Greetings from WUSTL, a premiere university in teaching and research that draws students to St. Louis from all 50 states in the US and more than 90 other nations.

St. Louis is the demographic center of the US and home to the Gateway Arch.

Brookings Hall administered the world’s fair in 1904.
Reaction Engineering Challenges

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Chemical Reaction Engineering Laboratory (CREL)
Energy, Environmental and Chemical Engineering (EECE) Department
Washington University in Saint Louis (WUSTL)
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SABIC, The Netherlands, September 6, 2012
Objectives of CREL since 1974

- Education and training of students in multiphase reaction systems
- Advancement of reaction engineering methodology via research
- Transfer of state-of-the-art reaction engineering to industrial practice

CREL Sponsors and Collaborators

Industrial Sponsors
- ADM
- ABB Lummus
- Air Products
- Bayer
- BP
- Chevron Texaco
- ConocoPhillips
- Corning
- Dow Chemical
- Dupont
- Enitechnologie
- Eastman Chemicals
- Exxon - Mobil
- IFP
- Ineos Nitriles
- Intevep
- Johnson Matthey
- Marathon Oil
- Mitsubishi
- Praxair
- Sasol
- Shell
- Statoil
- Syntroleum
- Total
- UOP

Governmental Sponsors
- DOE, NSF, USDA

Chemical Reaction Engineering Laboratory
Challenge: Addressing global energy, environmental and materials needs

- Role of reaction engineering in meeting societal needs
- Past and present practices
- Multi-scale science based approach
- Scientific challenges
- Other barriers
- Industry–university partnerships

Dudukovic, M.P., Science 325, 698, 2009;
Key Factors Affecting the Environment and Sustainability

- Total population
- Lifestyle

- Agricultural practices
- Mining practices
- Energy utilization

- Recreational activities
- Manufacturing practices
The Domain of Chemical Engineering

Challenges:
- Cleaner, sustainable processes
- Increased atom and energy efficiency
- Improved safety
- Ability to scale-up based on science
- Making environmentally benign processing profitable
Historically, **process technologies** have been viewed as means for more **effective utilization of the environmental resources** in providing alternate life styles and increased living standards of humankind.

The **role of process engineers** has been to ensure that **commercially practiced technologies** (in production of fuels, chemicals, materials, pharmaceuticals and in variety of consumer end products) are **profitable** and **operable**.

Promising chemistries were ‘**scaled-up**’ mainly based on **empiricism**. **Environmental and sustainability issues** were considered “post-facto”, if at all.

**CONTINUED USE OF THIS APPROACH USES GLOBAL RESOURCES INEFFICIENTLY AND IS NOT SUSTAINABLE!**
GLOBAL ENVIRONMENTAL IMPACT OF PROCESS TECHNOLOGY AND POSSIBLE WAYS OF REDUCING IT *

Global environmental impact $\propto (1 - \text{process efficiency}) (\text{consumption per capita}) (\text{population})$

Process inefficiency

1) Population control - unacceptable to two major religions
2) Reduction in per capita consumption - anathema to globalization
3) Increase in all types of process efficiency (atom, mass, energy)

---

*Dudukovic “Relevance of Multiphase Reaction Engineering to Modern Technological Challenges”, I&ECR 46, 8674 (2007)*
Requirements for the Future

• **Novel process technologies** that minimize the environmental imprint by improved efficiencies and that are sustainable. Require a science based multi-scale approach applicable over all industrial sectors.

• **Universities stay the course** in developing process engineers with expertise in science based multi-scale approach. This will allow innovation in many technologies.

• **Science based scale-up reduces the risk of novel technologies** and helps to close the current wide open loop-holes to profitability via old inefficient processes

Current Process Assessments

• Use flow charts that interconnect process units
• Use mass and energy balances resulting from conservation laws and estimated parameters from constitutive equations for transport and kinetics in each process unit
• The same basis used for economic and environmental impact assessment
Green Chemistry and Green Processing

**Plant Scale**
- Raw Materials
- Pretreatment
- Energy
- Reactor
- CRE
- Separator
- Waste or pollutants
- Energy

**Global Scale**
- Raw Materials
- Energy
- Value Added Products, Fuels
- Waste or pollutants
Synthesis & Natural Gas Conversion

MeOH, DME, MTBE, Paraffins, Olefins, Higher alcohols, ...

Energy
Coal, oil, gas, nuclear power plants

Petroleum Refining
HDS, HDN, HDM, Dewaxing, Fuels, Aromatics, Olefins, ...

In USA alone
Value of Shipments:
$US 640,000 Million

Bulk Chemicals

Aldehydes, Alcohol, Amines, Acids, Esters, LAB's, Inorg Acids, ...

Uses of Multiphase Reactor Technology

Polymer and Materials Manufacture

Polycarbonates, PPO, Polyolefins, Specialty plastics; semiconductors etc

Fine Chemicals, Pharmaceuticals, Nanomaterials

Ag Chem, Dyes, Fragrances, Flavors, Nutraceuticals

Energy

Syngas, Methanol, Ethanol, Oils, High Value Added Products

Biomass Conversion

De-NOx, De-SOx, HCFC’s, DPA, “Green” Processes ...

Environmental Remediation

In addition: Minerals processing via hydro and pyro metallurgy
Multi-Scale Chemical Reaction Engineering (CRE) Methodology

**Reactor choice determines plant costs; Need improved reactor selection and scale-up**

**MOLECULAR SCALE (RATE FORMS)**
- Strictly Empirical
- Mechanism Based
- Elementary Steps

**EDDY OR PARTICLE SCALE TRANSPORT**
- Empirical
- Micromixing Models
- DNS / CFD

**REACTOR SCALE**
- PFR/CSTR
- Axial Dispersion
- Phenomenological Models
- CFD

**PROCESS SCALE**
- Steady State Balances
- Dynamic Models for Control & Optimization

**Dudukovic, Larachi, Mills, Catalysis Reviews (2002), 44(1), 123-246**
Reactors Models

• All reactor models are based on the principle of conservation of mass, species mass, energy and momentum applied to a properly selected control volume in the system:

\[(\text{rate of accumulation}) = (\text{rate of input}) - (\text{rate of output}) + (\text{rate of generation})\]

NOTE: The reaction rate formulation to be used in the reactor scale model must properly incorporate the key features of all the smaller scales.

The control volume size and dimensionality of the model depend on the level of knowledge of the flow field, phase distributions and exchange rates between them. Models vary from assumptions of ideal flow fields (i.e. plug flow or perfect mixing on one end to CFD descriptions of the system.

Reactors of *High Volumetric Productivity* and *High Selectivity* are needed for efficient environmentally friendly technologies.
Reactor Volumetric Productivity = moles of product produced per unit reactor volume and unit time = average process rate for the reactor

Average reactor process rate is a function of:
- kinetic rate, which in turn depends on local temperature and composition distributions
- local mass and heat transfer effects on the kinetic rate
- reactor flow and contacting pattern which determines the composition-temperature field in the reactor

Reactor selectivity = f(kinetics, local transport effects and global contacting pattern)
Environmental Impact

Process industries that practice reaction engineering at a high level of sophistication have a much smaller adverse environmental impact as measured by the E-factor than those that do not; those that largely ignore reaction engineering have undesirably large impact factors as shown in the next table.
### Environmental Acceptability, as Measured by the E-Factor

<table>
<thead>
<tr>
<th>Industry</th>
<th>Product tons per year</th>
<th>Waste/product ratio by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil refining</td>
<td>$10^6 - 10^8$</td>
<td>~ 0.1</td>
</tr>
<tr>
<td>Bulk chemicals</td>
<td>$10^4 - 10^6$</td>
<td>&lt; 1 – 5</td>
</tr>
<tr>
<td>Fine chemicals</td>
<td>$10^2 - 10^4$</td>
<td>5 – 50</td>
</tr>
<tr>
<td>Pharmaceuticals</td>
<td>$10^0 - 10^3$</td>
<td>25 - &gt; 100</td>
</tr>
</tbody>
</table>
Waste Reduction (WAR) algorithm


WAR algorithm: determines the potential overall environmental impact of a chemical process including acidification, greenhouse enhancement, ozone depletion, photochemical oxidant formation, etc.
Available at: www.epa.gov/oppt/greenengineering/software.html

Based on Conservation Equations applied to the process flow sheet:
- using mass and energy balances along with chemical reaction engineering and engineering economics.
- accounting for the flow of potential environmental impact in and out of the process.
**Schematics of WAR algorithm**

Fig. 1. The waste reduction (WAR) algorithm is a methodology that aids in the environmental evaluation of chemical manufacturing processes. This is where the WAR algorithm fits into the overall life cycle of a product.

Final Comments on Current Methods for Environmental Impact Assessment

• Algorithms like WAR are very useful in taking the drudgery out of mass and energy balances and flow-sheeting. They establish a basis for comparison of designs.

• These algorithms, just like ASPEN or HYSIS and other of that type, cannot predict the actual performance of a reactor in a new process nor can they assess the effect of reactor type on this performance in absence of previous experiences. They also cannot accurately predict the effect of changes in process conditions on performance of existing reactors.

• To be able to do a better environmental assessment one needs improved reactor models and a systematic approach to reactor selection and optimal operation.

• Current algorithms provide no clues as to how to select the right reactor type and best operate it.
Steps Needed to Ensure Clean Processing (high atom, material and energy efficiency and minimum waste generation)

**Multiscale Process Engineering (MPE)**

- Selection of ‘green chemistry’ (12 Principles)
- Selection of right reactor type for implementation of green chemistry
- Exploring means for process intensification
- Use of modern scale-up methodology
To implement green sustainable process chemistry in industrial practice modern reaction engineering approaches MUST:

optimize the atom, material, and energy efficiency
minimize wastes
reduce the burden on separation units
minimize capital costs by process intensification
achieve safe operation

This requires full understanding of the multi-scale character of the reaction system at hand and a systems approach to reactor selection, scale-up, design and operation.
Making Friends with Chemical Reactors

by

Octave Levenspiel
Professor Emeritus – Oregon State University

Alias: Dr. Suess of Reaction Engineering

Narrated by: M.P. Dudukovic
Making friends with reactors and knowing their habits is important.
Texas cowboy

Buffalo

Barbecue
Omelette
Rule 1 For Single Reactions

Given $A \rightarrow R$, with rate $= kC_A^n$

$C_{Ao} \rightarrow \text{volume } V \rightarrow C_A, X_A$

to minimize $V$ keep $C_A$ as high as possible
HOMOGENEOUS SYSTEMS
(Optimizing Volumetric Productivity)

**Batch Reactor**

\[
\begin{align*}
t &= 0, \quad C_A &= C_{A0} \\
t &= t, \quad C_A &= C_{A0} (1 - X_A) \\
t_s &= \text{shutdown time} \\
t &= \int_{C_A}^{C_{A0}} \frac{dC_A}{R_A} = \text{reaction time}
\end{align*}
\]

\[
\frac{\text{Moles of A per unit time}}{t + t_s} = \frac{C_{A0} V X_A}{t + t_s}
\]

**Continuous Flow Stirred Tank Reactor (CSTR)**

\[
F_A = F_{A0} (1 - X_A)
\]

\[
T = \text{const.}
\]

\[
F_{A0} X_A = -R_A V
\]

**Plug Flow Reactor (PFR)**

\[
F_A = F_{A0} (1 - X_A)
\]

\[
(\frac{\text{Moles of A per unit time}}{X_A}) = \frac{F_{A0} X_A}{\int_{0}^{X_A} \frac{dX_A}{R_A}} V
\]

\[
= \left( \frac{1}{X_A} \int_{0}^{X_A} \frac{dX_A}{R_A} \right) V
\]
Rule 2 For Reactions in Series

Given $A \rightarrow R \rightarrow S \rightarrow T \rightarrow \ldots$

to maximize any intermediate do not mix fluids of different compositions
Rule 3  For Reactions in Parallel

\[ R \quad \cdots \quad r_R = k_0 \quad \cdots \quad \text{lowest order} \]

\[ A \rightarrow S \quad \cdots \quad r_S = k_1 C_A \quad \cdots \quad \text{intermediate order} \]

\[ T \quad \cdots \quad r_T = k_2 C_A^2 \quad \cdots \quad \text{highest order} \]

To maximize \( R \quad \cdots \quad \text{operate at lowest} \ C_A \)

To maximize \( S \quad \cdots \quad ? \)

To maximize \( T \quad \cdots \quad \text{operate at highest} \ C_A \)
Rule 4 Complex Reactions

These can be analyzed by their component simple reactions, for example

\[ \begin{align*}
A + B &\rightarrow R \\
R + B &\rightarrow S
\end{align*} \]
Industrial Example - Auto Antifreeze

$$
\text{EtO}_x + \text{H}_2\text{O} \rightarrow \text{EtO}_x \rightarrow 10\text{m}
$$

$$
\text{O}_2 \rightarrow \text{ch}_2-\text{ch}_2\text{oh} \rightarrow \text{EtO}_x \rightarrow \text{EtO}_x
$$

$$
\text{ethylene glycol} \quad \text{diethylene glycol}
$$

$$
\text{A} + \text{B} \rightarrow \text{R} \\
\text{R} + \text{B} \rightarrow \text{S}
$$
Given $A \xrightarrow{\text{cells}} R + C \quad \text{rate} = \frac{kC_A C_C}{C_A + C_M}$

which reactor could be optimum, and which can never be (optimum = minimize volume)
Fig. 2. Reactor superstructure with three CSTRs.

three interconnected mixed flow reactors
Examples 3 & 5

\[
\begin{align*}
\text{A} & \rightarrow \text{B} \quad \text{r}_B = 0.025 \\
\text{A} & \rightarrow \text{C} \quad \text{r}_C = 0.2 \, \text{C}_A \\
\text{A} & \rightarrow \text{D} \quad \text{r}_D = 0.4 \, \text{C}_A^2 \\
\text{C} & \rightarrow ? \quad \text{maximize} \left( \frac{\text{C}_C}{\text{C}_{\text{AD}} - \text{C}_A} \right)
\end{align*}
\]

\( \text{V} = 100 \, \text{lit/min} \)

\( \text{C}_{\text{AD}} = 1 \, \text{mol/lit} \)

From CRE

\[
\text{C}_{\text{Aopt}} = \sqrt{\frac{k_0}{k_2}} = \sqrt{\frac{0.025}{0.4}} = 0.25
\]

and \( \text{C}_R = 0.375 \quad \frac{\text{C}_R}{\text{C}_{\text{AD}} - \text{C}_A} = 0.5 \quad \text{V}_{\text{mixed}} = 750 \, \text{lit} \)
Example 3  Three different solutions

CES 45  595 (1990)
Example 7

Denbigh reactions

$C_{AD} = 6.0 \text{ mol/lit}$
$C_{B0} = 0.6 \text{ mol/lit}$
$V = 100 \text{ lit/hr}$

**Reactor**?

$C_{AD} = 6.0$
$C_{B0} = 0.6$
$V = 20.706 \text{ lit}$

$\frac{C_{B}}{C_{D}} = ?$

$\frac{C_{B}}{C_{D}} = ?$

$maximize \frac{C_{B}}{C_{D}}$

$CES 45 595 (1990)$
My First Assignment as a Process Engineer (1967)

EUROPEAN (WEST GERMAN) PROCESS:

\[ \text{CARBON} + \text{SULFUR} \rightarrow \text{CARBON DISULFIDE} \]

\[ \begin{align*}
C \quad & \quad 2S \\
\rightarrow \quad & \quad \text{CS}_2
\end{align*} \]

REACTOR: REFRACTORY LINED KILN WITH GRAPHITE ELECTRODES
Glowing Red Hot Coal !!!

Poisonous Gases !!!

VOLCANIC ERUPTIONS ONCE A WEEK (on the average) !!!

Reactor Clearly Environmentally Unfriendly !
Runaway caused by thermal instability and ‘hot spots’ in the reactor – not controllable

Recommendation of young engineers to the boss: “Pre-volatize the sulfur and suspend smaller coke particles in sulfur vapor – run the process in a fluidized bed”

Boss’s Response
“No way! You know nothing about fluidization technology! Go improve on the German kilns!”

Conclusion
The “improved design of the “German” kilns (positioning more bottom electrodes to expand the hot zone) led to “our” kilns erupting once every two to three weeks (a big improvement according to our boss)

MORALE
If pollution was part of the cost, risk would have been taken to go for new technology. Without it no new process.

Lessons still valid today: Aversion to risk, copying existing designs or expired patents, believing that western technologies are superior, lack of business incentives to innovate.
Reaction routes and reactors for alkylation

- Parafin (P) + olefin (O) = alkylate (A) – wanted

- Olefin (O) + olefin (O) = oligomers - unwanted

- Keep P high and O low!!

Traditional (WWII) technology

- Liquid phase acid catalysts such as HF or H2SO4
- Extensive waste generation
- Highly corrosive systems of high capital cost

Currently licensed technologies essentially the same (but with improved flow pattern) in spite of availability of solid acid catalysts
Homogeneous Systems (optimizing selectivity)

\[ A + B \rightarrow P \text{ (desired product)} \]
\[ A + A \rightarrow S \text{ (undesired product)} \]

- Which is the optimal flow pattern?
- What is the optimal selectivity?

(at fixed feed concentrations, feed ratio of \( F_{A0}/F_{B0} \) and conversion of B)

 initially only B

 initially only A
Alkylation: HF Catalyst (Old); Deactivating Solid Supported Liquid Catalyst or Solid Acid Catalyst (New)

OLD REACTOR: MIXER-SETTLER WITH EXTERNAL RECYCLE PUMP

OLD REACTOR: MIXER-SETTLER WITH EXTERNAL RECYCLE PUMP

PRODUCT \( t \approx 40 \text{min} \)

HF RECYCLE with a pump !!

NEWER REACTOR: “LIFT” PRINCIPLE: NO RECYCLE PUMP

NEWER REACTOR: “LIFT” PRINCIPLE: NO RECYCLE PUMP

PRODUCT \( t \approx 30 \text{sec} \)

HF INTERNAL RECYCLE
no pump !!
no leaky seals !!
Still HF is there!!

Simultaneous Development of Catalyst and Reactor Technology

Simultaneous Development of Catalyst and Reactor Technology

Porous support with liquid superacid catalyst

Thin film solid acid catalyst

Packed bed with moving active zone

Liquid-solid Riser

Fluidized bed

Need reactor model to assess selectivity and productivity
Example of ‘Best Available Technology’ in Alkylation:

**Application:** Combines propylene, butylene and pentylene with isobutane, in the presence of sulfuric acid catalyst, to form a high-octane, mogas component.

**Products:** A highly isoparaffinic, low Rvp, high-octane gasoline blend-stock is produced from the alkylation process.

**Installation:** 119,000-bpd capacity at 11 locations with the sizes ranging from 2,000 to 30,000 bpd. Single reactor/settler trains with capacities up to 9,500 bpsd.

**Licensor:** ExxonMobil Research & Engineering Co.
A System Approach to Multiphase Reactor Selection

Economics

Reactants

Reactor Type & Contacting Pattern?

Products

Process Requirements
• Maximum selectivity
• Maximum conversion
• Maximum productivity
• Stable
• Easy scale-up
• Operability

Environmental Constraints
• Minimum pollution

Why System Approach?
• Number of configurations extremely large
• Limits to intuitive decision making
• Innovations are possible
Example: Recovery of Oil From Oil Shale

Process Requirements (Wish List)

- Maximize “oil” recovery (99%+)
- Scale-up to mega-size units (≈ 500 kg/s feed)
- Minimize reactor volume
- Handle fines well

>200 G-S Reactor Configurations possible!

After Krishna (1989)
Decisions to be made:

I. Particle Size

II. Contacting Pattern
   a. Overall contacting flow pattern of gas and solid phases:
      - (A) counter-current
      - (B) co-current
      - (C) cross-current
   
   b. RTD of each phase:
      - Gas Phase: plug flow, well-mixed
      - Solid Phase: plug flow, well-mixed

III. Gas-Solid Fluidization Regime

Downflow Moving Beds
Raw Shale

\[ \downarrow S \uparrow G \]

- Paraho
- Kiviter
- Tosco
- Petrox (11 mtd)

Packed moving bed

Spent shale

Volatiles

Cold product gas

Air or product gas

Superior Oil's
Horizontal Moving Bed (merry-go-round)

Still

Air + fuel recycle

Fresh shale

Spent shale

Recycle gas

\[ d_p = 50 \text{ mm} \]

TOSCO II (ball mill)

Still

\[ d_p = 10 \text{ mm} \]

Lurgi - Ruhrgas (meat grinder)

\[ d_p = 5 \text{ mm} \]

Hot recycler gas

Steam seal

Downflow of gas

Shale + C

Volatiles

Rock pump pushes shale upward

TOSCO II

Fuel + air

Volatile

Pyrolysis drum

Shale to carbon burn up

Lift pipe

Raw shale

Hot waste gas

Combustion in lift pipe

Mixer pyrolyzer

Waste

Solid recycle ratio 2 to 4

Air & fuel
Shell’s SPHER 3 Bed Concept

Chevron’s STB (staged turbulent bed)
The “Ideal” Reactor: Multi-Stage Cross-Current Fluidized Bed

Meets the criteria:
- Small particles
- Plug flow of solids
- Short vapor residence time (cross-flow)
- Good mixing and heat transfer
- Scale-up possible – study one train

Shell Shale Retorting Process
(Shell Research)

Krishna (1992)
Multi-Scale Chemical Reaction Engineering (CRE) Methodology

**REACTOR PERFORMANCE** = f ( input & operating variables ; rates ; mixing pattern )

**Reactor choice determines plant costs; Need improved reactor selection and scale-up**

**MOLECULAR SCALE (RATE FORMS)**

10^{-10} m

- Strictly Empirical
- Mechanism Based
- Elementary Steps

**EDDY OR PARTICLE SCALE TRANSPORT**

- Empirical
- Micromixing Models
- DNS / CFD

**REACTOR SCALE**

- PFR/CSTR
- Axial Dispersion
- Phenomenological Models
- CFD

**PROCESS SCALE**

10^2 m

- Steady State Balances
- Dynamic Models for Control & Optimization

*PFR/CSTR*

_Dudukovic, Larachi, Mills, Catalysis Reviews (2002), 44(1), 123-246*
By advancing the scientific basis of the multi-scale reaction engineering methodology CREL demonstrated its value in numerous and diverse technologies such as:

• desulfurization of heavy crudes

• hydrogenation of commodity and specialty chemicals

• polysilicon and single crystal silicon production

• manufacture of long fiber reinforced resins

• conversion of gas to liquid fuels

• synthesis of pharmaceuticals, etc

CREL also demonstrated the value of the approach in diverse reactor types (packed beds, trickle beds, slurries, mixed tanks, bubble columns, etc)
Steps Needed to Ensure Clean Processing (high atom, material and energy efficiency and minimum waste generation)

**Multiscale Process Engineering (MPE)**

- Selection of ‘green chemistry’ (12 Principles)
- Selection of right reactor type for implementation of green chemistry
- Exploring means for process intensification
- Use of modern scale-up methodology
Improved and more efficient reactor performance is sought by different means of process intensification

**COMBINATION OF REACTION AND SEPARATION**
- Reactive / catalytic distillation
- In situ adsorption
- Membrane reactors

**MINIATURIZATION AND TRANSPORT ENHANCEMENT**
- Micro Reactors
- Rotating packed bed
- Structured packing

**DYNAMIC FORCED PERIODIC REACTOR OPERATION**
- gas–solid exothermic reactions,
- gas-solid exothermic and endothermic reaction coupling,
- gas-liquid-solid systems (trickle beds)

**USE OF SOLVENTS AND SUPERCritical MEDIA**
- phase transfer catalysis
- enhancement of selectivity and ease of catalyst separation
OLD --------- and ---- NEW

MeOH + AcOH = MeAC + H2O
Catalytic Distillation (CD) in Industrial Practice
(Larry Smith  AIChE Industrial practice Award 2006)

• Concept well proven - *MTBE, ETBE, TAME, CDHydro, EB and Cumene, CDHDS+
• More than 25 “*first-of-a-kind*” CD Processes
• 113+ units in operation (CDTech)
• Pilot units run at up to 1 TPD or 5-10 BPD
• Successful scale-up to 58,000 BPSD

Typical CD Advantages

Lower Capital Cost
- Reduced equipment count; -Built-in heat integration

Higher Conversion
- Reaction equilibrium overcome by product separation
  - Isothermal operation
  - Improved mass transfer

Longer Catalyst Life
- Self-cleaning system
Rule 4  Complex Reactions

These can be analyzed by their component simple reactions, for example

\[
\begin{align*}
A + B &\rightarrow R \\
R + B &\rightarrow S
\end{align*}
\] \Rightarrow

\[
\begin{align*}
A &\rightarrow R \rightarrow S \\
B &\leftrightarrow R \\
B &\leftrightarrow S
\end{align*}
\]
REATIONS IN ETHYLENE GLYCOL PRODUCTION

ETHYLENE GLYCOL MANUFACTURE:

REACTION SCHEME:

EO + W = MEG
EO + MEG = DEG
EO + DEG = TEG

CONVENTIONAL THINKING:

\[ W \xrightarrow{+EO} MEG \xrightarrow{+EO} DEG \xrightarrow{+EO} TEG \]

\[
EO \begin{cases} 
+W & \rightarrow MEG \\
+MEG & \rightarrow DEG \\
+DEG & \rightarrow TEG 
\end{cases}
\]
CONVENTIONAL PROCESS:
1. Plug flow reactor
2. Large excess water in the feed
3. Optimal residence time
4. Downstream separation – large separation train

PROPOSED PROCESS:
1. Reactive Distillation

ADVANTAGE:
Remove wanted product in situ as it is formed;
Make excess water available in reaction zone
OPTIMAL DISTRIBUTED FEED REACTIVE DISTILLATION COLUMN FOR ETHYLENE GLYCOL SYNTHESIS

Ciric et al. AIChEJ 1999
A train of bubble columns (sparged reactors) through which liquid toluene and chlorinated products flow in series while chlorine is added into each column and hydrogen is removed from the column.

Typical selectivity to benzyl chloride: 90% But Toluene conversion is less than 30%. **Can one do better?**

Process Intensification via Multi-functionality by Reaction – Separation Coupling: Proposed Technology Configured into a Semi-Batch Mode

Schematic of Photo Reactive Distillation System

Allows in situ product removal and toluene recycle.

Selectivity to benzyl chloride: 96% + up to toluene conversion of 98%.

Product In Situ Removal
-Membrane Reactors
-In Situ Adsorption
-Trickling Solids Adsorbent Reactor

Novel concept in which fine particles of solid adsorbent flow countercurrent to gas (reactant and product) through packed catalyst bed (Ross and Van Swaaij, 1979; Claus, Vergnes and LeGoff, 1976)

*In-situ* product removal overcomes equilibrium limitations effectively

100% conversion of syngas to methanol demonstrated (Kuczinski and Westerterp, 1987)

- $CO + 2H_2 = CH_3OH$
Standard adiabatic fixed bed for exothermic reaction leads to monotonically rising temperature profile and low exit conversion.

F. Cottrell (U.S. Patent, 1938)-Foul Gas Deodorizer

An inverted U shaped temperature profile in a bi-directional FBR.
Overcomes equilibrium limitations.
Achieves high temperatures with dilute feed.

- Matros (1989)
- Van de Beld & Westerterp (1996)
- Eigenberger & Nieken (1988)
Reverse Flow Process for Exo and Endo Reaction Coupling Wrong-Way Coupling (Kulkarni and Dudukovic (1996-1998))

Exo: Methane combustion
Endo: Methane Steam Reforming

Additional studies on exo-endo coupling in reverse flow by Kuipers et al (Twente) and Eigenberger et al (Stuttgart) etc.
Steps Needed to Ensure Clean Processing (high atom, material and energy efficiency and minimum waste generation)

**Multiscale Process Engineering (MPE)**

- Selection of ‘green chemistry’ (12 Principles)
- Selection of right reactor type for implementation of green chemistry
- Exploring means for process intensification
- Use of modern scale-up methodology
Bench scale achieved desired conversion, yield, selectivity, productivity

Scale-up

Commercial production

Alternatives:

1. Scale-up in parallel (Scale-out, scale-up by multiplication.)

2. Scale-up vertically – account for effect of change in equipment scale on multi-scale interaction of transport and kinetic phenomena.
TWO KEY SCALE-UP REQUIREMENTS

• Match mean residence time (mean contact time)
• Match [or account for the change in] dimensionless variance of residence (contact) times

– For **scale-up in parallel** this is achieved by ensuring the same amount and state of catalyst in each channel and uniform flow distribution that provides equal flow in each channel (e.g. wall cooled packed tubular reactors, micro-reactors, monoliths, etc)

– For **vertical scale-up** one needs to know the physics of flow to be able to assess the effect of reactor scale on the above two parameters
Direct Scale-up of Tubular and Packed Bed Wall-Cooled Reactors: Scale-up by Multiplication

Single tube of diameter $d_t$ and length $L$ at given feed conditions $(P_0, T_0, C_0)$ and given feed rate $Q$ (l/h), produces the desired product at the rate of $F_{P_L}$ ($mol P/h$) and the desired selectivity.

Identical tubes of diameter $d_t$ and length $L$ produce then the commercial production rate $F_{p_C} (S = F_{p_C} (F_{P_L}))$, using identical feed conditions and flow rate, at the desired selectivity.

Possible Problems: - External heat transfer coefficient
- Flow manifold for flow distribution

SAME PRINCIPLE USED IN MICROREACTORS
Advantages of Micro reactors

- High surface-to-volume area; enhanced mass and heat transfer;
- High volumetric productivity;
- Laminar flow conditions; low pressure drop

- Residence time distribution and extent of back mixing controlled
- Low manufacturing, operating, and maintenance costs, and low power consumption
- Minimal environmental hazards and increased safety due to small volume
- “Scaling-out” or “numbering-up” instead of scaling-up
Multiphase Flows in mFluidic Systems

- Multiphase flows are important
  - Reactions – oxidation, hydrogenation, fluorination, ...
  - Materials synthesis – crystallization, nanoparticles, colloids, ...
  - Separation – extraction, gas-liquid separation, ...

- Performance = f(understanding and ability to manipulate)
Silica Synthesis: Laminar Flow Reactor

- Wide particle size distribution (PSD) at low residence times
  - Particle growth is fastest, and hence most sensitive to residence time variations
- PSD at high residence times approaches batch synthesis results (8% vs. 5%)

Khan, et al., Langmuir (2004), 20, 8604

Pratsinis, Dudukovic, Friedlander, CES(1986) effect of RTD on size pdf
Silica Synthesis: Segmented Flow Reactor

- SFR enables *continuous synthesis* with results that mirror those obtained from batch synthesis

Khan, et al., Langmuir (2004), 20, 8604
Review of gas-liquid, gas-liquid-solid contacting patterns and transport properties in micro-reactors

- falling film
- falling film on catalytic wall
- overlapping channel and mesh micro reactor
- micro bubble columns
- foam micro-reactors
- packed bed micro-reactor
- wall cooled micro-reactor

Improved mass and heat transfer coefficients, much larger interfacial area, controllable RTD, increased volumetric productivity, ease of scale-out

Applications demonstrated in lab scale
- direct fluorinations
- oxidations with fluorine
- chlorinations
- sulphonations
- hydrogenations

Hessel et al, I&EC Research, 44, 9750-9769 (2005) also presented at CAMURE-5 & ISMR-4
Disadvantages of Micro Reactors:

- Short residence times require fast reactions
- Fast reactions require very active catalysts that are stable (The two most often do not go together)
- Catalyst deactivation and frequent reactor repacking or reactivation
- Fouling and clogging of channels
- Leaks between channels
- Malfunctioning of distributors
- Reliability for long time on stream

Challenge of overcoming inertia of the industry to embrace new technology for old processes

Most likely implementation of micro-reactors in the near term:
- Consumer products
- Distributed small power systems
- Healthcare
- In situ preparation of hazardous and explosive chemicals
Illustrations of the need for understanding multiphase flow fields to build predictive reactor models for scale-up

• Trickle beds
Does the industry have a predictive model for design? No.

• Solid acid alkylation (riser)
Choice of liquid-solid riser as reactor is often only justified if liquid and solids are in plug flow. Are they? Current design manuals say so but while liquid is close to plug flow solids are not.

• Partial Oxidations in Circulating Fluidized Beds (CFB)
Is there a scientific basis for scale-up of CFBs? (The maleic anhydride story indicates otherwise.) Important for chemical looping, partial oxidations, redox reaction systems, etc.
TBR Performance Assessment: Multi-Scale Approach

- TBR performance affected by particle scale & reactor scale flow phenomena
- Need to couple: 1) reactor scale CFD model; 2) particle scale models

**Reactor scale:**
- Phase distributions
- Mal-distribution
  Can observe via CT (CREL)

**Phenomenological analysis:**
- Flow structures
- Description of phase interactions
  - "Rivulet flow"
  - "Film flow"
  Can observe via NMR; Gladden et al.; X-ray, Nicol et al.

**Particle scale model:**
- Influence of local hydrodynamics
- Phase contacting and interphase mass/heat transport
- Intraparticle mass/heat transport (single or multi component) and reaction

**Complete catalyst wetting**

**Incomplete wetting**
Example of Improper TBR Scale-Up
Aldehyde Hydrogenation, Scale-up done based on equal LHSV

<table>
<thead>
<tr>
<th>DATA</th>
<th>PLANT</th>
<th>LAB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Height (m)</td>
<td>19.4</td>
<td>0.235</td>
</tr>
<tr>
<td>Diameter (m)</td>
<td>0.455</td>
<td>0.0341</td>
</tr>
<tr>
<td>LHSV (hr(^{-1}))</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>(U_L) (LSV) (mhr(^{-1}))</td>
<td>26</td>
<td>0.26</td>
</tr>
<tr>
<td>H(_2) FLOW (STD) (m(^3)hr(^{-1}))</td>
<td>1000</td>
<td>0.067</td>
</tr>
<tr>
<td>GHSV (hr(^{-1}))</td>
<td>312</td>
<td>312</td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>Temperature (C)</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>Bed porosity</td>
<td>0.425</td>
<td>0.425</td>
</tr>
<tr>
<td>Catalyst tablets</td>
<td>3/16 x1/8</td>
<td>3/16 x 1/8</td>
</tr>
<tr>
<td>Conversion ((x_B))</td>
<td>0.4</td>
<td>0.9</td>
</tr>
<tr>
<td>Contacting efficiency</td>
<td>1.0</td>
<td>0.51</td>
</tr>
</tbody>
</table>

\[
\frac{H_P}{H_L} = 100 \frac{L_P}{L_L} \quad \frac{\eta_{EP}}{\eta_{EL}} \approx 3
\]

\[
L_L = 0.06 \text{kg/m}^2 \text{sec} \quad L_P = 6 \text{kg/m}^2 \text{sec}
\]

\[
k_{app} \approx 0.44k_{appL}
\]

For gas limited reaction, need both LHSV = constant and \(H_R\) = constant
Available Approaches

- Prediction of global bed properties like liquid holdup, pressure drop, transport coefficients using the expert system and most comprehensive database assembled by Larachi and colleagues (Multi_R_Designer, Larachi et al. 2000)

- Using statistical description of bed porosity distribution for prediction of flow and holdup distribution by CFD (Euler-Euler) or minimization of energy dissipation (Holub, Jiang, Guo –CREL). Develop 2-D cell network model (Jiang, Guo- CREL)

- Using more detailed mass and energy balances on particle scale and reactor scale and detailed transport to describe steady and transient TBR behavior (Khadilkar –CREL)

- Detailed statistical description of packing, micro scale flow description coupled with macro scale bed CFD (Combest –CREL)
Simulation Results: Multiplicity Effects

- Hysteresis Predicted
- Two Distinct Rate Branches Predicted (As Observed by Hanika, 1975)
- Branch Continuation, Ignition and Extinction Points
- Wet Branch Conversion (~30 %)
- Dry Branch Conversion (> 95 %)

- Wet Branch Temperature Rise (~10-15 °C)
- Dry Branch Temperature Rise (~140-160 °C)

Data from Hanika et al., (1976) and Khadilkar et al. (1998)
Intra-reactor Wet-Dry Transition

- Abrupt drop in liquid flow
- Temperature rise after liquid-gas transition

- Abrupt change in catalyst wetting
- Cyclohexene and cyclohexane mole fraction show the effect of evaporation and reaction

Khadilkar (CREL), 1998
Performance Enhancement by Periodic Operation

Hydrogenation of α-Methylstyrene to Cumene
-under gas limited conditions at different cycle splits

(Khadilkar et al., 1999)
2-D Rectangular Bed (Liquid Holdup Snapshot)

LIQUID PERIODIC OPERATION

Dimensions: 29.7 cm x 7.2 cm
33 cells (z) x 8 cells (x)
Distributor: 2 cells (L); 8 cells (G)
Velocities: 0.1 cm/s (L)-time averaged
10. cm/s (G)

60s cycle time = 15s turn-on + 45s turn-off

Jiang et al, AIChEJ 2001
Cross-sectional liquid holdup and exit liquid distribution are compared in the region close to the reactor bottom. Results are in good qualitative agreement even though two different parameters (i.e. liquid holdup and exit liquid fluxes) are compared but that is not always the case. CFD predictions remain a challenge!
Consequences of Liquid Maldistribution: Simulated Hot Spot for Low Flow Region
(3.3 inch Diameter Low Flow Region)

- In presence of hot spot catalyst dry-out may occur leading to rates 100-500 times higher due to reduced diffusional resistance – *this feeds the hot spot*
Eulerian CFD Model Overview and Solution Procedure

Mueller correlation & CT data

Sectional porosity distribution (MATLAB)

Porosity map (UDF)

3D Grid (GAMBIT)

FLUENT Eulerian Multiphase Model

Capillary closure (UDF)

Particle scale model & Species balance:
- Interphase reactant transport
- Catalyst effectiveness factor
- Total effectiveness factor
- Reaction rate

Interphase momentum exchange (UDF)

Statistical hydrodynamic model:
Determine $k_L = f(\varepsilon_L, Re_{MIN})$
3D Hydrodynamic Eulerian CFD Model

Model setup:

• Volume averaged equations on the computational grid
• Porosity distribution on the computational grid (CT data; Gaussian)
• Phase interactions closures (two fluid model, statistical hydrodynamics and relative permeability model)
• Account for pressure difference between gas and liquid phase (“capillary closure”)
• Solution strategy (Fluent/Gambit with Matlab and C codes)

Basic input parameters:

• Ergun parameters ($E_1$, $E_2$ for the bed of interest via one phase flow experiments)
• Contact angle (determines likelihood of film vs. rivulet flow)
• Liquid phase relative permeability
Predictions: Extent of Hysteresis

**Experimental pressure drop in Levec mode, kPa/m**

Levec prewetting mode:

Flood the bed; drain, and then initiate gas and liquid flow

\[ f_H = 1 - \frac{(\Delta P/L)_{\text{Upper branch}}}{(\Delta P/L)_{\text{Lower branch}}} \]

Kuzeljevic (2007)
Comparison with Exp Data*: Gas Limited

\[
\frac{C_{LD_{\text{eff},L}}}{C_{GD_{\text{eff},G}}} \gg 1
\]

- 1/16” 0.5% Pd on alumina

Kuzeljevic (2008)

**Hydrogenation of α-methylstyrene (to cumene) in hexane**

- Wetting Efficiency (El-Hisnawi, 1981):

\[
\eta_E = 1.61 \cdot 10^{0.146} \cdot \Re_{L}^{-0.071} \quad \text{(Locally predicted by CFD model)}
\]

\[
\eta = 1 - \eta_{CE} \eta_{\text{dry}} + 2 \left(1 - \eta_{CE} \eta_{CE_{\text{halfwetted}}} + \eta_{CE_{\text{fullywetted}}}^{2}\right)
\]

(Beaudry, 1987 model)

* Experimental data of Mills et al., 1984
Further Improvement in TBR Model by Micro-Scale Modeling of Packed Beds

- New Monte-Carlo packing algorithm makes producing random domains of cylindrical based particles possible.

- Simulations include complete local scale of catalyst particles modeled with Navier-Stokes equations explicitly.

- Packed beds are loosely packed and can produce courser meshes than tightly packed beds

- Radial porosity distributions are comparable to those seen experimentally

Combest (2011)
Micro-Scale Modeling of Packed Beds

- 2-D multiphase flows are modeled with the Volume of Fluid (VOF) method.
- 3-D VOF results are difficult to obtain due to computational requirements.
- 3D single phase flows with turbulence are beginning to be available.
- Key feature is that no Ergun-type pressure closure relations necessary for modeling.
- More advanced models incorporating heat and mass transport within the catalyst particle are possible using a coupled matrix approach that includes intra-particle transport.

Combest (2011)

Horizontal cross-section
Z-Velocity Profile
Micro-Scale Modeling of Packed Beds

Packing
• Randomly packed domains of \((10^2-10^3)\) cylindrical particles are made from a Monte-Carlo packing algorithm.
• Because the exact location of the faces of the particles are known, computational meshes are accurately constructed.

Modeling
• Micro-scale models of packed beds are based on the Navier-Stokes equations without an Ergun-type pressure closure relation
• More complex conjugate heat transfer models (including heat transport in solids) are being developed

Advanced Hardware Integration
• Because of the size of the sparse matrices produced by these meshes, a computational paradigm shift is necessary to leverage new technology in widely used CFD software.
• Integration of Graphics Processing Units (GPU) to solve these sparse linear systems is being performed with multiple times speedup compared to CPU based linear system solvers.
• Integration of GPU based solvers into OpenFOAM code is currently available.
CREL TRICKLE BED WORK MAIN CONTRIBUTORS:

- J. SCHWARTZ (1975) - Amoco / BP
- A. EL-HISNAWI (1981) - L.A.E.A
- E. BEAUDRY (1985) - Solarex
- P. HANRATTY (1988) - D.M.C. / Aspen / ExxonMobil
- R. HOLUB (1991) - Ethyl / Albemarle
- M. AL-DAHANN (1993) - Xytel/WUSTL/ MST
- M. KHADILKAR (1998) - General Electric/SABIC
- J. WU (1998) - Wuhan Institute of Technology
- Y. JIANG (2000) - Conoco / Corning
- J. GUO (2004) - UOP
- Z. KUZELJEVIC (2010) - SABIC
- D. COMBEST (2012) - Engys Ltd.
SOLID ACID ALKYLATION

- Solid acid catalysts are more environmentally benign but deactivate rapidly on stream.
- This requires reactors with solids recirculation and regeneration such as in CFBs.
- Catalyst activity and selectivity in the liquid–solid riser is determined by its residence time distribution in the riser. Design manuals say its plug flow.
  - Experiments requiring specialized techniques (university–industry partnership) show otherwise.
  - CFD model validation based on experiments provides robust model for design.
Radioactive Particle Tracking (CARPT) Provides Solids Velocity and Mixing Information

Computer Tomography (CT) Provides Solids Density Distribution

Tracer Studies Confirm Liquid In Plug Flow (N > 20) Solids Flow and Distribution
Quantification of Flow Field by CARPT


Distance vs. Count map from Calibration + Counts from Detectors

Eddy diffusivity

Instantaneous Positions \((x, y, z, t)\)

Sojourn Time Distributions

Instantaneous Velocities

Mean Velocities

Fluctuating Velocities

Turbulent Kinetic Energy

Moslemian (1986); Devanathan (1990); Degaleesan (1996); Chaouki, Larachi, Dudukovic (1997);
SOLIDS RESIDENCE TIME DISTRIBUTIONS

Trajectories

Total Number of Trajectories = 1473
\[ \sigma_D = 0.23 \]

Total Number of Trajectories = 877
\[ \sigma_D = 0.46 \]

Total Number of Trajectories = 1833

\[ U_i = 15 \text{ cm/s; } S/L = 0.15 \]

\[ U_i = 20 \text{ cm/s; } S/L = 0.10 \]

\[ U_i = 23 \text{ cm/s; } S/L = 0.20 \]

\[ 2 \leq N_{\text{solids}} < 6 \]

\[ 0.18 \leq \sigma_D^2 \leq 0.61 \]

OVERALL

CHEMICAL REACTION ENGINEERING LABORATORY
CARPT Results

Trace over 38 s (1900 positions)

Z = 125 cm

Z = 100 cm

Time Average (25 - 100 s)

CFD Results

Comparison of CFD with Data

Axial Solids Velocity, cm/s

Radial Position, cm

Solids Holdup

Granular Temperature, cm²/s²

Radial Position, cm

Final 2-D Convection Diffusion Reactor Model for the Riser

Ready for plant design, optimization and model based control.

Improved Atom and Mass Efficiency in Maleic Anhydride Synthesis—Green Process in Textbooks is not so green in reality

Atom economy is a measure of how efficiently raw materials are used. (Benzene route 18/42=.43; n-butane route 9/17=0.53)

Example: Mass economy of Maleic anhydride production via benzene & n-butane route.

**Benzene route:**

\[
2\text{C}_6\text{H}_6 + 9\text{O}_2 \xrightarrow{V_2\text{O}_5 \text{MoO}_3} 2\text{C}_4\text{H}_2\text{O}_3 + \text{H}_2\text{O} + 4\text{CO}_2
\]

\[
\text{Mass Efficiency} = \frac{2(4)(12) + 3(2)(16) + 2(2)(1)}{2(6)(12) + 9(12)(16) + 2(6)(1)} \times 100 = 44.4\% 
\]

**n-Butane route:**

\[
\text{C}_4\text{H}_{10} + 3.5\text{O}_2 \xrightarrow{(\text{VO}_5\text{P}_2\text{O}_5)} \text{C}_4\text{H}_2\text{O}_3 + 4\text{H}_2\text{O}
\]

\[
\text{Mass Efficiency} = \frac{(4)(12) + (3)(16) + (2)(1)}{4(12) + 3.5(2)(16) + 10(1)} \times 100 = 57.6\% 
\]
Partial Oxidation or Butane to Maleic Anhydride  
(Replaced Benzene Oxidation)

\[
C_4H_{10} + \frac{7}{2} O_2 \rightarrow C_4H_2O_3 + 4H_2O \\
C_4H_2O_3 + O_2 \rightarrow 4CO + H_2O \\
C_4H_{10} + \frac{11}{2} O_2 \rightarrow 2CO + 2CO_2 + 5H_2O \\
\]

Vanadium Pentoxide Catalyst

All reactions are exothermic and the heat is removed using cooling of reactor wall (tubular reactor) or via heat exchange pipes (fluidized bed reactor). The amount of butane in the feed (1.8% for packed beds and 4% fluidized beds) is controlled as not to form an explosive mixture. Hence, low concentration of butane results in low yield of maleic anhydride (1% in product) which requires costly separation of product mixture.

**Industrial reactors:**

1. Packed beds
2. Fluidized beds
3. CFB reactor
Circulating Fluid Bed (CFB) Reactor for Butane Oxidation

Off-gas (CO\(_x\), H\(_2\)O,..)

Regen

Riser

Air

Solids Flow Direction

Butane Feed Gas

Reoxidized Catalyst

Maleic Anhydride

Reduced Catalyst

Inert Gas

Main Reaction

\[ \text{O}_2 \]

\[ \text{V}^{+5} \]

\[ \text{HC} \rightarrow \text{HC} \]

Catalyst Redox

\[ \text{O}_2 \leftrightarrow \text{V}^{+3} \leftrightarrow \text{V}^{+4} \leftrightarrow \text{V}^{+5} \]

Riser
Example: Butane to THF Process

\[ \text{n-C}_4 \text{H}_8 + \text{O}_2 \rightarrow \text{C}_4\text{H}_4\text{O}_4 \]
\[ \text{C}_4\text{H}_4\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{C}_4\text{H}_6\text{O}_4 \]
\[ \text{C}_4\text{H}_6\text{O}_4 + \text{H}_2 \rightarrow \text{C}_4\text{H}_8\text{O} \]

Pilot Plant Reactor

n-C\textsubscript{4} Oxidation Reactor

Maleic acid Hydrogenation Reactor

Purification Train

Commercial Plant
CFBs Scale-up requires at matching the mean and variance of contact times in the riser and in the fluidized bed for the pilot and plant scale

- This is hard to do when solids holdup in the two vessels is not precisely known and when solids circulation rate is unknown

- CT and CARPT can determine this and provide a data base for CFD validation in prediction of these important parameters

- The issue is who will provide the funds needed for capitalization and operation of such experimental facilities.
Meeting the Challenge: Conclusions

Reaction engineering methodology is the enabling discipline that offers multi-scale avenues for innovations in developing “greener” more sustainable processes. Multiscale approach is essential.

In adoption of green chemistry principles it is vital to master the scale-up methods based on fundamental reaction engineering principles.

Incentives should be provided globally for taking the risk to implement new more efficient technologies that utilize process intensification concepts on a multitude of scales.

Miniaturization provides opportunities for scale up in parallel. Quantification of multiphase flow fields reduces the risk of vertical scale up. Both are needed for rational process intensification.
Key Reaction Engineering Challenge

Improved science-based general scale-up methodology for transfer of molecular discoveries to sustainable processes in meeting the future energy, environmental, food and materials needs of the world

Development of reliable tools for implementation
Reactor Models Based on Science through Multi-scale Approach Allow:

Risk reduction of novel reactor technology or of existing reactors for new applications
- Improved safety of existing and novel reactor types
- Proper more accurate assessment of the environmental impact of new process technology

ALL OF THIS REDUCES THE ENVIRONMENTAL IMPACT OF THE TECHNOLOGY AND ENCOURAGES NOVEL SOLUTIONS
Technical Barriers: 
Manufacturing companies and engineering contractors lack expertise in multi-scale multiphase reaction engineering. Designs are based on old correlations and integration of multi-scale concepts is missing. Universities are not doing research and producing people in multi-scale areas.

Non Technical Barriers: Chase for short terms profits encourages:
- Use of old ‘best available technologies’ which are inefficient
- Use of familiar reactors and separations (contractors)
- Building the plant with minimal scale-up expenditures
- Current IP policies
As a result when new chemistry is chosen one often experiments with the plant to determine ‘best conditions’. Very costly. Rarely successful.

In summary, as long as everyone practices the old ways and old designs and licensing of old technologies leads to profits no one wants to invest in innovation and introduction of science into their routine design methods. Globalization provides the means for continued use of suboptimal methods.
Acknowledgement of Financial Support and Effort in Advancing Multiphase Reaction Engineering and Establishing Unique CARPT/CT Techniques

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Designing environmentally responsible molecules, products, and processes – from the molecular scale to the plant scale.

**Lead Institution:** University of Kansas (KU)

**Core Partners:** University of Iowa (UI); Washington University in St. Louis (WUStL); Prairie View A&M University (PVAMU)

**Director:** Bala Subramaniam (KU); **Deputy Director:** Daryle Busch (KU)

**Associate Directors:** John Rosazza (UI); Milorad Dudukovic (WUStL); Irvin Osborne-Lee (PVAMU)
Environmentally Beneficial Catalytic Engineered Systems

TG1: Catalyst Design and Preparation

TG2: Media and Catalyst Supports

TG3: Experimental Design and Advanced Measurements

TG4: Multi-scale Process Model
- Quantum effects
- Molecular dynamics
- Rate theories
- Solvent thermodynamics and kinetic effect
- Micromixing
- Multi-component transport
- Turbulence
- Mixing
- Computational fluid dynamics
- Reactor simulation
- Plant simulation
- Control
- Optimization

CEBC – U. of Kansas, U. of Iowa, CREL-WUSTL, Prairie View A&M University (PVAMU)
Environmentally Benign Processing ...

**Art**

Past & Present...

Science Based Multi-scale Engineering

**Science**

... Future
Alternatives to Multiscale CRE Approach

CONVENTIONAL APPROACH: End-of-the-pipe-clean-up, improved house-keeping, waste reduction, retrofitting, recycle, environmentally benign processing.

UNCONVENTIONAL INNOVATIVE IDEA DISCUSSED BY TWO GENTLEMEN ABOVE: “The only other solution is that, with the help of genetic engineering, we may evolve into a species immune to all this junk”.
The **scope** and **expected outcome** of the MPE3 program is as follows: Development of a set of tools which will allow rational and efficient scale up of multiphase processes in today’s world where energy, environment and profits interact.

Partnering between industry and academia will ensure the tools are practical and provide the means for training people to use them.
An Invitation to Join

Department of Energy, Environmental & Chemical Engineering
Washington University in St. Louis

Multi-Scale Process Engineering for Energy and Environment: An Industry-University Partnership

VISION
An Industry-University partnership program to generate a unique knowledge base and graduates capable of leading the efforts in implementation of modern, efficient process technology in a broad spectrum of industrial sectors.

MISSION
1. Develop and organize science based tools for dealing with multi-scale and multiphase aspects of kinetics—transport interactions, catalyst or biocatalyst selection, design, testing and process scale up.
2. Develop the needed metrics for evaluating the impact of process technologies on energy and materials efficiency and the environment.
3. Apply these to a variety of problems relevant to Industry.

STRATEGY
1. Nurture long-term research interaction with industries in a broad spectrum of activities (e.g. energy and environment sector, fuels, fossil and renewable energy, biotechnology, nanotechnology, environmental technology, and catalysis).
2. Develop strong partnerships with industry to build expertise and knowledge initially in the following focus areas: reaction engineering, renewable energy & storage, aerosol technology, biotechnology, and environmental technologies.
3. Speed up applications of academic research to solution of industrial problems.
4. Provide education and training for industrial researchers via courses, sabbaticals, and other innovative programs.
5. Develop government funded centers and projects to maximize leveraging of resources and positively impact the societal needs.

CURRENT INVESTMENTS
The Department of Energy, Environmental and Chemical Engineering (EECE), was organized as the first of its kind in 2006. In 2010, Brauer Hall, a 70 million dollar building, was completed to house EECE. Washington University in St. Louis (WUSTL), also initiated the McDonnell Academy Global Energy and Environmental Partnership (MAGEEP), a collaborative program with 28 leading universities. This across-the-globe program was designed to develop synergistic approaches to global energy and environmental issues. In October 2010, Chancellor Wrighton hosted a five day conference dedicated to Global Energy Future. A one day symposium at this meeting on Multiscale Process Engineering for Energy and Environment, where contributed papers were followed by panel discussions, provided inspiration for this proposed industry-university partnership program. The partnership program would have access to the network of 28 universities with a global outreach. Faculty and students from the various universities are collaboratively working on several projects funded by MAGEEP, the Consortium for Clean Coal Utilization (Industry supported), and the DOE Energy Frontier Research Center.

FACILITIES
The EECE Department has state-of-the-art research facilities such as the Advanced Clean Energy Research Facility, Nano Research Facility (part of the National Nanotechnology Infrastructure Network), Johns Instrumentation Laboratory, Chemical Reaction Engineering Laboratory (CREL), and several more laboratories within Brauer Hall. Further growth of faculty and of facilities for EECE is planned.

LONG TERM COMMITMENT TO CORE DISCIPLINES
Our long term goal is to maintain excellence through a critical mass of faculty in the core disciplines of multiscale process and product engineering, such as, but not limited to, the molecular basis for transport and kinetics, transport phenomena (fluid mechanics, mass and heat transfer), reaction engineering of multiphase systems, control, metabolic engineering, aerosol engineering, science and technology, rational basis for green processing and waste reduction, environmental engineering science, and others. The utilization of fundamental principles and introduction of most recent scientific discoveries in important novel technologies will be continuously pursued by our entire faculty (e.g. in areas such as aerosol reactors, solar energy and cleaner utilization of coal, sustainable clean water and clean air technologies, biotechnology for conversion of biomass to energy and products, clean fuels).

PAST INDUSTRY PARTNERSHIP BENEFITS
In the past, our uniquely qualified graduates created value for industry sponsors by providing them with engineering solutions. This expertise was converted in-house towards increasing profitability of operations and installation of new technologies in a variety of applications. Examples of D.Sc. theses that led to novel processes of much higher material and energy efficiency:
1) fluidized bed production of poly-silicon from silane rather than chlorosilanes, which is still in operation; 2) novel model based control for manufacture of long fiber composites in aircraft manufacture that save millions in manufacturing costs; 3) development of scientific basis for scale-up of trickle bed reactors in hydro-processing, hydro-dereszulfurization and chemical syntheses; 4) unique experimental facilities for validation of computational fluid dynamics codes in opaque multiphase systems which provided a scientific basis for selection of most appropriate reactors in the petrochemical industry and dramatically reduced the risk and costs of scale-up; 5) advanced lower cost mercury control technologies using nanostructured sorbents; 6) novel sorbents for removal of heavy metals from combustion exhausts; 7) aerosol reactors for synthesis of metallic and composite nano materials (small business spun-off, and acquired by a major corporation); 8) spectrum of nanoparticle instrumentation that were invented and later commercialized; including miniaturization of size distribution measurement equipment; 9) novel technologies based on soft-x-ray irradiation for high efficiency capture of particles; including inactivation of bio-agents; 10) water purification technologies for arsenic removal; 11) single stage thin film deposition technologies for solar energy applications; 12) metabolic engineering of microbial pathways for biofuel synthesis.

EXPECTED INDUSTRIAL COMMITMENT
It is of vital interest to each progressive company to maintain the best educated work force capable of incorporating innovative approaches in the technologies it employs. Thus, the companies should commit to:
• assign one or two advisories for the program that will actively participate in structuring the program so as to meet broad industrial needs; they should also serve as catalysts to encourage interactions between their colleagues and specific faculty members in EECE
• attend every six months a review meeting at WUSTL (and plan on more frequent visits in some areas); • consider joint proposals with EECE faculty for federal funding
• consider EECE as partner for contract work to further develop an idea resulting from the above program
• consider our students for summer internships and graduates for permanent jobs
• provide sabbaticals for their top technical contributors to pursue research at WUSTL as Industrial Fellows in Residence and offer sabbaticals to our EECE faculty
• make a financial contribution in the form of an annual membership fee
• encourage company employees to attend our short courses