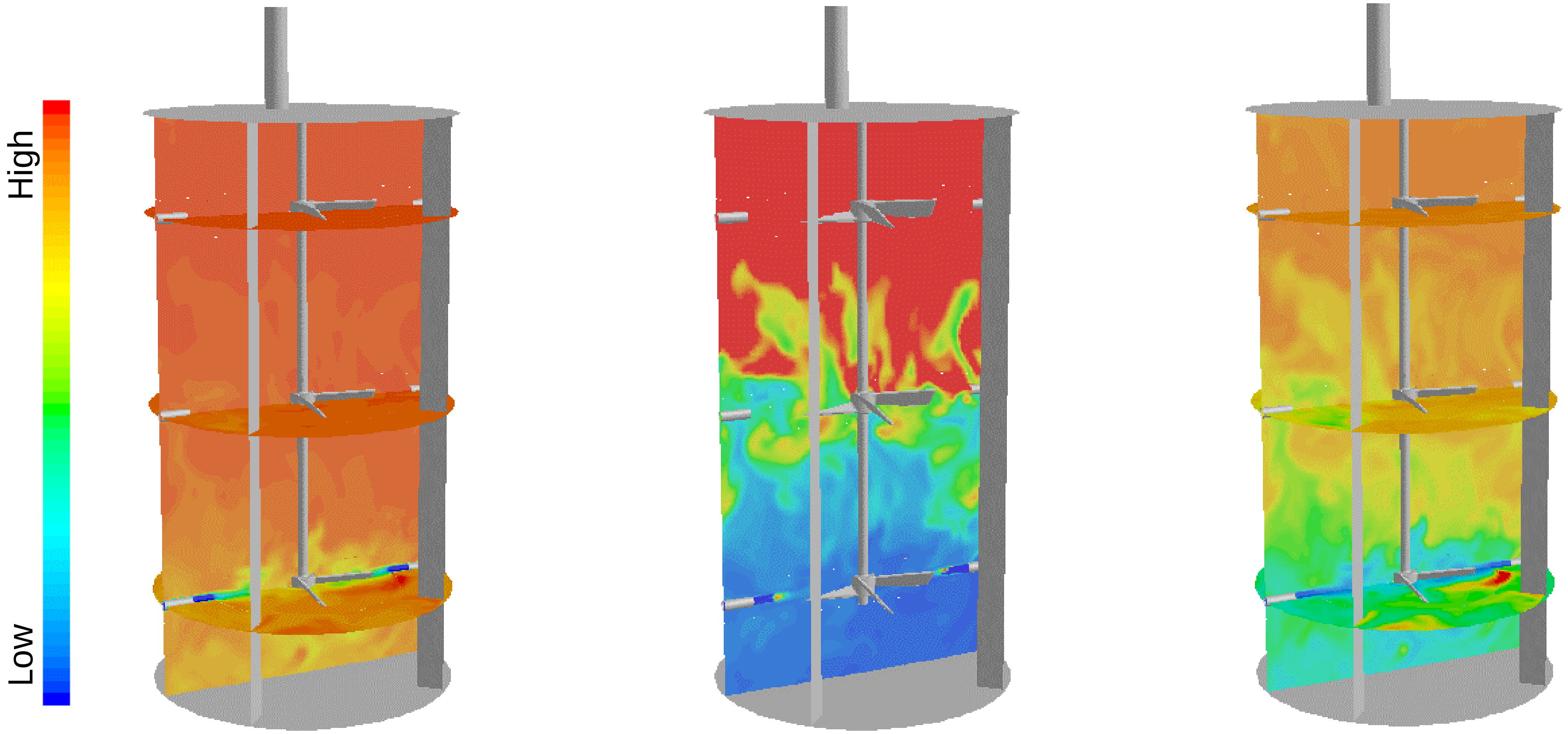
- Validation through various means
  - Cold flow experiments:
    - Velocity distributions (LDV)
    - Circulation measurements (LDV)
    - Blend time (PLIF)
    - Torque
  - Bench and pilot plant and commercial reactor data
    - Reactor exit temperatures
    - Monomer and co-monomer conversion
    - Co-monomer incorporation
    - Molecular weight distribution







CFD Model – Typical Results



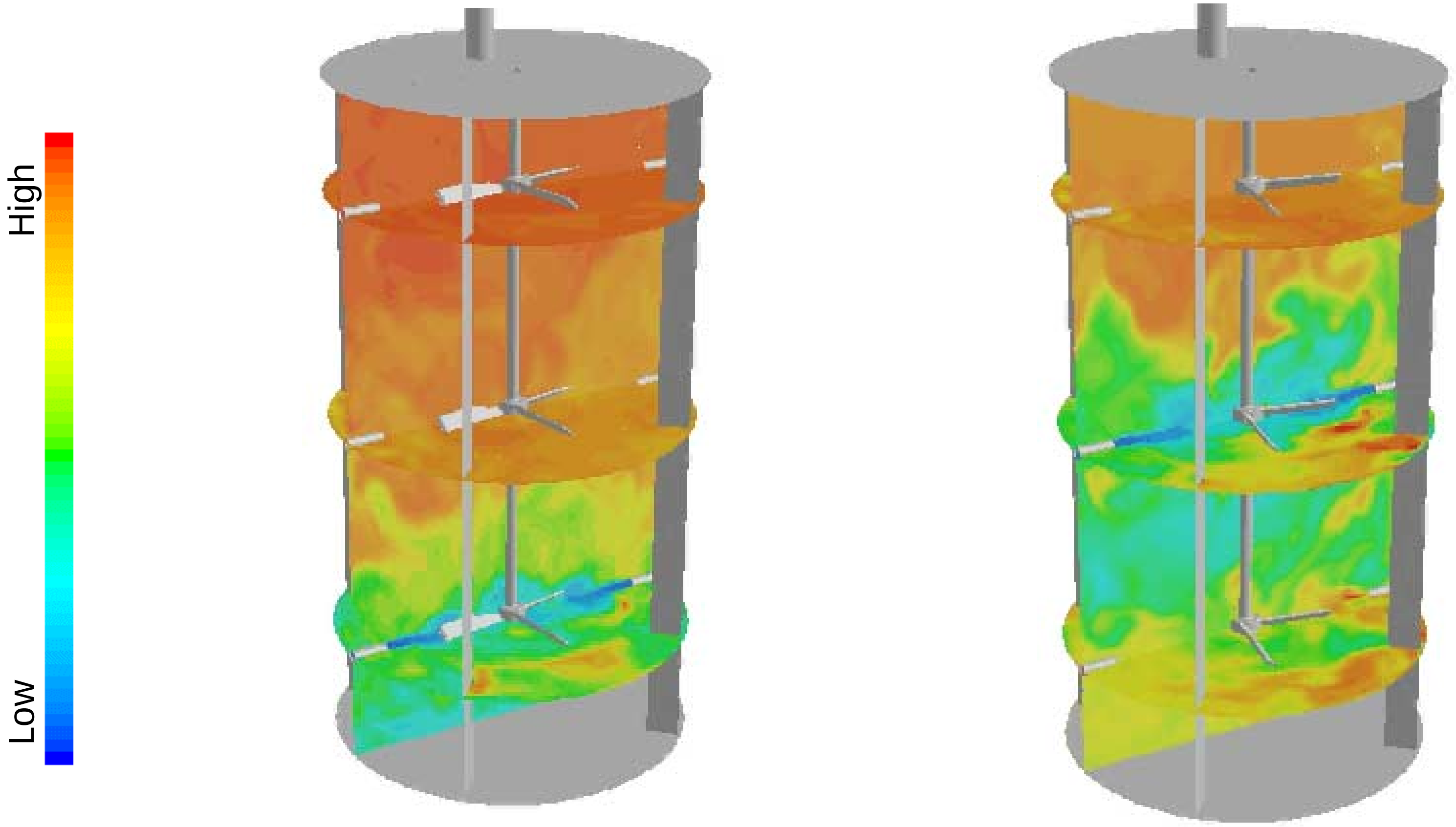
Temperature Distribution

Local Molecular Weight

Polymer Density
(Branches per 1000 carbons)

CFD Model – Typical Results

Branches per 1000 Carbons (related inversely to density)



Bottom Side Feed

Middle Side Feed

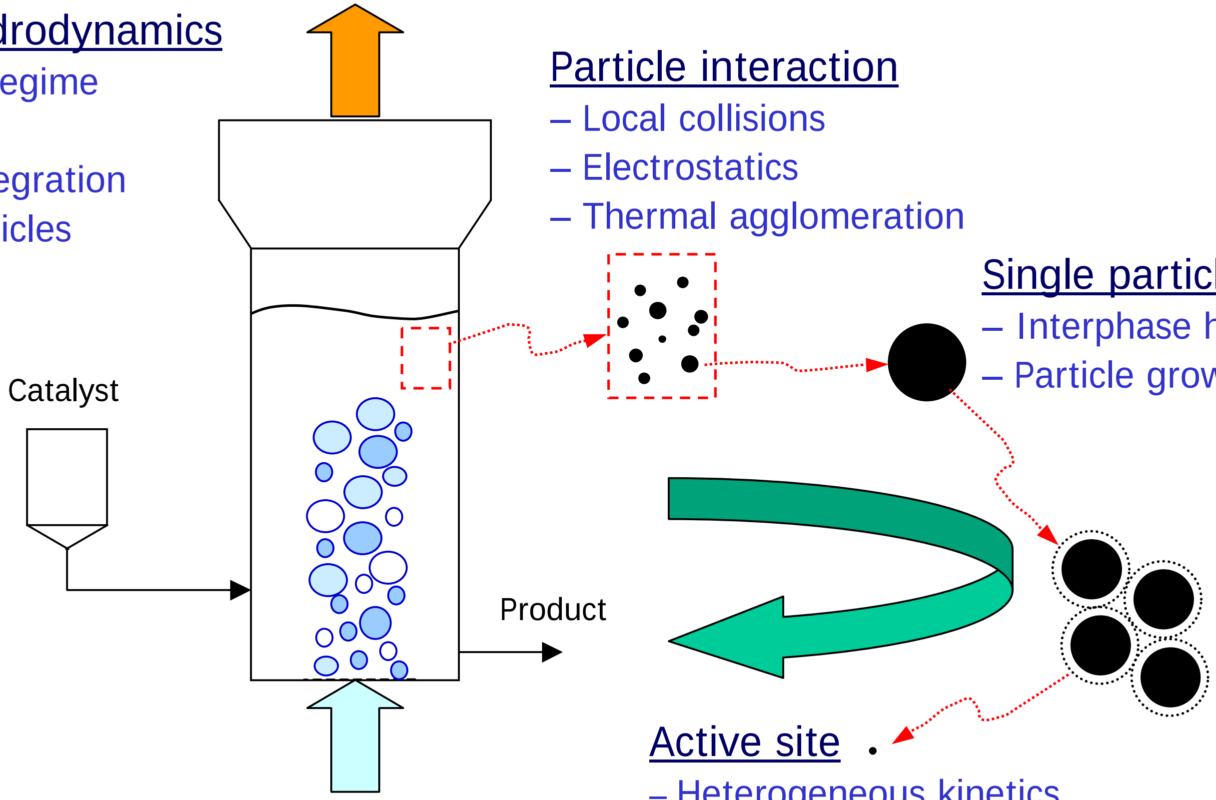
Gas Phase Technology

- Gas phase reactors are widely utilized for polyolefin production
  - Gas-solid fluidized bed reactor process operating at relatively low pressure & temperature.

- NOVA Chemicals has two commercial gas phase assets
  - LLDPE plant at Joffre (~1300 Mlbs/yr)
  - HDPE plant at Moore (~500 Mlbs/yr)

- CFD is a promising tool to improve our understanding of these complex reactors
  - A reliable (validated) CFD model of these reactors could lead improved unit operability
  - Improved ability to commercialize new catalysts

Commercial Gas Phase Reactor



Gas-solid hydrodynamics
- – Fluidization regime
- – Mixing, RTD
- – Particle segregration
- – 10^9-10^{12} particles

Particle interaction
- – Local collisions
- – Electrostatics
- – Thermal agglomeration

Single particle
- – Interphase heat/mass transfer
- – Particle growth

Sub-particle
- – Morphology
- – Porosity

Active site
- – Heterogeneous kinetics

The Challenges

- Comprehensive CFD model is certainly feasible, Fan et al. (2003)
  - Granular, multi-fluid Eulerian model with multiple solid phases
  - DQMOM to track the population balance
  - Inter-phase mass & heat transfer with a polymerization kinetics
- CFD models for isothermal gas-solid flows are still under development and require further validation
  - Rely on granular, multi-fluid (continuum) models, which have additional assumptions
  - Most work to-date has focused on ideal particles using 2-D simulations
  - Gas-solid hydrodynamics in commercial reactors; Gobin *et al*. (2003)

Validation

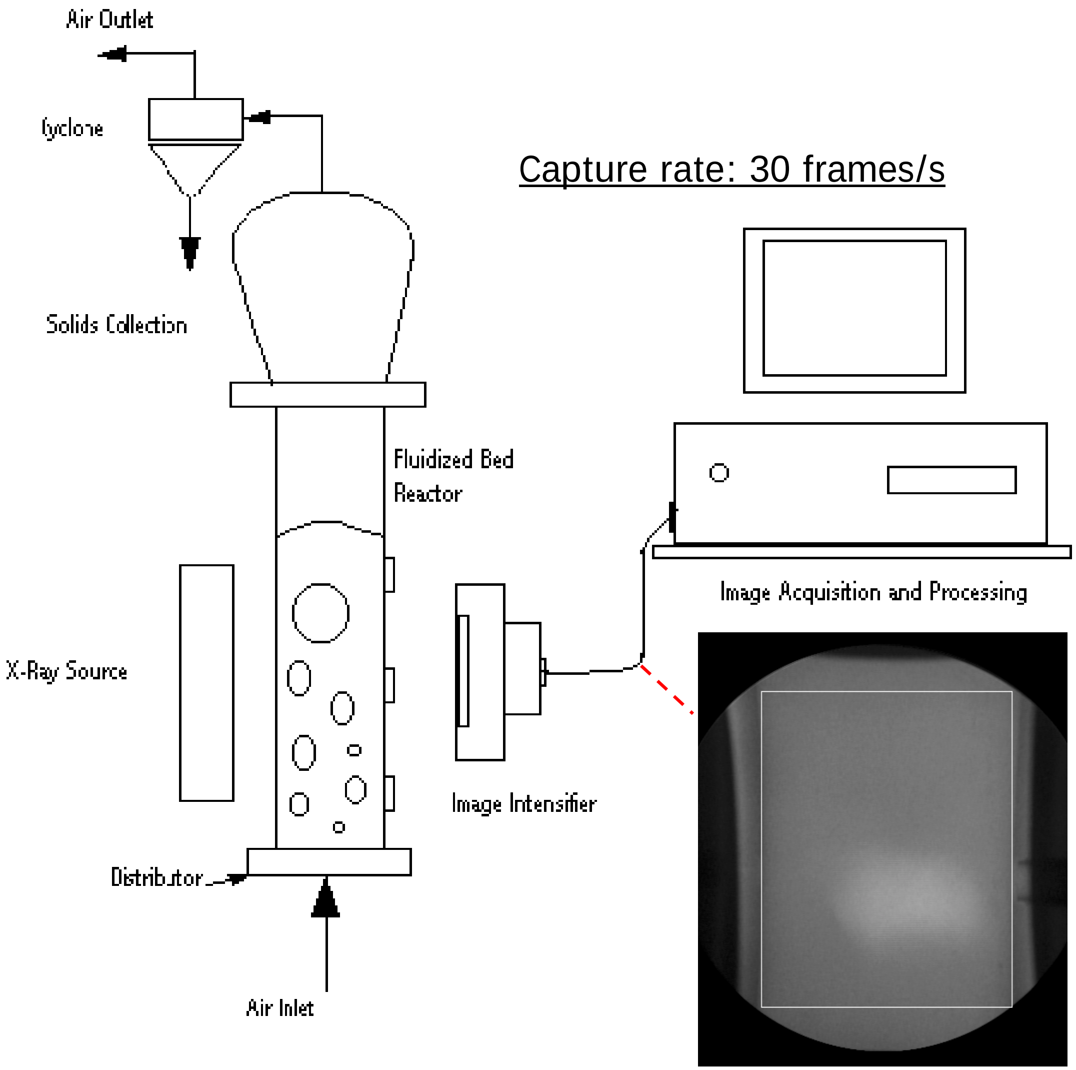
- Limited means to validate model on commercial reactors
  - Mean (wall tap) pressure drop measurements along the length of the bed are readily available on commercial reactors
  - Need to validate on more than just mean ΔP along the bed
- Rigorous validation involves comparing CFD results with non-intrusive measurements of the bed hydrodynamics
- Grid refinement is also important
  - Might get lucky and match exp. results using a single mesh
  - It is important to understand what happens on finer meshes
  - Limitations in computing power have hindered efforts in the past

University Collaboration

- Dr. Apostolos Kantzas and his imaging group at the University of Calgary have developed several non-intrusive measurement techniques
  - High-frequency pressure fluctuation data
  - High-speed CAT scans
  - **X-ray fluoroscopy and image processing**
  - Radioactive particle tracking

- These techniques have been applied on bubbling fluidized beds in small-diameter, low pressure air columns and results have been compared with CFD models (MFIX & Fluent)
  - Hulme (2003) compared bubble properties from 2-D CFD simulations (FLUENT) with the x-ray fluoroscopy experiments & image processing
  - Chandrasekaran (2004) repeated this with MFIX and also compared pressure fluctuation data (power spectra and auto-correlation)
  - Have worked with a variety of particles, e.g. glass beads, polyethylene
  - Achieved fairly good agreement using relatively coarse 2-D meshes but discrepancies appear using finer meshes (AIChE 2004)

Experimental Setup



Capture rate: 30 frames/s

Solid particles

Type: Glass beads

Size: 150-250 microns

Density: 2480 kg/m^3

Gas

Type: Low-pressure air

Velocity: 18.6 cm/s (2x U_{mf})

Column dimensions

I.D.: 10 cm

Bed height: 40 cm

Non-dimensional parameters

Re_{column}: 1230

Re_p: 2.5

Ar: 721

d_p*: 9.0, u*: 0.28 (bubbling)

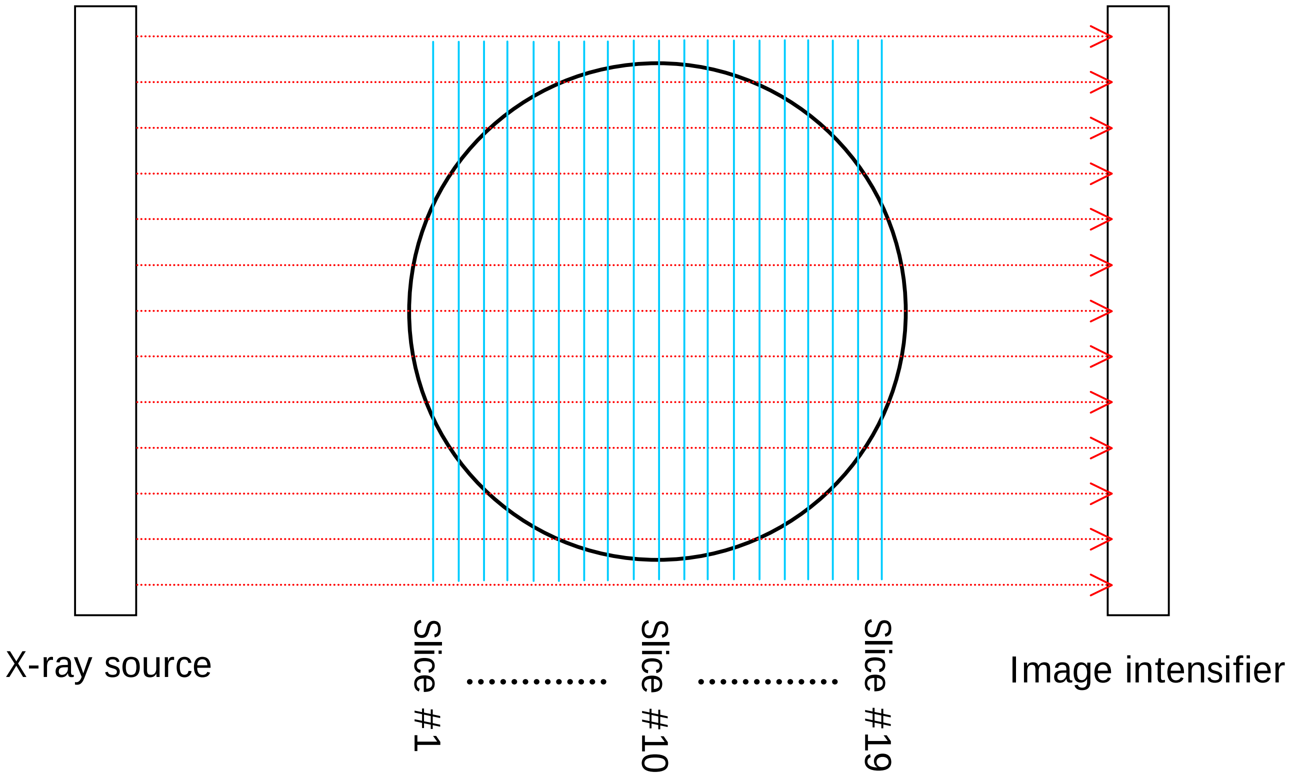
3-D CFD Simulations

- Long run-times even on 30 – Intel P4 processors
  - Need to simulate ~30s to get stationary bubble statistics
- Similar bubbling behaviour as 2-D beds
- Bulk bed properties such as mean ΔP and bed expansion well predicted (within 3%) – an improvement over 2-D
- Question:
  - Which slice should we use for comparison with the x-ray fluoroscopy results?
  - Center slice is a logical choice but will miss bubbles out-of-plane

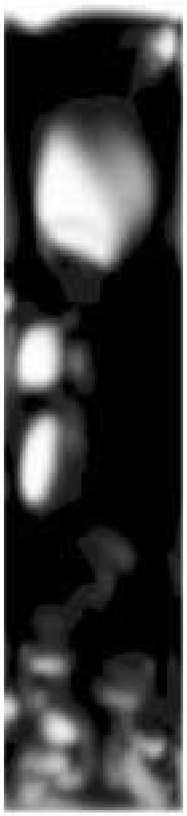
Numerical X-Ray Technique

- Compute attentuation of x-ray from slice-to-slice according to Beer-Lambert relationship

$$I = I_o \exp[-(\kappa_g \rho_g \varepsilon_g + \kappa_s \rho_s (1-\varepsilon_g))\Delta x]$$



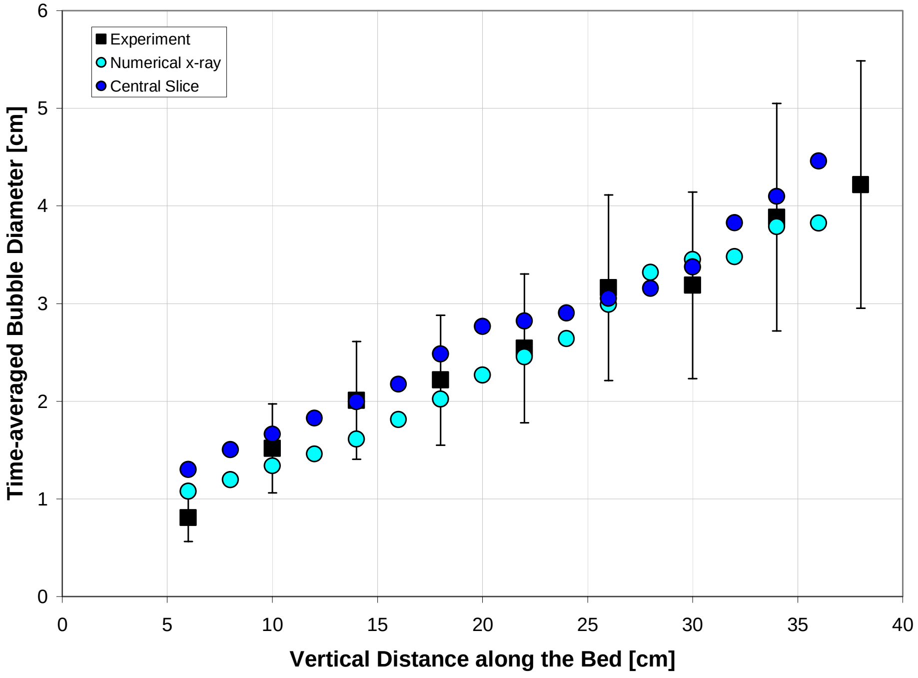
3-D Bubbling Fluidized Bed

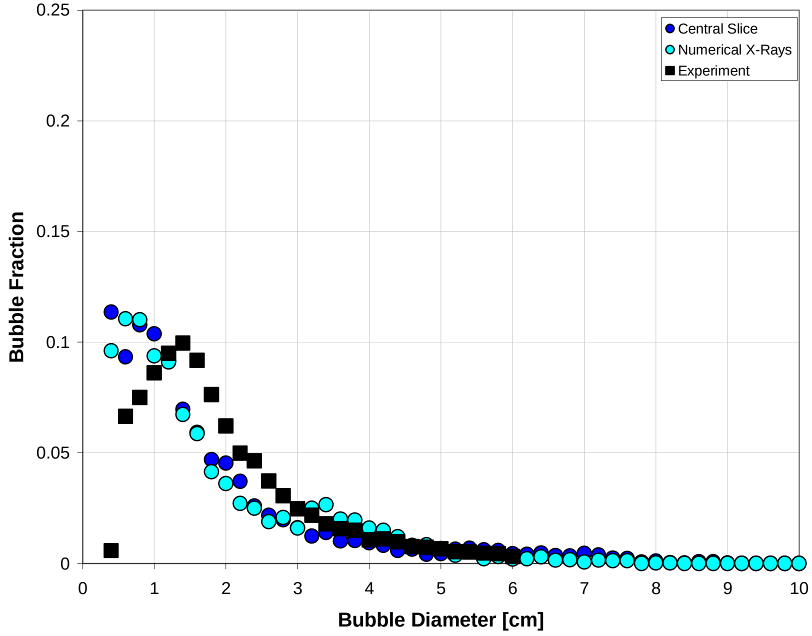


Centre Plane

Numerical x-ray

3-D Bubbling Fluidized Bed Results



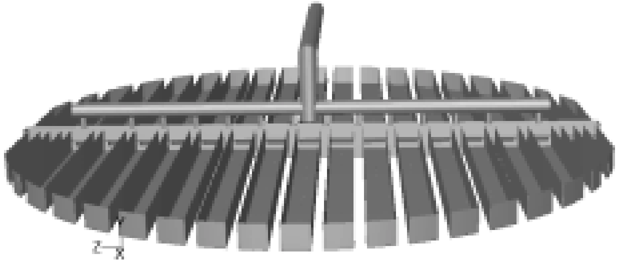


Commercial Reactor Hydrodynamics

Centre Plane

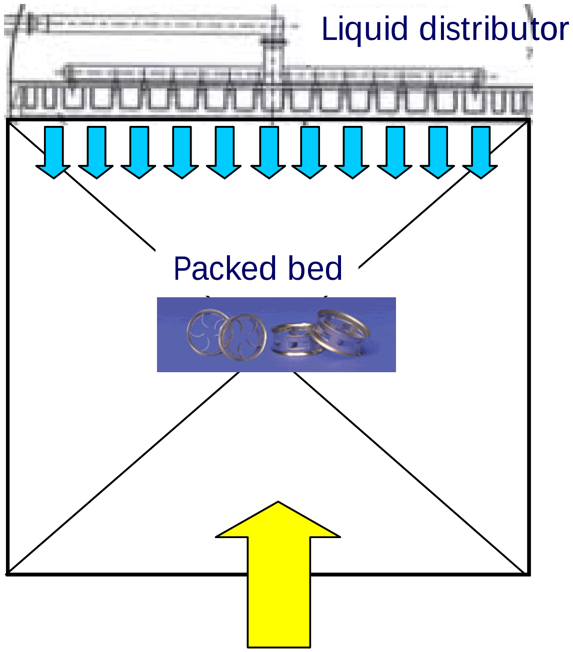
Reactor Wall

Gasoline Fractionator Fouling Study



<u>Background:</u>

- Excessive fouling in the upper packed bed inside a gasoline fractionator at an ethylene plant
  - Packing must be cleaned or replaced during turnarounds
  - Poor separation efficiency
- Research program was initiated to experimentally study the fouling mechanism in the packed bed
- Questions were raised about the uniformity of the liquid flow distribution into the packed bed
  - Liquid maldistribution can lead to a loss of separation efficiency and promote fouling in low flow regions; Hoek *et al*. (1986), Bonilla (1993)



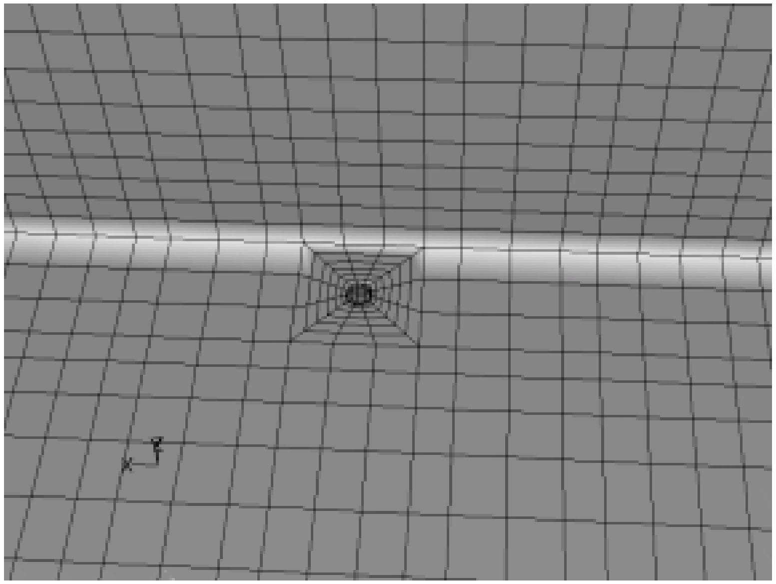
<u>Objective(s):</u>

- Perform simulations to evaluate effect of channel unlevelness on the liquid flow distribution into the upper bed

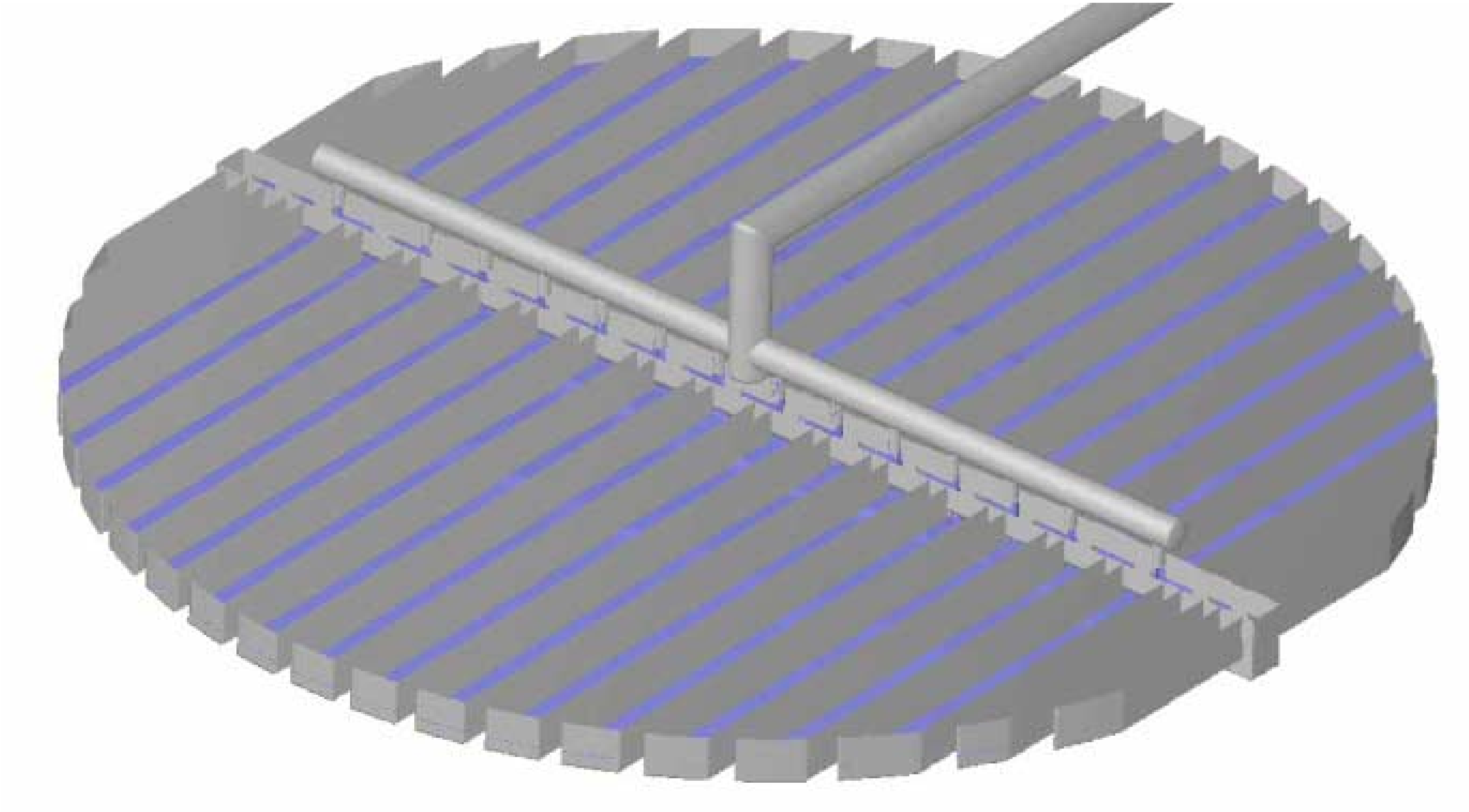
CFD Model

Approach:

- Transient, 3-D CFD simulations with Fluent v6.1
  - Eulerian Volume-Of-Fluid model
    - Interface capturing schemes
    - Interface reconstruction scheme (PLIC)
  - Different turbulence models were used
- Multi-block, structured mesh with >3M hexahedral cells
  - Limited mesh refinement

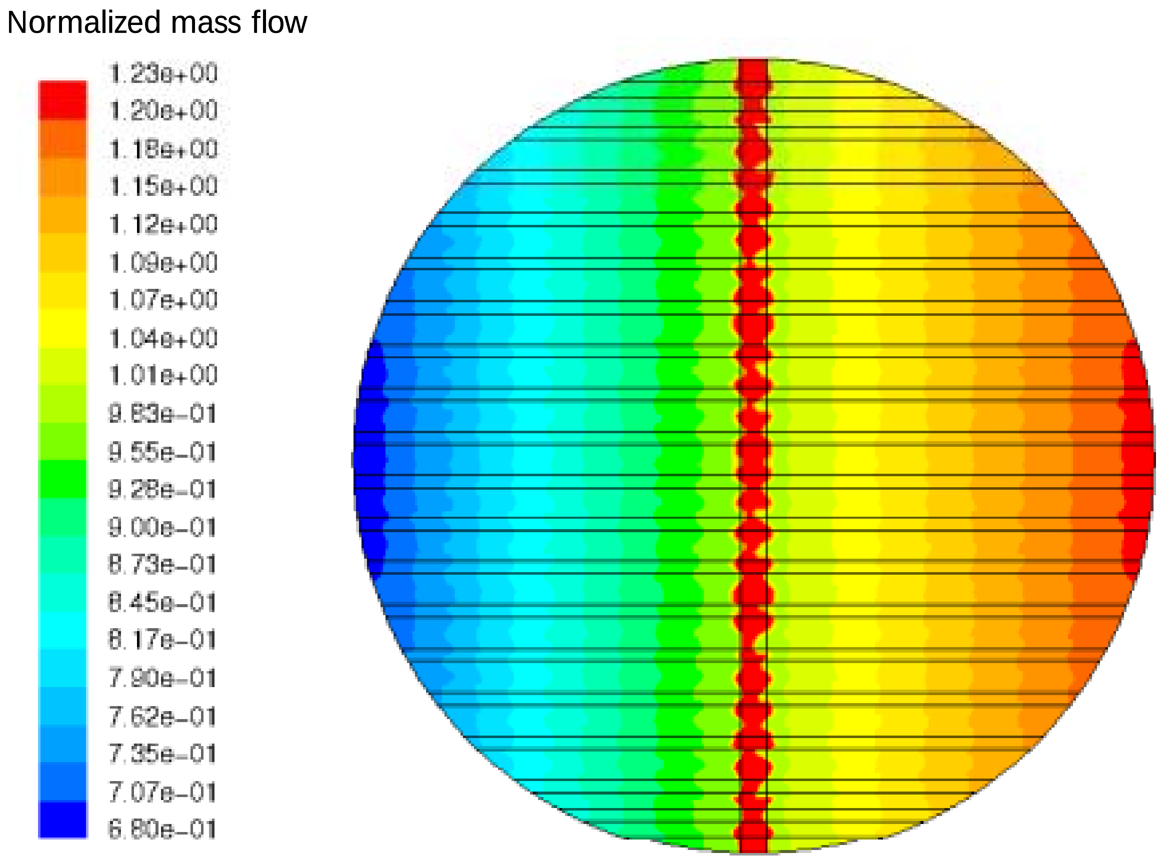


Model Results



Model Results

- Small degree of unlevelness (< 1°) can yield substantial maldistribution in liquid flow in a large diameter column



Flare Burn Back Study

Background:

- Investigation of a flare burn back event that occurred during a power failure at night
  - Air-assisted flare
  - Lost blowers + dampers fail closed!

Objective(s):

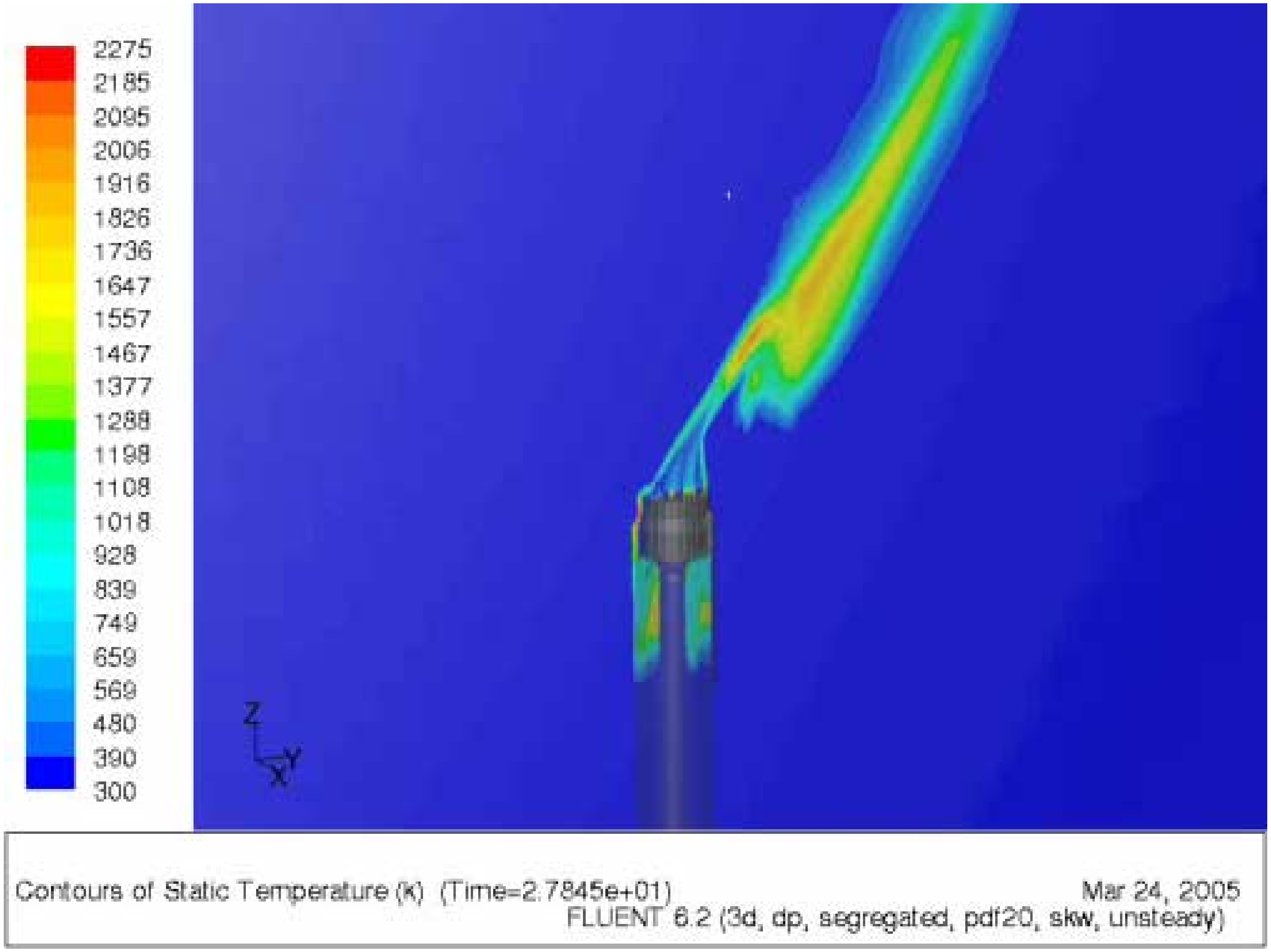
- Use CFD to help us understand what happened
  - Is this a one-time event or is it repeatable?
- Evaluate possible solution(s) to avoid this in the future

Flare Burn Back Study

Approach:

- Transient, 3-D CFD simulations
  - Including large region around flare stack
- Non-premixed turbulent combustion
  - Mixture fraction model with β–pdf
  - Equilibrium chemistry
- Neglect radiation and heat transfer
  - Adiabatic system

Flare Burn Back Study



Contours of Static Temperature (k) (Time=2.7845e+01) Mar 24, 2005
FLUENT 6.2 (3d, dp, segregated, pdf20, skw, unsteady)

General Remarks

- CFD has come a long way over the past 15 years due to:
  - Tremendous increases in low-cost, computing power
  - Improved meshing algorithms and more accurate numerics
  - Advanced models, e.g. LES, multi-phase, combustion, chemical reactions in turbulent flows, moving mesh, population balance methods
- CFD is now an accepted, engineering tool in the chemical industry
  - Trouble-shooting plant problems
  - Designing new equipment and evaluating vendor designs
  - Understanding and improving unit operation

General Remarks

- Successful development of comprehensive CFD models requires:
  - Good understanding of the underlying process
  - Collaboration with experts across different fields, e.g. rheology, thermodynamics
  - Validation, validation, validation!!!
- Try to strike a balance between long-term technology development and plant support
- CFD is just a tool!
  - In industry, we need to be engineers first
  - Listen to the plant engineers and really try to understand their problem(s)
  - Decide on the best approach in consultation with the plant
  - Don't overpromise!

Acknowledgements

- Our colleague, Mohammad Shariati, who contributed significantly to this presentation
- Other colleagues in Fluid Dynamics, across Technology and engineers/operators at the plants, who put up with our seemingly endless requests for data
- University collaborators:
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- Support from various experts at FLUENT:
  - Graham G., Sofiane B., Madhava S., Ahmad H., Lanre O., Wei Z.
- NOVA's Technology Leadership
  - Paul C., Daryll H., Umesh K., Bill T., Andrzej K.
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