

*Pacifichem 2010: Polyolefins Chemistry & Beyond - From Bench to Commercial Scale*



***Commercialization of Polyolefin Catalyst Systems: Synergistic Interaction Between Chemistry & Engineering***

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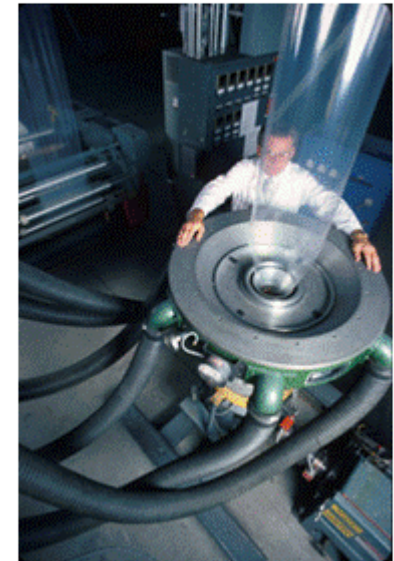
# Agenda

- NOVA Chemicals Corporation overview
- New Product Development - Market pull or Technology push
- Blend of science & engineering skills
  - ▶ Invent – catalyst synthesis/process innovations
  - ▶ **Scale up**
    - Right tools & equipment
  - ▶ Commercialization



# NOVA Chemicals Corporation

- NOVA Chemicals is focused on plastics and chemicals that make everyday life safer, healthier and easier
- Our 2500 employees develop and manufacture materials for customers worldwide that produce consumer, industrial and packaging products
- Our innovation and technology create value for our customers, their products and the markets they serve
- NOVA Chemicals is owned by the International Petroleum Investment Company (IPIC) of the Emirate of Abu Dhabi



# NOVA Chemicals Business Structure

Olefins/Polyolefins
Ethylene
Advanced SCLAIRTECH™ Technology producing SURPASS® & SCLAIR® Polyethylene
Polyethylene
Chemical co-products

Performance Styrenics
Styrenic Performance Polymers
North American EPS
EPS-Based Business Ventures
Styrene Monomer Equity Position*

INEOS NOVA
North American Styrene Monomer & SPS
SPS Based Specialty Polymers
European SPS/EPS



Polyethylene Barrier Film Food Packaging



ARCEL® Advanced Foam Resin

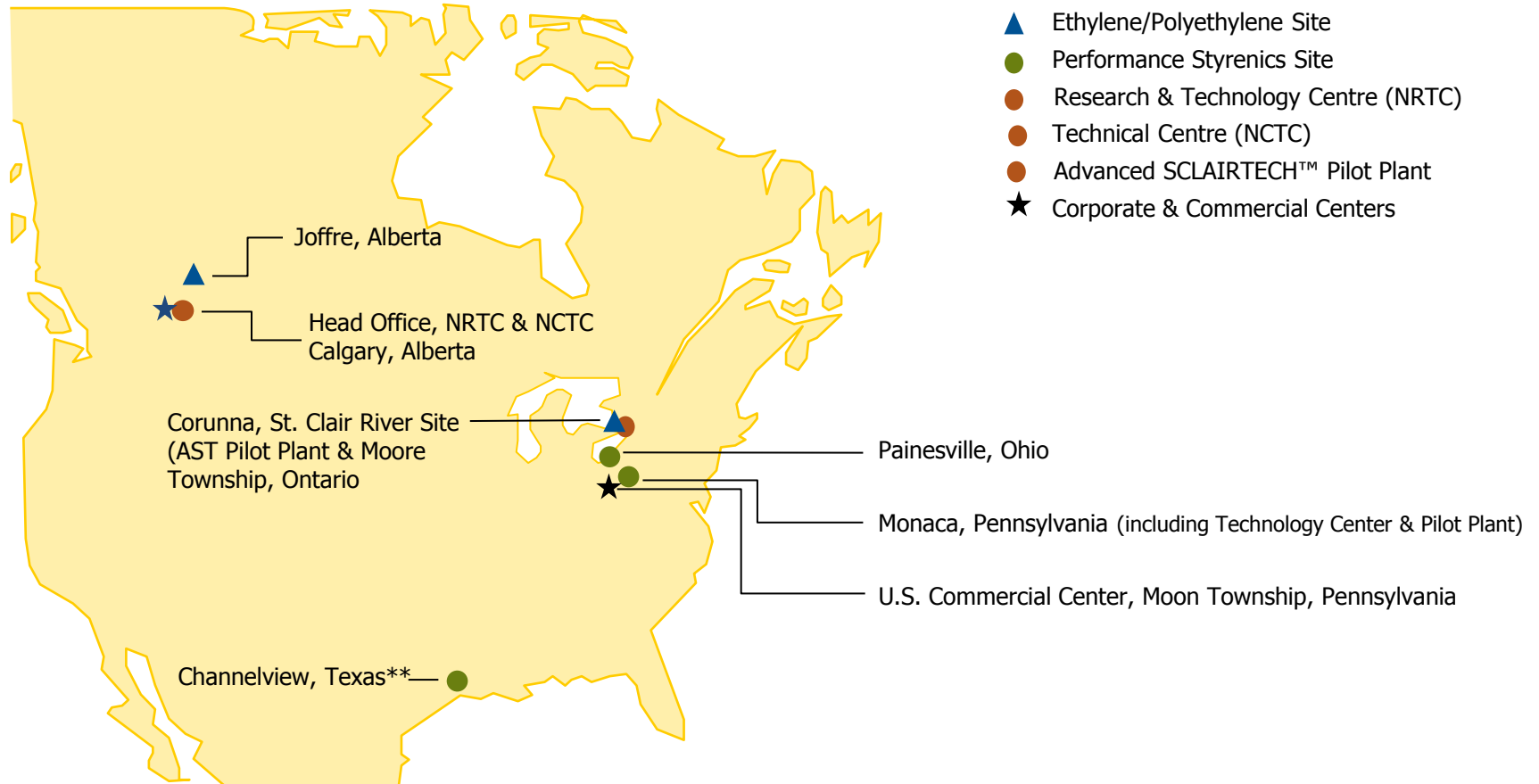


INEOS NOVA Polystyrene Resin

\*Equity position in Lyondell's Channelview styrene plant.

# NOVA Chemicals Manufacturing & Technology Sites

Nine locations in North America\*



\*Excludes INEOS NOVA sites

\*\*Long-term tolling arrangement with LyondellBasell Chemical Company

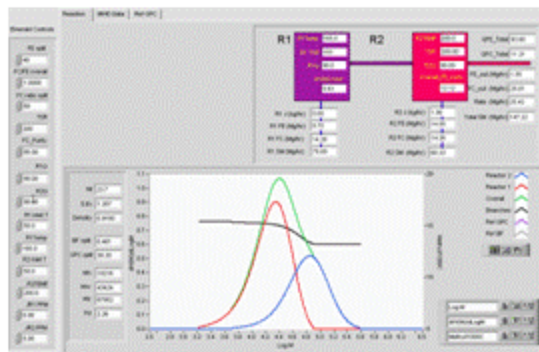
# Advanced SCLAIRTECH™ Technology

- Solution polyethylene technology
- Dual reactor technology
- Proprietary Single Site or Ziegler-Natta catalysts
- Comonomer - Octene
- Wide density range
  - ▶ 0.905 to 0.967 g/cm<sup>3</sup>
- Wide melt index range
  - ▶ 0.40 to 150 g/10 min
- Tailored molecular weight distributions
  - ▶ Very narrow to broad
- Rapid transitions & low inventories

# Product Development Process

## Technology Push or Market Pull

### Focus on Translating Customer Need to Value-Added PE



Model the ideal structure & operating conditions



Develop at Pilot Plant



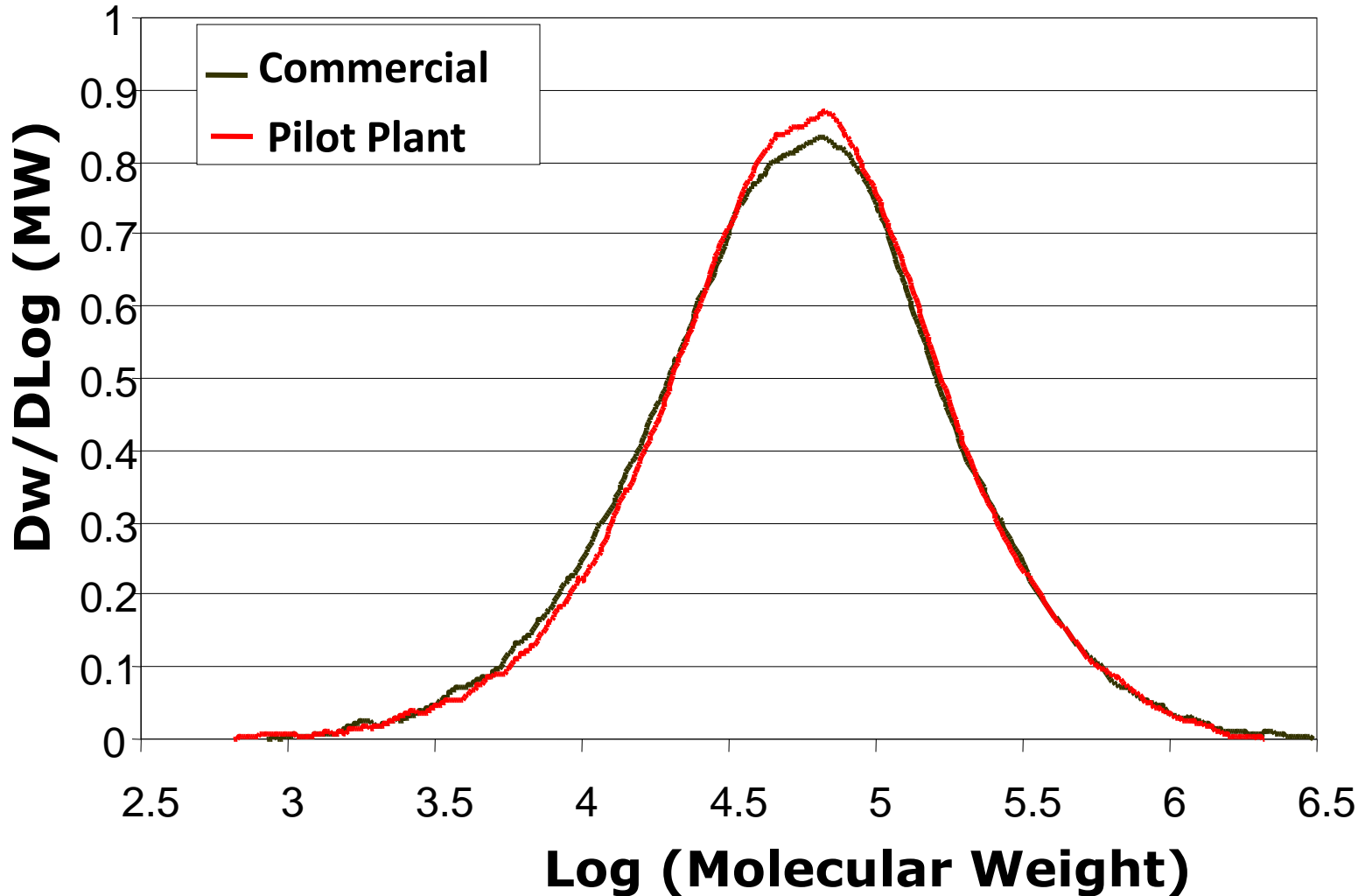
Produce commercially

Customer Need



Test in the labs

# Pilot Plant vs. Commercial Resin (1MI, 0.912g/cc)

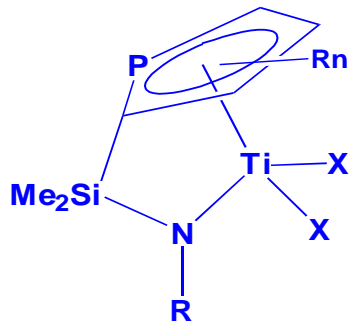


# Advanced SCLAIRTECH Technology

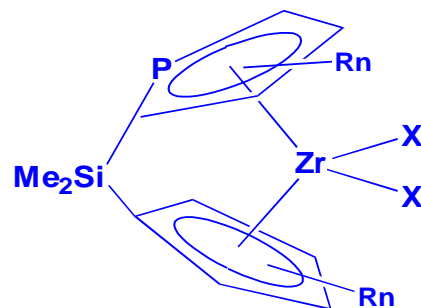
## Product/Process Development - Catalyst

- Novel catalyst structure - batch lab/continuous polymerization scale
- Synthetic route/process optimization – target properties
- Commercialization:
  - ▶ Pilot plant/commercial facilities - as is/modify/new
  - ▶ Catalyst supply chain – self manufacture/toll
  - ▶ Legal/IP – freedom to act/operate
  - ▶ Regulatory compliance/toxicology – FDA approval
  - ▶ Technical feasibility - robustness (impurities)
  - ▶ Business case – initial value proposition/formal D&RA

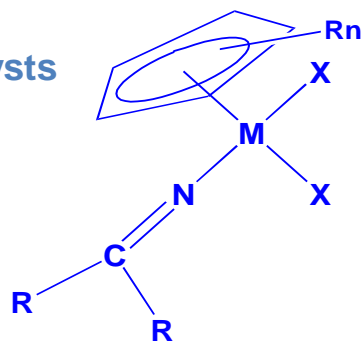
# NOVA Chemicals Single Site Catalysts



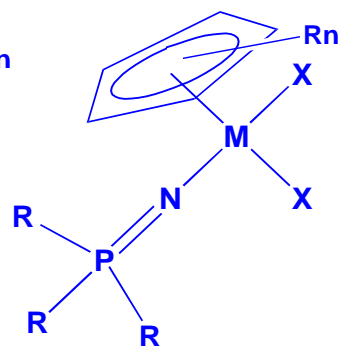
Phosphole Catalysts



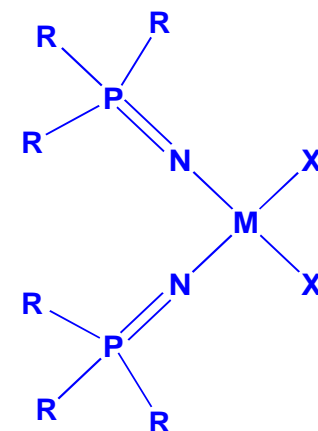
Phosphinimine Catalysts



Ketimide Catalysts

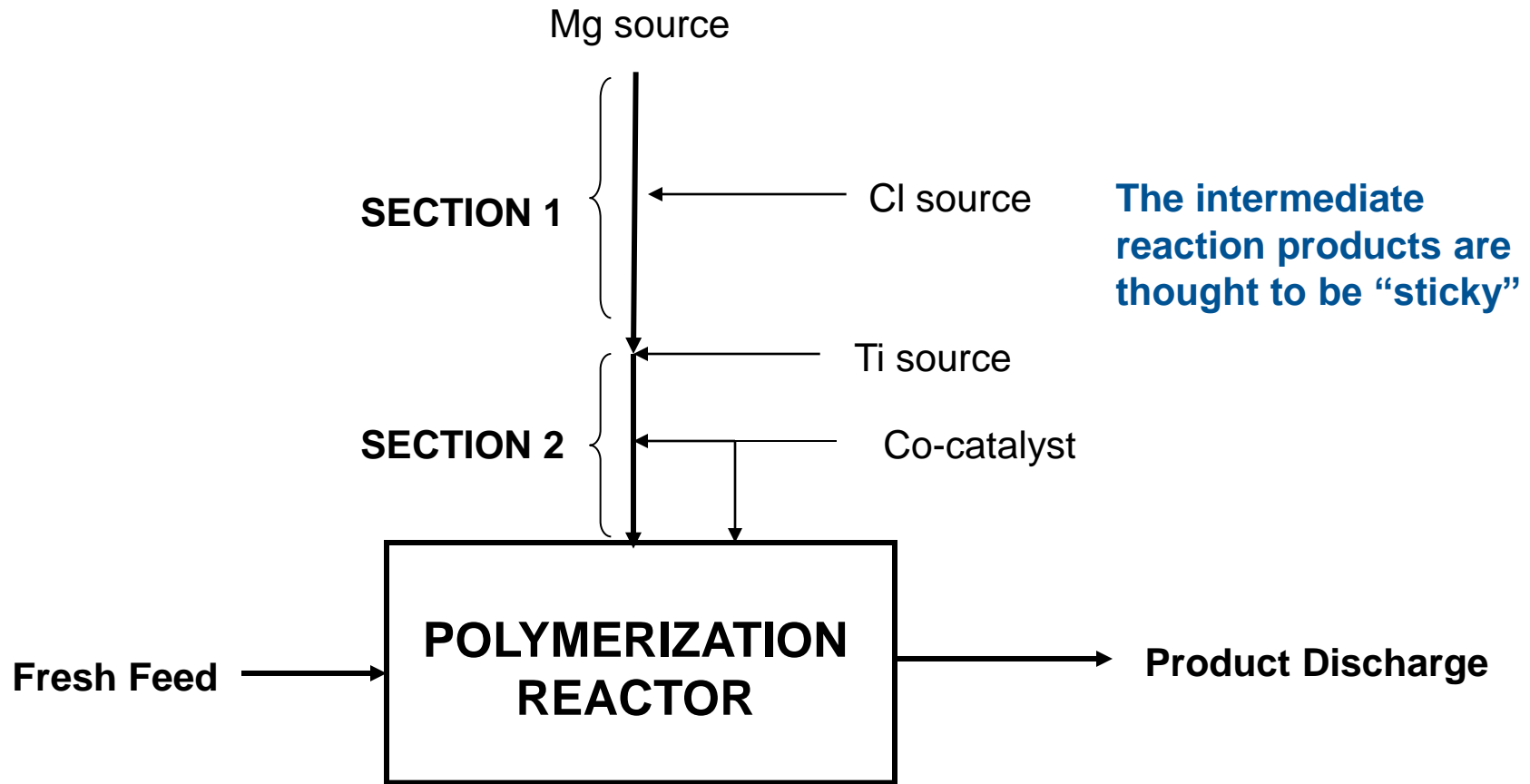


Siloxane Catalysts



# Advanced SCLAIRTECH Technology: Ziegler-Natta Catalyst

Polymerization catalyst supported on solid particles formed *in-situ*



The intermediate reaction products are thought to be “sticky”

If ONLY Life Was That Simple!

## Advanced SCLAIRTECH Technology: Z-N Catalyst

- On scale up: both Section 1 & 2 plugged often
  - ▶ The catalyst flows would become uncontrollable/stop
  - ▶ Section 1 plug – appeared to be catalyst residue; could not be flushed out with hot solvent
  - ▶ Section 2 plug - appeared to be polymeric in nature - hot solvent flushing helped but could not be completely removed
- Two-pronged approach:
  - 1) Catalyst Formulation Change
    - Significantly reduced polymeric build-up in Section 2
    - Reduced deposits in Section 1 to lesser degree
  - 2) Alternate mixing style/philosophy for catalyst formation

# Z-N Catalyst Delivery System Design Basis

## ■ Two Coaxial Mixers in Series

1. Diameter & velocity ratios
  - Prevent recirculation downstream of injector tip
2. Turbulent flows but not too intense
  - Control mixing such that reaction occurs away from the wall & in the core of the pipe as rapidly as possible
3. Prevent & minimize disturbances to the flow
  - Minimize the number & effects of penetrations (flanges, TIs & PIs) plus use polished/smooth walls & sharp injector tips
4. Orient the mixer vertically
  - Prevent solid settling or accumulation at the wall
5. Large bore mixing sections

## ■ Modular design

- ▶ Replace/modify either section: may not be the final solution

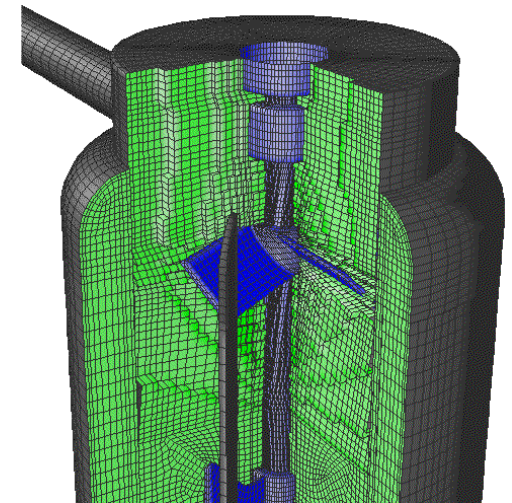
# Computational Fluid Dynamics:

- Computational Fluid Dynamics (CFD)

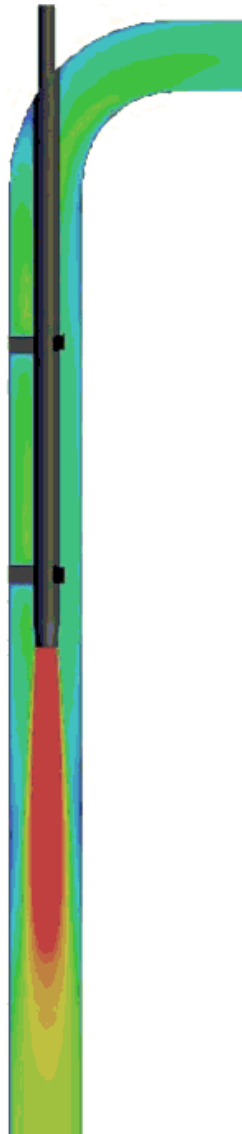
CFD is the science of predicting fluid flow, heat transfer, mass transfer, chemical reactions & related phenomena by solving the mathematical equations which govern these processes using a numerical process

- ▶ Plant support by troubleshooting unit operations
- ▶ Design new equipment & evaluate vendor designs
- ▶ Consider different operating scenarios
- ▶ Root-cause failure analysis
- ▶ Address safety concerns
- ▶ Understanding reactor scale-up

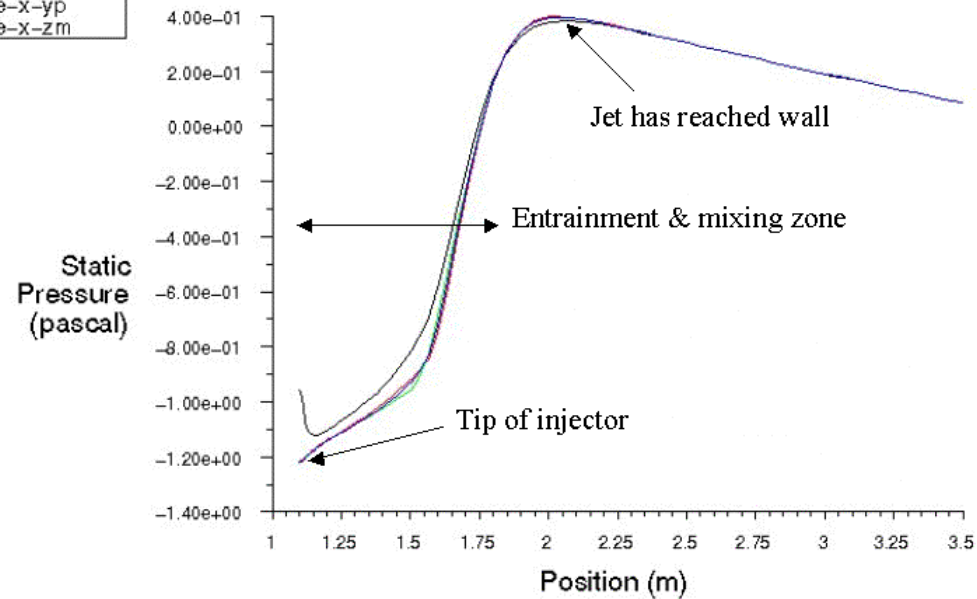
- A useful engineering tool



# Catalyst Delivery System - Section 1 CFD



- line-x-axis
- line-x-ym
- line-x-yp
- line-x-zm

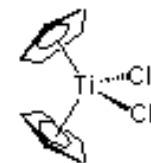


## Why Model with CFD?

- Scale-Up
  - ▶ Aids scale-up process across three orders of magnitude in reactor volume (bench -> pilot -> commercial)
- Improve existing products & aid in product development
  - ▶ Identify source(s) of undesirable product characteristics grease or high MW tails
  - ▶ Mixing to adjust MWD & co-monomer incorporation
- Design & diagnostics
  - ▶ Design of new & modification to existing reactors
  - ▶ Provide data for mechanical design: impeller forces, shaft torque, temperature distributions, etc.

# CFD - The Challenges

- Complex kinetics
  - ▶ Fast, multi-step co-polymerization reactions in laminar & turbulent flows
  - ▶ Require many rate constants & mechanisms
  - ▶ Needed to predict product MWD & co-monomer incorporation
  
- Solution physical properties
  - ▶ Reactors operate at high temperature & 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 & temperature
  
- Complex geometry
  - ▶ Multiple, complex proprietary impellers; large diameter ratio
  - ▶ Multiple monomer & catalyst feed nozzles, nozzle from 1<sup>st</sup> reactor to 2<sup>nd</sup>



# CFD Model – Complex Kinetics

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



Bench Scale Reactor

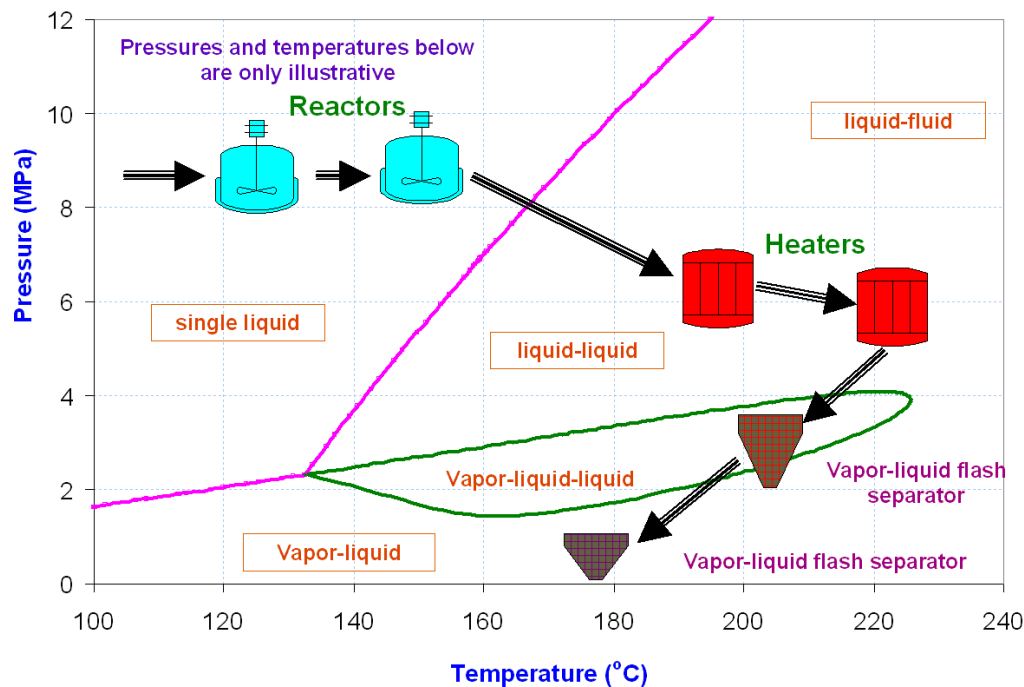


Sarnia Pilot Plant

# CFD Model – Physical Properties

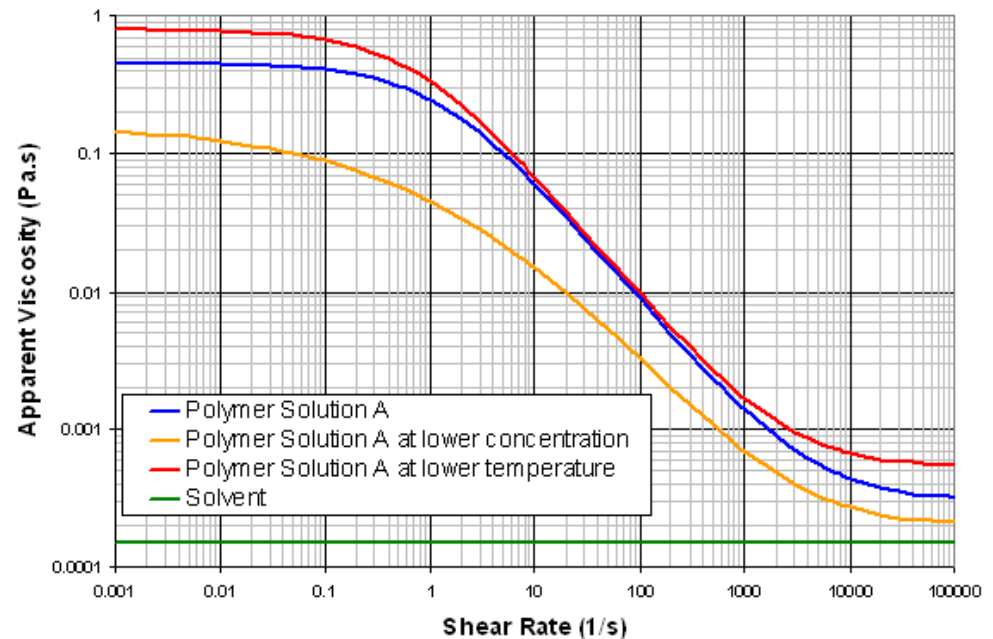
- PC-SAFT Equation of State

- ▶ Prediction of phase envelope, pure component & mixture densities for polymeric systems
- ▶ Validated in collaboration with the University of Dortmund, Rice University & University of Calgary

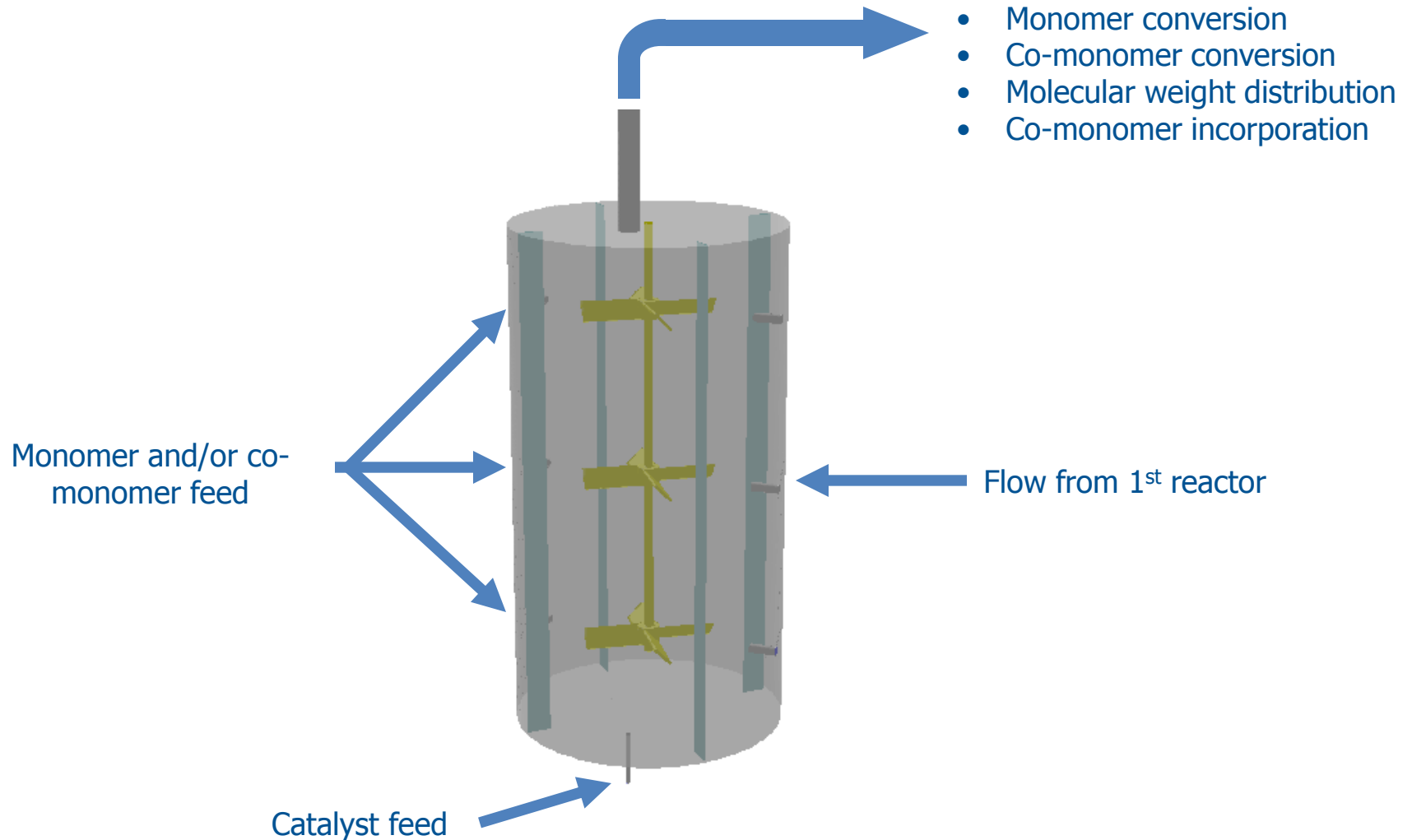


# CFD Model – Physical Properties

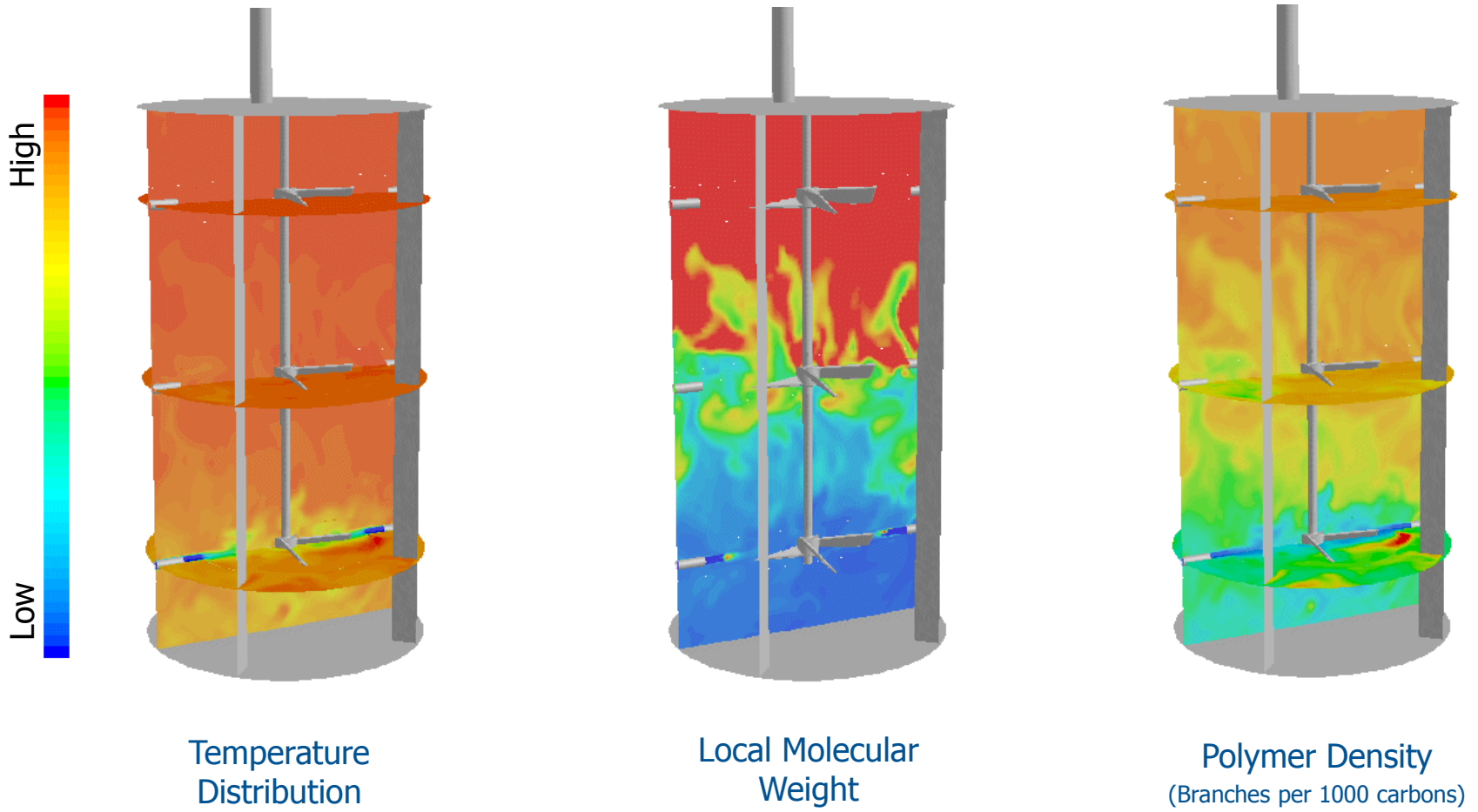
- Viscosity
  - ▶ Solvent & pure component viscosities as a function of temperature & pressure from the University of Mainz
  - ▶ Solution viscosity determined using Multi-Pass Rheometer (MPR), which provides viscosity measurements at reactor conditions



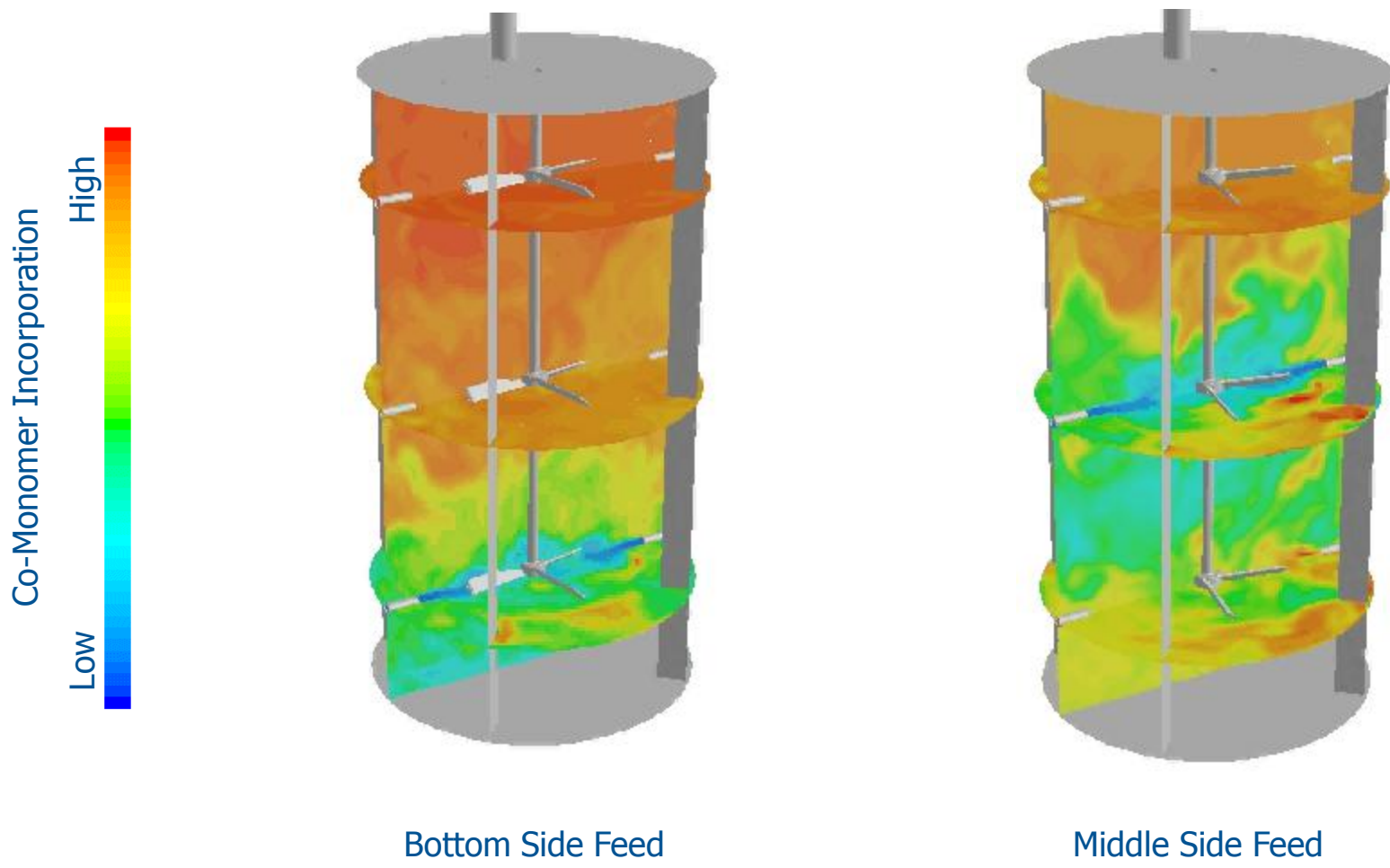
## Example Reactor



# CFD Model – Typical Results



# CFD Model – Typical Results



## Keys To Rapid Development & Commercialization

**The right blend of science & engineering skills with the right tools & equipment are needed to succeed in the commercialization of a new process**

- **Technical Creativity**
- **Investment in Fundamental R&D**
- **Pilot Plant facility**
- **Multi-discipline interactions**
- **Chemistry & Engineering**
- **“Human Resources”**



## ***Acknowledgements***

**Our colleagues: Eric Cheluget, Steve Brown, Larry VanAsseldonk**

**Numerous University collaborators**

**SCLAIRTECH Process Team**

**Fluid Dynamics Team**

**NRTC/NCTC Support Groups and Pilot Plant personnel**

**NOVA Chemicals Technology Leadership Team**