

# Reaction Engineering for Environmentally Benign Processing



## Module 1: Chemical Reaction Engineering, the Environment, Pollution Prevention, Sustainable Development and Green Processing

**M.P. Dudukovic**

Chemical Reaction Engineering Laboratory (CREL)  
Washington University  
St. Louis, MO 63130, USA

- ↪ Introduction
- ↪ Pollution Prevention Strategies
- ↪ Role (Current and Future) of CRE in Pollution Prevention and Green Processing
- ↪ Conclusions



**SLIDE 1.** In this one unit course, that will be team taught, we will strive to introduce you in a modular fashion to concepts and tools needed to do modern reaction engineering in accordance to the principles of green chemistry and green processing. The ultimate goal is sustainable development.

The objective of today's lecture is to discuss what constitutes chemical reaction engineering and its relevance to the environment, pollution prevention, green processing and sustainable development. First, I will introduce you to this topic and demonstrate that there is a strong relationship between the many terms in this long title. I will briefly review pollution prevention strategies next, and then focus on the role of chemical reaction engineering in pollution prevention and green processing before making a few concluding remarks.

- CHEMISTRY** - The science that treats of the composition of substances and of the transformation which they undergo.
- REACTION** - Act of chemical change.
- ENGINEERING** - The art and sciences by which the properties of matter and the sources of power in nature are made useful to man in structures, machines and manufactured products.
- ENVIRONMENT** - That which environs; The surrounding conditions, influences and forces.  
- The aggregate of all external conditions and influences affecting the life and development of an organism.
- POLLUTE** - To make or render unclean or impure.
- SUSTAINABLE DEVELOPMENT** ⇒ Meeting the needs of the present without compromising the ability of future generations to meet their needs.











(Definitions from Webster Dictionary)



**SLIDE 2. To explain the relationship between various terms, the best place to start is the Webster Dictionary which defines:**

- 1) Chemistry as “the science that treats of the composition of substances and the transformations which they undergo”,**
- 2) Reaction as the act of “chemical, change”, i.e., transformation at the molecular level**
- 3) Engineering as “the art and science by which the properties of matter and the sources of power in nature are made useful to man in structures, machines and manufactured products”, (often today we tend to forget what engineering is supposed to be as we chase molecular discoveries in the realm of pure science).**
- 4) The environment as “the aggregate of the external conditions and influences affecting the life and development of an organism”,**
- 5) To pollute is “to make or render unclean or impure”.**

**By the term “sustainable development” we mean meeting the needs of the present without compromising the ability of the future generations to meet their needs. We will leave the discussion of the principles of green processing for a little later. Let us address the question as to why and how are all the above terms connected?**

Key Factors Affecting the Environment and Sustainability	
↗ Total population	↗ Lifestyle
 <ul style="list-style-type: none"> <li>• Agricultural practices</li> <li>• Mining practices</li> <li>• Energy utilization</li> </ul>	  <ul style="list-style-type: none"> <li>• Recreational activities</li> <li>• Manufacturing practices</li> </ul>
  	    

S3

**SLIDE 3.** Clearly, the two key factors that affect the environment and sustainability of our practices is the total number of people and their life style.

**Agricultural practices, clearing of forest for durable land, irrigation of deserts, use of herbicides and pesticides, etc., obviously are important.**

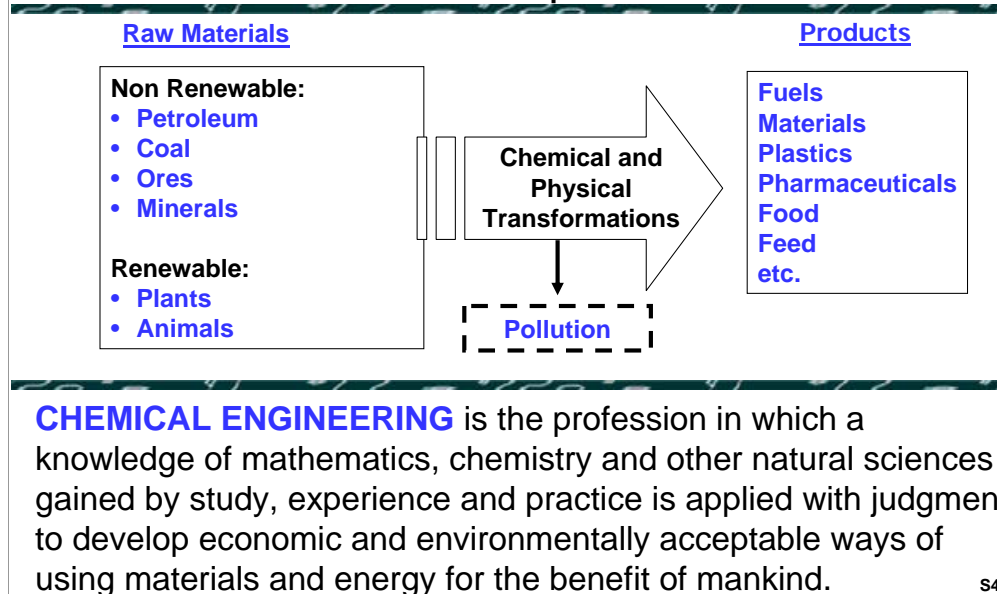
**Mining for finite mineral or energy resources, strip, deep shaft, etc., affect the environment.**

**Energy utilization, drilling for oil in pristine areas and oceans, use of hydroelectric power, etc., have environmental impact.**

**Recreational activities, do you country ski or drive a snow mobile, walk or use a dune buggy, have environmental consequences.**

**As important as all of the above are, it is the manufacture of products from fuels to chemicals, plastics, pesticides, etc. that make alternate life styles possible and that is the realm of chemical and process engineering, which we need to discuss.**

The domain of chemical engineering consists of chemical and physical transformation of starting materials to products



**SLIDE 4.** In chemical engineering (or chemical processes) we deal with the chemical and physical transformation of non-renewable and renewable resources into a variety of products useful to man to which advanced technological society like ours is absolutely addicted. It is self evident that materials with new properties are created by the chemical change, i.e., by the transformation in atomic content or configuration of a molecule. In the process of accomplishing these transformations, we inadvertently create undesirable changes which, if not checked, can result in pollution of the environment. Both the degradation of the environment and heavy reliance on non-renewable fossil based raw materials threatens to render our technologies unsustainable over the long run.

To change this is the responsibility of chemical and process engineers who are predominantly in charge of all such transformations.

Process engineers have always been aware of the “11th commandment” “your process should make profit”, so that the recently added “12th commandment” “do not pollute” is easier to implement if to do otherwise leads to dire economic consequences, i.e., has a negative effect on the fulfillment of the 11th commandment, which is an integral part of the definition of chemical engineering.

Moreover, in assessing the environmental impact of our processes and/or products we should include the life cycle analysis of the product to truly understand the consequences of making it in the first place. The ‘cradle to grave’ consequences on the environment should be addressed but this is not part of CRE.

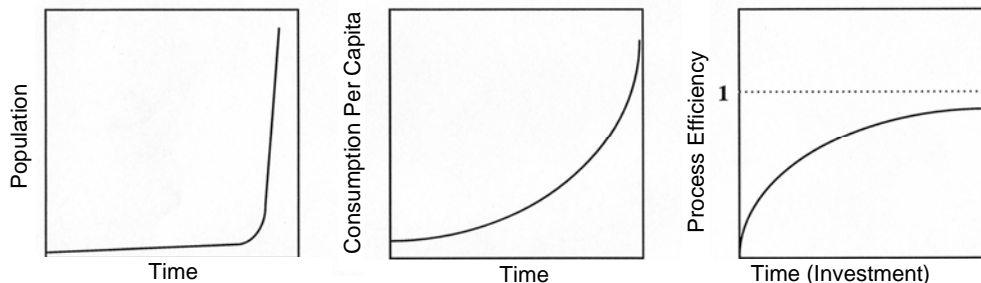
# GLOBAL VIEW

## Pessimistic Assessment

$$\text{Pollution} \propto \frac{(\text{consumption per capita}) (\text{population})}{(\text{process efficiency})}$$

## Optimistic Assessment

$$\text{Pollution} \propto \underbrace{(1 - \text{process efficiency})}_{\text{process inefficiency}} (\text{consumption per capita}) (\text{population})$$



**SLIDE 5. One can simplify the global view of the pollution generalized by manufacturing activities either into a pessimistic assessment that the total pollution generated is the product of consumption per capita and population divided by process efficiency. Or one can be an optimist and present the total pollution as a product of consumption per capita, population and process inefficiency = 1 – process efficiency. Whichever view you take, it seems self-evident that pollution can be reduced by controlling population growth, and/or by reducing consumption per capita. In contrast, process efficiency increases only asymptotically to unity. Hence, from the pessimistic point of view that alone cannot provide a serious impact on total pollution. One should also note that further increases in process efficiency require considerable investment of capital and time. Improving efficiency of one process may lead to inefficiency elsewhere. Hence, a holistic system's approach and life cycle analysis are needed.**

**Since population control is anathema to two major religions and reduction in consumption the capita is hereby to the free market system, the only realistic road to the future is decreasing pollution and preserving the environment is via increases in process efficiency. It is in that regard that chemical reaction engineering (CRE) has a vital role to play.**

- GLOBALLY, Pollution prevention and reduction will ultimately depend either on population and consumption control or on introduction of environmentally benign and highly efficient sustainable technologies.
- LOCALLY, or on a national level, the focus has been on waste reduction via
  - Better education and operation practices at existing manufacturing facilities (*more than pays for itself*)
  - Retrofitting of existing facilities (*done only if resulting in improved profitability*)
  - Installation of pollution abatement equipment (*done only if under regulatory or peer pressures*)
  - Moving and opening new manufacturing facilities off-shore (*let them have our pollution while we manage money – service industry*)
  - Development and installation of cleaner processes (*requires substantial capital expenditures and new unit operations and new concepts needed for ultra pure systems*)

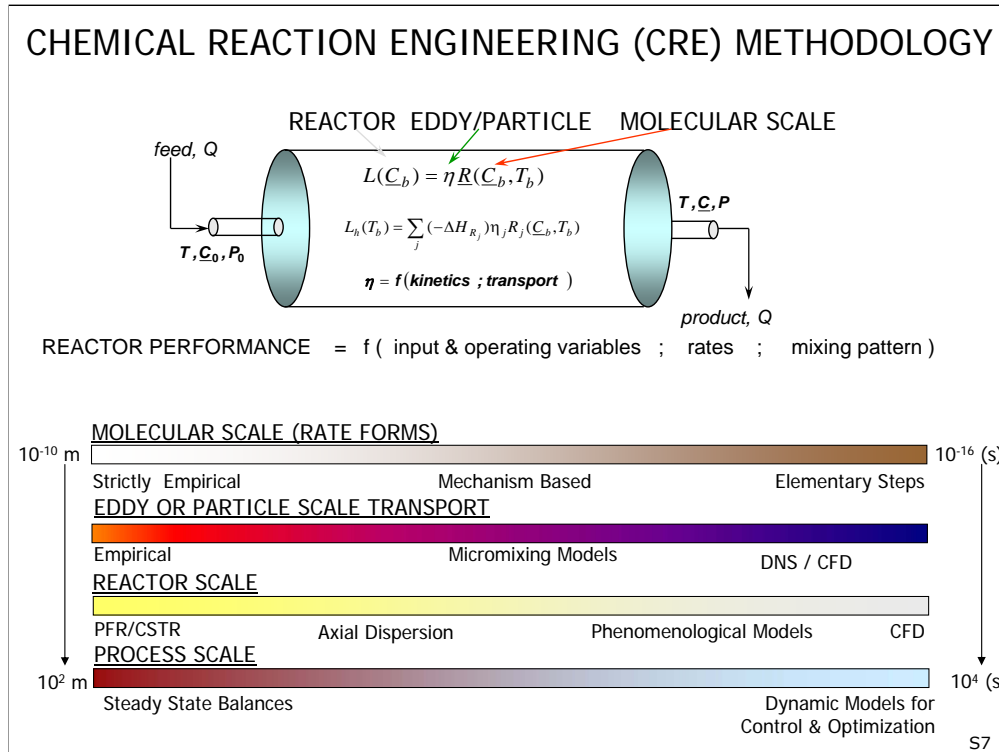
S6

**SLIDE 6.** Let us summarize then the current situation. Globally, pollution prevention and reduction, and sustainable development will ultimately depend either on population and consumption control or on introduction of environmentally benign highly efficient sustainable technologies. Unfortunately, at the moment there are no incentives to pursue either of these strategies. We seem to be in denial.

Locally, and on the national level, the focus has been on waste reduction via better house-keeping (that always pays for itself), retrofitting of existing facilities (if it leads to better profits). Installation of pollution abatement equipment is done only under regulatory or peer pressure. Moving facilities, or building new plants based on existing technologies, offshore is a wonderful US idea of giving others our pollution while we manage their profits! Development and installation of new technology for green processing is the best answer but is seldom tried, as it requires substantial capital expenditures and introduction of new, previously untested, concepts.

Introduction of clean processes based on new sustainable technology has been remarkably rare in the production of fuels, commodity chemicals and even specialty chemicals. The green chemistry presidential awards go to new pharmaceutical or specialty processes, and even some of those are not implemented on US soil. What we are witnessing is the loss of the manufacturing base in the US. It is evident that the current pollution reduction methods were implemented only when they increased profitability (due to waste recovery) or were required by regulations, which in turn, allowed raising the prices to accommodate increased cost. Hence, only globally uniform environmental regulations will speed up introduction of sustainable production methods in the US and the world.

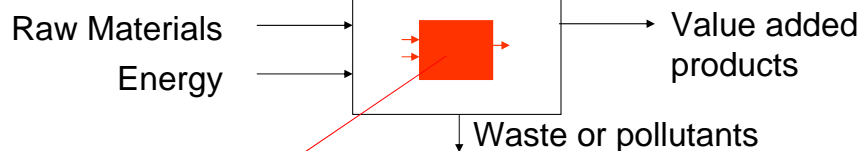
We should note, however, that in all the current and future methods of pollution reduction, chemical reaction engineering plays a pivotal role. That is true in retrofitting activities, in end-of-the-pipe treatment and certainly to the highest degree in the development of cleaner new green processes.



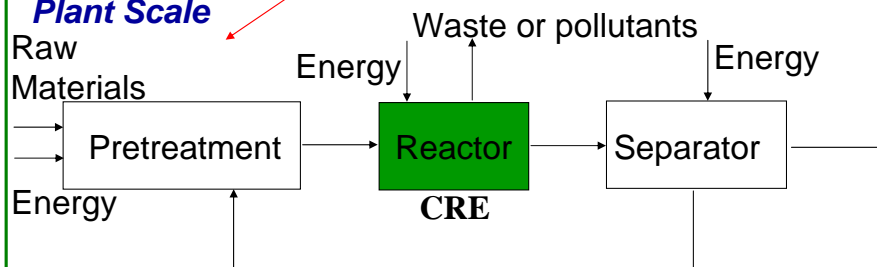
**SLIDE 7. Let us now consider why CRE is so important. The CRE methodology provides a scientific basis for quantifying the chemical reactor performance, as measured by volumetric productivity, selectivity, material and energy efficiency and environmental impact as a function of input and operating variables, kinetic and transport rates and mixing and flow pattern. An appropriate model of the reactor must be multi-scale in character and describe a wide range of length and temporal scales. The molecular scale events determine the mechanism and kinetic rates. Their description is rapidly moving from the empirical to transition theory and quantum mechanics based calculations. Micro and meso-scale, such as transport in a turbulent eddy or in a single catalyst particle, determine local transport effects on the reaction rates and provide the source terms in the species mass and energy balance equations. Their description is being advanced from the empirical to DNS/CFD type models. To complete the reactor model, which rests on mass and energy conservation laws, a reactor flow pattern must be assumed or calculated. These descriptions are usually still at the primitive ideal reactor level, for reasons to be described later, and need to be addressed. Full dynamic model based process control and optimization also rests on a reliable reactor model.**

## Green Chemistry and Green Processing

### Global Scale



### Plant Scale




S8

**Slide 8. Clearly, the choice of the reactor and how it operates affects the number of separation units needed upstream and downstream and has a profound environmental impact. Those that practice CRE at the high level control wastefulness better than those who are using an ad-hoc approach to reactor design.**



Environmental Acceptability, as Measured by the E-Factor		
Industry	Product tons per year	Waste/product ratio by weight
Oil refining	$10^6 - 10^8$	~ 0.1
Bulk chemicals	$10^4 - 10^6$	< 1 - 5
Fine chemicals	$10^2 - 10^4$	5 - 50
Pharmaceuticals	$10^0 - 10^3$	25 - > 100


**CHEMICAL REACTION ENGINEERING LABORATORY**
S9

**SLIDE 9.** The enclosed table illustrates the so-called E factor of various industries. Clearly, those that practice CRE at the high level produce the fewest undesirable products per unit desired product. So-called high tech industries, which are really high value added industries, like the electronic industry used to be and pharmaceutical industry is now, have terribly high E-factors and are not high tech at all from the environmental standpoint.

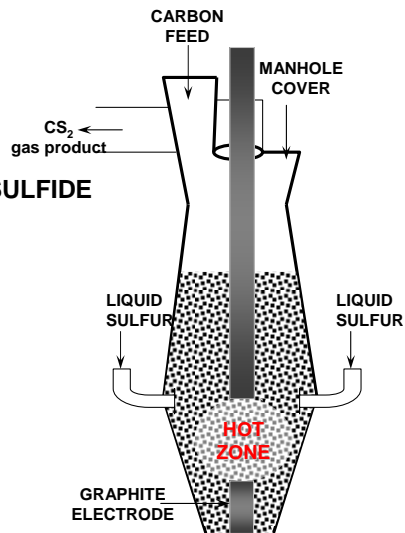
The other point that should be understood is that the so-called principles of green chemistry are just one of the prerequisites for a green process. Whether the process will be successful or not, depends on selection of proper reactor type and its proper operation. A great number of new processes is often abandoned due to inability to scale up reliably. Hence, understanding of all scales of events in reactors is essential for proper scale-up and design.

## My First Assignment as a Process Engineer (1967)

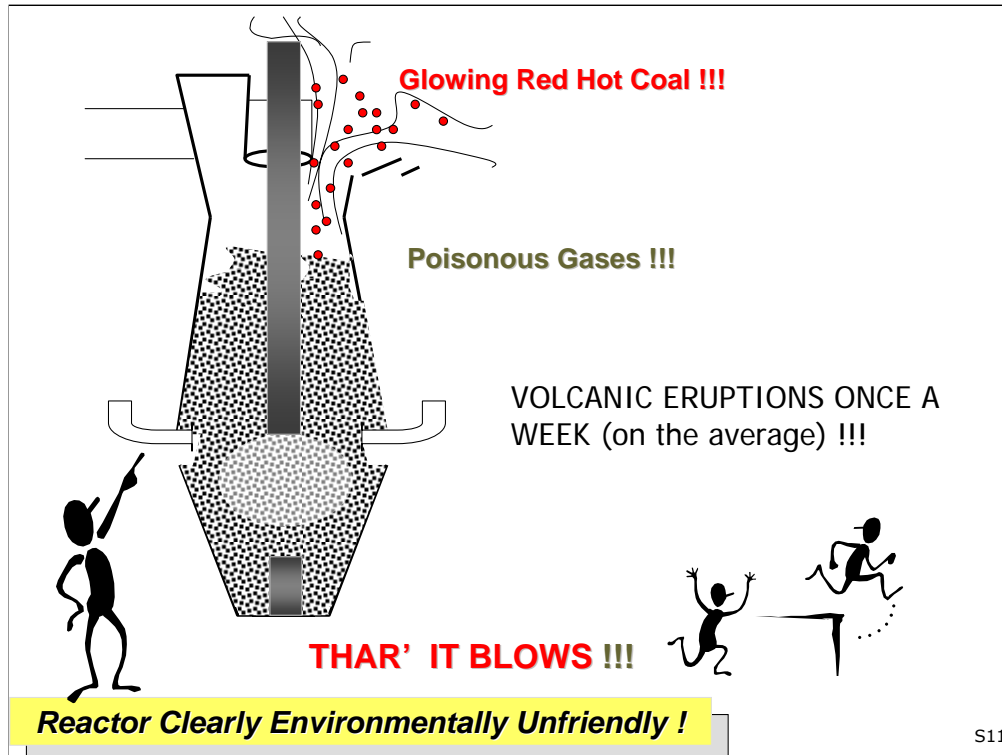
EUROPEAN (GERMAN) PROCESS:



**REACTOR: REFRACTORY  
LINED KILN WITH  
GRAPHITE ELECTRODES**



**SLIDE 10.** To illustrate the pivotal role of reaction engineering in pollution prevention let me use an example from personal experience. My first assignment as process engineer was to expand the capacity for production of rayon fibers which utilized carbon disulfide as a solvent. In Eastern Europe at that time, an expired German patent (that utilized coke contacted by liquid sulfur in a refractory kiln heated by an electric arc between two graphite electrodes) was the state-of-the-art technology for production of CS<sub>2</sub>. Please, note that atom efficiency is 100% so the process is from that point of view better than producing CS<sub>2</sub> from methane and sulfur, as the practice was and is in the US! The reactor operated essentially at atmospheric pressure and our task seemed very simple – to replicate the design of the existing kilns in order to increase the plant capacity. As we inspected the kilns in operation we soon discovered that the existing manhole was not for cleaning purposes during shutdowns, as we originally surmised.



**SLIDE 11. Without any warning often that manhole cover would open up and discharge the glowing coal (coke) all over the place together with a mass of toxic gases. You could not run for cover when the eruptions happened because you would lose the respect of the operators then. So you had to sort of look over your shoulder and nonchalantly say “Thar it blows!”. This environmentally unfriendly reactor had very dire health consequences for the operators who were exposed to this on a daily basis since each kiln erupted about once a week and there were 5 of them!**

• Runaway caused by thermal instability and 'hot spots' in the reactor – not controllable  
 • Recommendation of young engineers to the boss: "Prevolatize the sulfur and suspend smaller coke particles in sulphur 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.

EPILOGUE  
 Four years after our recommendation a Japanese company proved fluidized bed concept viable.

S12

**SLIDE 12. The point is that the reactor was selected poorly for the process. It was the wrong reactor. Nevertheless, when we suggested that a fluidized bed reactor with pre-volatized sulfur feed would not have a hot spot problem and would be stable and work reliably, our suggestion was dismissed as too risky (sounds familiar)? The aversion towards the risk of adopting a new technology (not to replace but even to expand the plant capacity!) led to the order that we improve on the existing kilns. We re-designed the hot zone the best we could, only to achieve 1 blowout of the new kilns on the average of once in two weeks as opposed to one in every five days for the old ones. That was considered a great success by our management (they achieved their goal of increased capacity). So I came to the US in the hope that reaction engineering here would be done right! I was proven wrong. There is a morale and epilogue to the story. The old kilns are now out of business.**

## The Twelve Principles of Green Chemistry

1. Waste prevention
2. Atom Economy
3. Less Hazardous Chemical Syntheses
4. Designing Safer Chemicals
5. Safer Solvents and Auxiliaries
6. Design for Energy Efficiency.
7. Use of Renewable Feedstocks
8. Reduce Derivatives
9. Catalysis
10. Design for Degradation
11. Real-time analysis for Pollution Prevention
12. Inherently Safer Chemistry for Accident Prevention

S13

Slide 13. Now we need to discuss how to incorporate the established 12 principles of green chemistry into process development and design.

The first principle of waste prevention clearly guides us towards chemistries of high atom and mass efficiency. As reaction engineers we still need to identify conditions of pressure, temperature and composition that yield high rates and selectivity on a micro scale and determine the flow pattern most conducive to high selectivity.

The second principle of high atom efficiency is self evident as well as the 3<sup>rd</sup> that requires use of less hazardous chemicals. These as well as 4<sup>th</sup> and 5<sup>th</sup> that call for use of safer chemicals and solvents are the domain of the chemist! Design for high energy efficiency (No 6) and use of renewable feedstocks (No. 7) should be considered by chemists and engineers at the start of the process development. Reducing unneeded derivatization (No. 8) and using catalysts (No. 9) wherever possible are also taken into account early in conceptualizing the process. Design of products that can be naturally degraded (No. 10) should be one of the key strategies used in consumer product development. Real time analysis for pollution prevention (No. 11) deals with implementation of appropriate control methodologies for prevention of toxic fields, discharges, and reactor runaways is essential in modern plants. Inherently safer chemistry for accident prevention (No. 12) calls for elimination of hazardous solvents by more benign ones.

## *Green Chemistry and Green Processing*

---

### **Better Housekeeping**

- Raw material selection
- Equipment maintenance
- Temperature control
- Pressure control
- Vent and relief system tuning

---

S14



**Slide 14. The green chemistry concepts lead to hierarchical strategies for pollution prevention which culminate in more efficient process technologies that minimize waste and pollution and use novel process intensification concepts.**

## *Green Chemistry and Green Processing*

---

### **Guidelines for Improved Reactors**

- Use non-hazardous raw materials.
- Use renewable resources.
- Reduce by-products and generate less waste
- Produce products easy to separate.
- Recycle un-reacted materials.
- Reduce use of solvents.
- Use benign solvents.
- Improve atom efficiency.
- Improve energy efficiency.
- Use heat integration.
- Replace liquid phase routes by solid catalyzed routes.
- Do not over-design.

S15



**Slide 15. Green chemistry principles result also in the common sense guidelines for selection of environmentally friendly processes.**

## ***Successes in Process Changes***

### ***Example***

#### **Ethylbenzene synthesis from Benzene and Ethylene (390,000 t/y):**

OLD:

1. Liquid Phase Process (  $AlCl_3$  Catalyst)  
3,900 tons  $AlCl_3$  to be handled
2. Vapor Phase Process ( $BF_3/Al_2O_3$  Catalyst)  
500 t/y solid waste  
800 t/y liquid (benzene saturated) waste

NEW:

3. New Process (H-ZSM-5)  
35 t/y solid waste  
265 t/y liquid waste

S16

**Slide 16. Implementation of new more environmentally benign process like for example achieved in synthesis of ethyl-benzene results in dramatically reduced burden on the environment in terms of waste disposal.**



## Green Chemistry and Green Processing

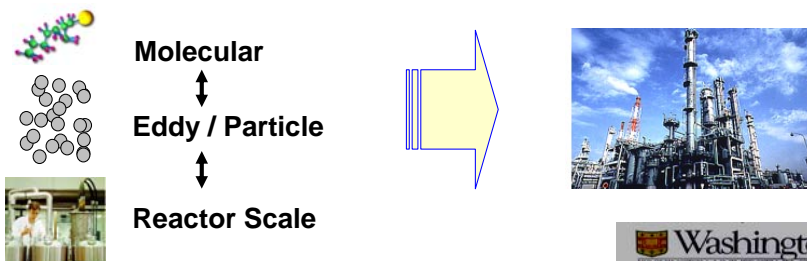
### OLD APPROACH:



Scale-up In Size

### NEW APPROACH:

Apply fundamentals on:



S17

**Slide 17. To achieve efficient implementation of new processes one must replace the old approach of sequential scale-up with a new parallel multi-scale approach on the molecular level (choice of chemistry, catalyst, media), eddy particle scale (effect of transport on kinetics) and reactor scale where effect of flow pattern and contacting pattern of phases is decided upon.**

## *Green Chemistry and Green Processing*

### REACTION ENGINEERING...

*Art*



Past & Present...

*Science*



... Future

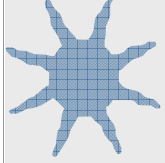
S18

 **Washington**  
WASHINGTON UNIVERSITY IN ST. LOUIS  
School of Engineering & Applied Science

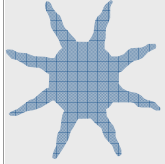
**Slide 18. Only the use of firm scientific concepts and appropriate modeling will allow one to move CRE from the state of art to the state of science which is needed in developing environmental benign processes.**



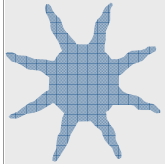
## REACTION ENGINEERING ENCOMPASSES A MULTITUDE OF SCALES



- Molecular scale (micro)
- Small eddies and particle scale (meso)
- Reactor scale (macro)



All of these scales can affect reactor performance and hence the overall process performance and its environmental impact.

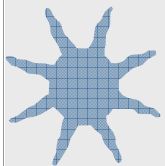
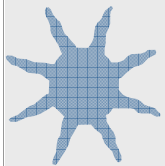
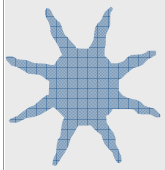


S19

**Slide 19. One should reiterate that diverse scales can affect reactor performance and dealing with all these scales is required to optimize reactor performance and minimize negative environmental impact.**



## MICRO-SCALE TECHNIQUES

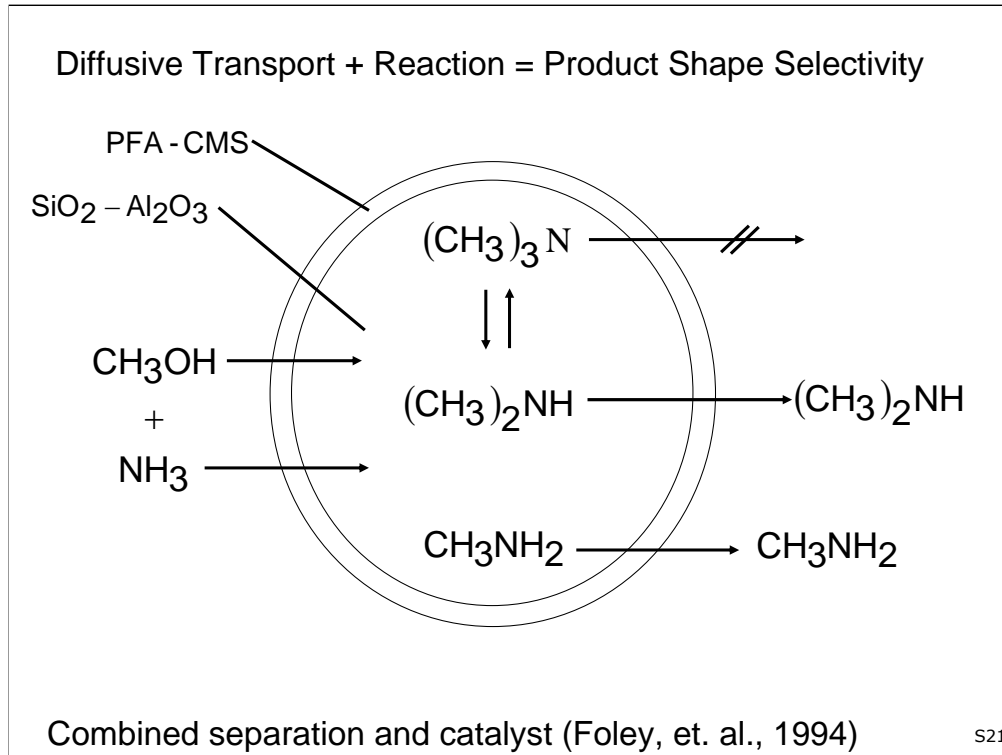


1. Molecular Synthesis:  
e.g. solvent replacement group contribution approach
2. Reaction Path Synthesis:
  - Understanding current reactions and mechanisms of pollutant formation
  - Establishing synthesis pathways for new compounds
3. Catalysis Design:
  - Rational development of new catalysts that will result in cleaner technologies

S20

**Slide 20. Micro scale techniques involve methods for solvent replacement and molecular synthesis as well as rational development of new catalyst.**

**Methods of molecular modeling are important.**



**Slide 21. On a single particle scale one can use the concept of hindered diffusion to combine reaction and separation. The desired MMA and DMA can diffuse through the layer deposited on the outside of the silica-alumina catalyst. TMA cannot come out and due to reactions in the pellet can be reconverted to DMA and MMA. Clearly, diffusion and reaction concepts are important on the pellet scale.**

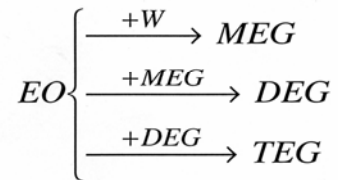
# REACTIONS IN ETHYLENE GLYCOL PRODUCTION

## ETHYLENE GLYCOL MANUFACTURE:

### REACTION SCHEME:



### CONVENTIONAL THINKING:



S22

**Slide 22. Innovations are possible also on reactor scale. Classic process for ethylene glycol manufacture can be viewed as a set of competitive reactions for EO. Large excess of water helps promote the desired reaction to MEG. Clearly water takes part in consecutive reactions so plug flow should be used at optimal residence time to maximize the production of the desired intermediate, MEG.**

**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:**

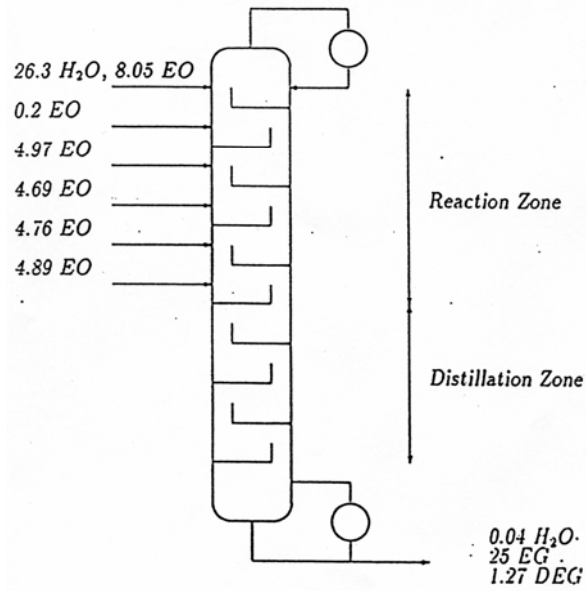
Remove wanted product in situ as it is formed;  
Make excess water available in reaction zone

S23

**Slide 23. The conventional process does indeed use a tubular reactor, large excess of water in the feed but requires large separation train and enormous recycle of water at 100:1 W to EO may be used.**

**The innovation is to use reactive distillation, remove the desired MEG in situ and make excess water available in the reaction zone.**

OPTIMAL DISTRIBUTED FEED REACTIVE DISTILLATION COLUMN FOR ETHYLENE GLYCOL SYNTHESIS



S24

**Slide 24. The small single unit process is shown here. However, before one should embark on building new EO plants one needs to ask a question whether MEG is really optimal to use as anti freeze? What should replace it that has less undesirable environmental impact?**



## Green Chemistry and Green Processing

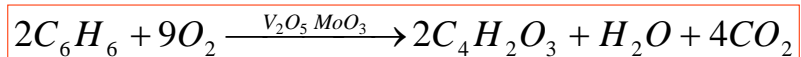
### Concept of Atom and Mass Economy

Atom economy is a measure of how efficiently raw materials are used.

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

#### Benzene

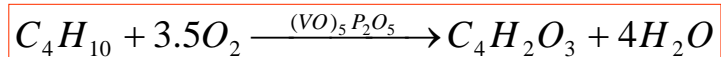
##### route:



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

#### n-Butane

##### route:



$$\text{Mass Efficiency} = \frac{(4)(12) + (3)(16) + (2)(1)}{4(12) + 3.5(2)(16) + 10(1)} \times 100 = 57.6\%$$

S25

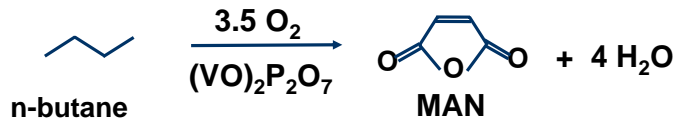
**Slide 25.** We should consider now how multi-scale efforts are required in development of new processes.

Clearly, considerations of mass atomic efficiency lead to a preference for butane as raw material for synthesis of maleic anhydride over the benzene route.

For the advantage to hold one must assure that the new process operates at high yields of maleic formation and further oxidation losses of hydrocarbon to CO and CO<sub>2</sub> must be suppressed.

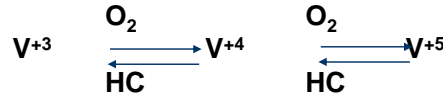
This requires a new catalyst. Then comes the realization that traditionally used packed bed reactor is not good because of hot spots (pronounced temperature profile) and due to rapid catalyst deactivation.

## Butane Oxidation Over VPO



- Active catalyst is a mixture of phases, including  $\alpha_{\text{II}}\text{-VOPO}_4$ ,  $\delta\text{-VOPO}_4$ ,  $\gamma\text{-VOPO}_4$  and  $(\text{VO})_2\text{P}_2\text{O}_7$

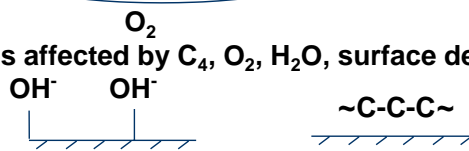
- Catalyst oxidation state is variable



- Both heterogeneous and homogeneous reactions occur



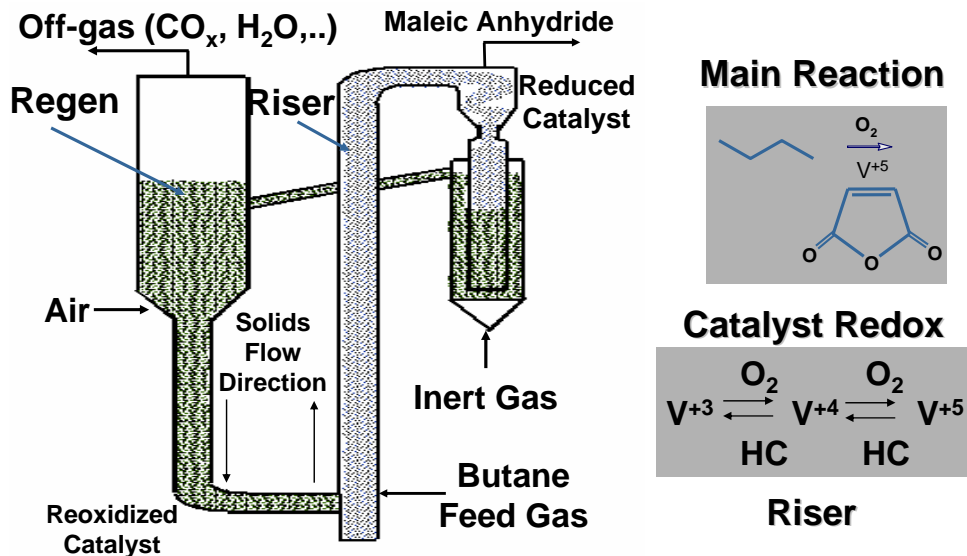
- Intrinsic rates affected by  $\text{C}_4$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , surface deposits, ...



S26

**Slide 26. Extensive research revealed that vanadium pentoxide catalyst possesses a number of phases, undergoes oxidation-reduction and only one type of oxygen is active. Thus, to optimize catalyst activity and selectivity one cannot use traditional steady state operation but must expose the catalyst to periodic reaction conditions. Feed swinging in packed bed is not good due to hot spot. Thus fluidized bed riser is selected.**

## Circulating Fluid Bed (CFB) Reactor for Butane Oxidation



S27

Washington  
WASHINGTON UNIVERSITY IN ST. LOUIS  
School of Engineering & Applied Science

Slide 27. In the riser re-oxidized catalyst is exposed to butane, upon separation of MAN the reduced catalyst is re-oxidized in the regenerator.

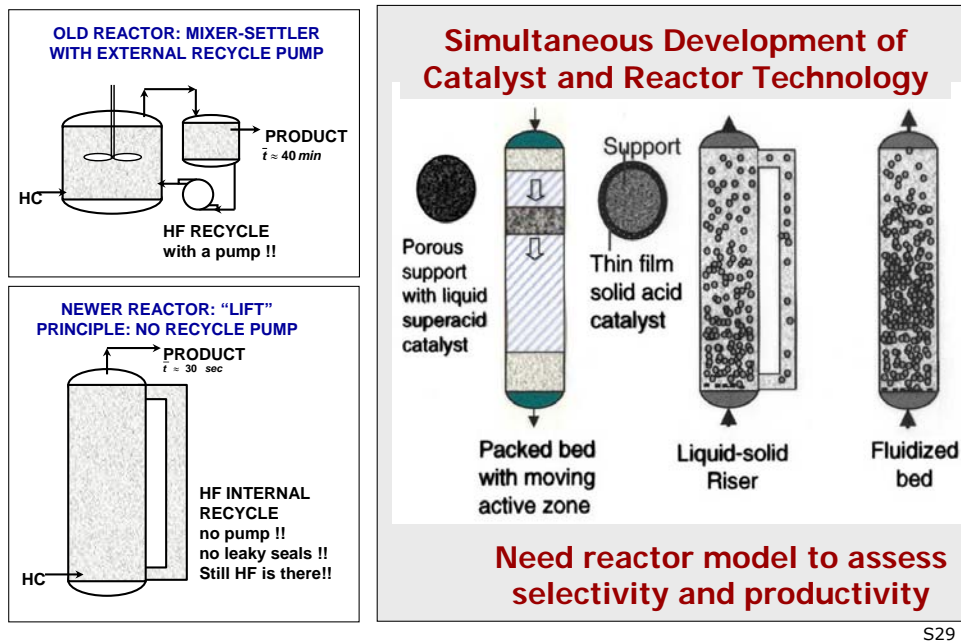
To withstand attrition, a special attrition resistant, highly porous, layer is deposited successfully on the catalyst particles. Pilot plant results were excellent but plant performance is dubious. The technology is viable but requires advances in knowledge in scale-up of circulating fluidized bed reactors which is a demanding problem. Understanding reactor scale, such as hydrodynamic effects on catalyst back-mixing, hold the key to success.

### **Traditional Routes for Alkylation**

- **Traditional routes use liquid phase acids such as HF or  $\text{H}_2\text{SO}_4$  or Lewis acid metal halides:  $\text{AlCl}_3$  and  $\text{BF}_3$**
- **Stoichiometric quantities often needed leading to waste generation**
- **Disposal of spent catalysts such as  $\text{BF}_3$  needed**
- **Corrosive systems → Capital cost**

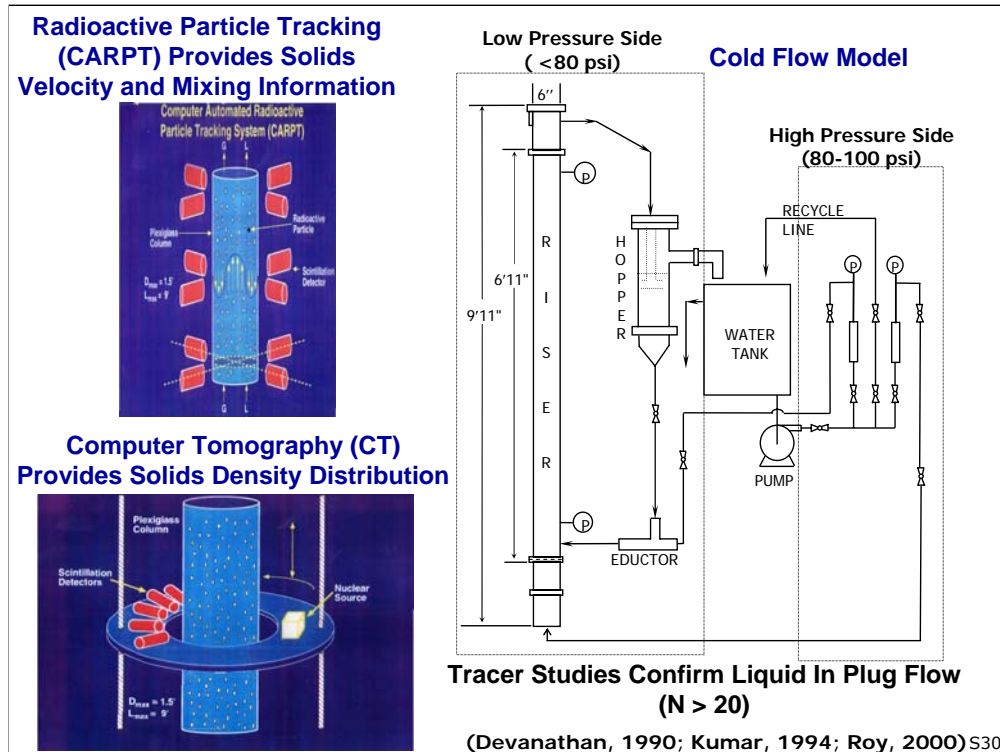
**Slide 28. Let us consider alkylation reactions as another example in need of multi-scale approach. Traditional routes use liquid acids or halides and create a serious spill and disposal hazards.**

## Alkylation: HF Catalyst (Old); Deactivating Solid Supported Liquid Catalyst or Solid Acid Catalyst (New)



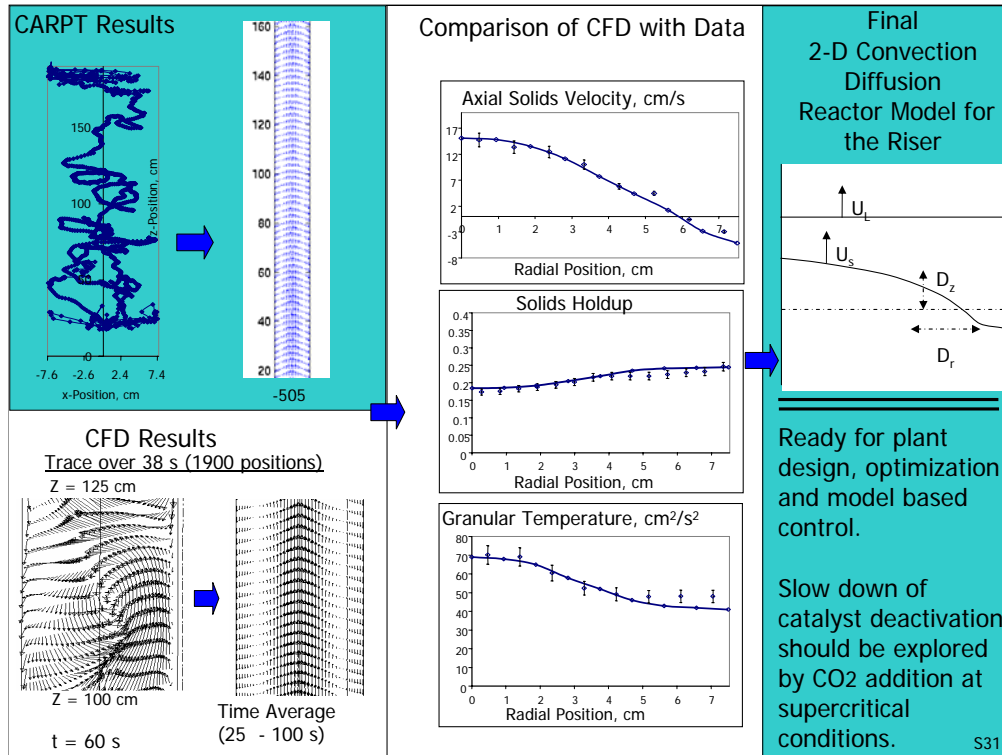
**SLIDE 29.** The original process used stirred tanks (mixer settlers with heat exchanger) in which HF used as the catalyst was recycled with the external pump. The hydrocarbon paraffin-olefin mixture and HF form two liquid phases. Low concentration of olefins had to be maintained for good selectivity so micromixing and point of introduction of olefins feed are reaction engineering issues. Many stirred tanks in parallel are used. However, the process is environmentally unfriendly due to HF use and leaky seals on the pump and reactor mixing shaft. For that particular chemistry a lift type reactor, that avoids the rotating shafts, and accomplishes mixing by utilizing the buoyancy force created in the mixture of a light and heavy phase is to be preferred.

Quantum jump in technology, and its environmental friendliness, occurs with the invention of super-acid liquid catalyst, that can be contained on porous solid support, and with solid acid catalyst deposited on solid support. New reactor configurations suitable to deal with deactivating solid catalyst are now required. We focus here on the liquid-solid riser arrangement. Proper reactor modeling needed for scale-up can only be done if information on solids volume fraction (holdup) distribution and solids velocity and mixing, as well as that of the liquid, is known. This information is necessary to be coupled with kinetics of the reaction and deactivation.



**SLIDE 30.** By building a prototype cold flow model of the riser, one can execute appropriate studies to obtain the needed information and validate the CFD code that can be used to predict liquid and solid mixing and holdup distribution. Liquid tracer studies (with KCl as tracer and electroconductance probes) quickly reveal that liquid is essentially in plug flow ( $N > 20$ ). At the time of this study in 2000 the prevailing assumption was that solids are uniformly distributed and are in plug flow. The slip velocity was assumed to be correlated with mean solids holdup via Richardson Zaki correlation. This information proved inadequate for precise design.

Our Computer Aided Radioactive Particle Tracking Facility (CAPT) was then used to obtain full information about solids flow and mixing pattern. An array of 28 2" NaI detectors monitors the motion of a single radioactive particle (containing Sc 46) of the same size (2 mm) and density as the solids used in the riser at a sampling frequency of 50 Hz. Gamma ray computer tomography, with a single Cs 137 source and a fan beam of NaI detectors that rotate 360° around the riser, yield the density distribution in various planes.



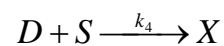
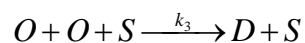
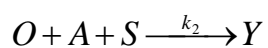
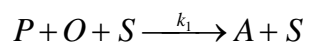
**SLIDE 31.** CARPT results reveal that a trajectory of a tracer particle during its single sojourn through the riser is anything but a straight line! Hence the individual particle does not experience plug flow but meanders in a helical irregular path as it travels through the riser. However, upon obtaining instantaneous velocities from 2000 trajectories of the tracer particle and upon ensemble averaging them, a regular flow pattern with solids rising in the middle and falling by the walls emerges. CFD computations confirm that the instantaneous solids Eulerian velocities form a complex 3D swirly pattern. Time averaging, however, confirms CARPT results of solids rising in the middle and descending by the walls. A quantitative comparison of time (ensemble) averaged axial solids velocity from CFD and CARPT is in excellent agreement, as is the CFD prediction of the CT determined time averaged solids holdup distribution. Remarkably, solids kinetic energies determined by CARPT are also predicted well by CFD. CARPT also provides diffusivities from first principles from the Lagrangian particle trajectories.

This now provides the basis for a reactor flow pattern and mixing model that can be coupled with kinetics of reactions and deactivation. The model assumes liquid in plug flow, solids with their axial velocity profile and superimposed eddy diffusivities. All parameters can be calculated from CFD and are verified experimentally. Still the issue of how to introduce olefins and keep their concentration low needs to be resolved.

Moreover catalyst still deactivates rapidly, so slow down in deactivation or periodic regeneration via CO<sub>2</sub> at close to critical conditions, needs to be explored.

## Green Chemistry and Green Processing

### Alkylation Reaction Scheme\*



P - Paraffin

O - Olefin

A - Alkylate

D - Dimer

S - Active site

X - Complex blocking an acid site

Y - Complex blocking an active site

#### Model Predictions

- Olefin conversion
- Selectivity to alkylate
- Catalyst activity profile
- Discerning important deactivation step

\* deJong et. al., CES (1996), Volume 51, 2053-2060

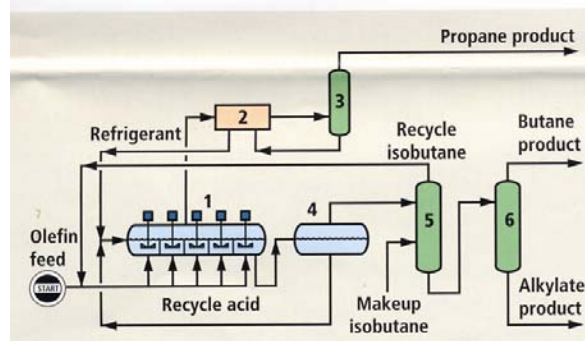
S32



**Slide 32. The current understanding of the alkylation scheme is shown here. Conventional thinking dictates high paraffin to olefin concentration in the feed, plug flow for paraffin and alkylate with side gradual addition of olefin.**



## System to Beat 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.

**Licensors:** ExxonMobil Research & Engineering Co.

S33

**Slide 33. This is captured in the ExxonMobil process that utilizes the old sulfuric acid catalyst.**

### Solid Acid Catalysts

#### Common Types

- Beta zeolites
- Ion exchange resins such as silica supported nafion.
- Heteropoly acids such as tungsto- phosphoric acid.

#### Limitations/Challenges

- Catalyst Deactivation
- Reactivation of catalyst needed
- Complex reactor types
- Pore diffusion
- Loss of selectivity

Developing stable solid acid catalyzed processes as environmentally benign alternatives to liquid acid based processes has been a major challenge for over three decades

S34

**Slide 34. To beat the ExxonMobil and other similar processes on environmental grounds and economically one must develop a solid acid based process which will be highly selective and economical. This will require development of active and selective catalyst that either deactivates slowly or can get regenerated rapidly and easily.**

## *Green Chemistry and Green Processing*

---

### **Pore Diffusion**

- Zeolites and other solid acids have macro-micro pore structure
- Out-diffusion rate of alkylate affects selectivity.
- Out-diffusion rate of dimer affects catalyst activity.
- Solvent tuning to alter diffusion coefficients.
- Model based design of catalyst structure and target goals for diffusivity.

---

S35



**Slide 35. It is essential to understand the diffusion mechanism in the catalyst and its support and the effect of catalyst structure on adsorption/desorption and diffusion.**

## *Green Chemistry and Green Processing*

---

### **Reactor Types**


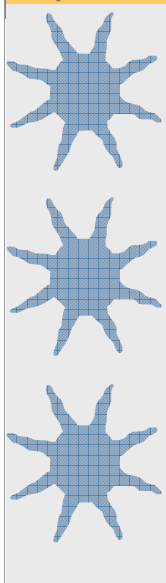
- **Circulating fluid beds**
- **Packed beds with periodic operation**
- **Stirred tanks with or without catalyst baskets (provision for switching)**
- **Chromatographic type of reactors**

---

S36



**Slide 36. At the same time plausible mode of operation – periodic packed bed feed, or CFB or stirred tanks must be considered.**

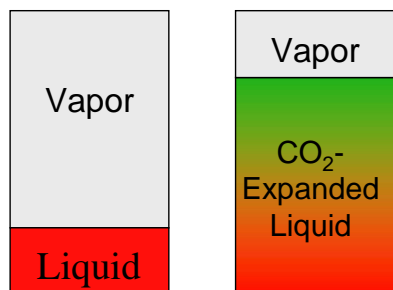
	<p><b>ATTRACTIVE OPTIONS FOR IMPROVED REACTOR PERFORMANCE ARE:</b></p>
	<ul style="list-style-type: none"> <li>• <b>Dynamic operation swing adsorption</b></li> <li>• <b>Periodic (symmetric) operation of packed beds with exothermic reactions</b></li> <li>• <b>Coupling of an exothermic and endothermic reaction in a periodically operated (asymmetric) packed bed</b></li> <li>• <b>Induced pulsing in trickle beds</b></li> <li>• <b>Counter current flow in gas-liquid-solid catalyzed systems</b></li> </ul> <p><b>IN SITU REACTOR SEPARATIONS ARE ATTRACTIVE AND CAN BE ACHIEVED VIA</b></p> <ul style="list-style-type: none"> <li>• <b>Catalytic distillation</b></li> <li>• <b>Membrane reactors</b></li> <li>• <b>Flowing solids adsorbent</b></li> <li>• <b>Expanded solvents</b></li> </ul>

S37

**Slide 37. Additional attractive options for improved reactor performance are listed here. Some have reached commercialization and some have not in spite of decades of research.**

**University of Kansas is particularly strong in using expanded, via CO<sub>2</sub>, solvents.**

## (CXLs) CO<sub>2</sub>-Expanded Liquids



- High miscibility of CO<sub>2</sub> with most organic solvents
- Pressure tunable transport and solvent properties
- Mild pressures (relative to scCO<sub>2</sub>)

Add CO<sub>2</sub>

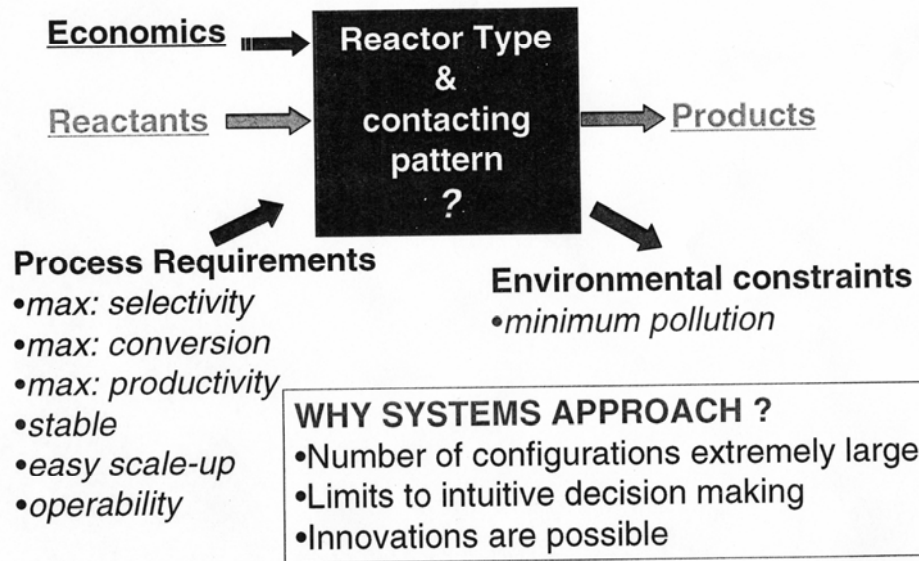
### CXLs successfully applied in homogeneous catalysis<sup>1,2</sup>

<sup>1</sup> Wei, M. *et al.*, *J. Am. Chem. Soc.*, **124** (2002) 2513.

<sup>2</sup> Rajagopalan, B. *et al.*, *Ind. Eng. Chem. Res.* **42** (2003) 6505.

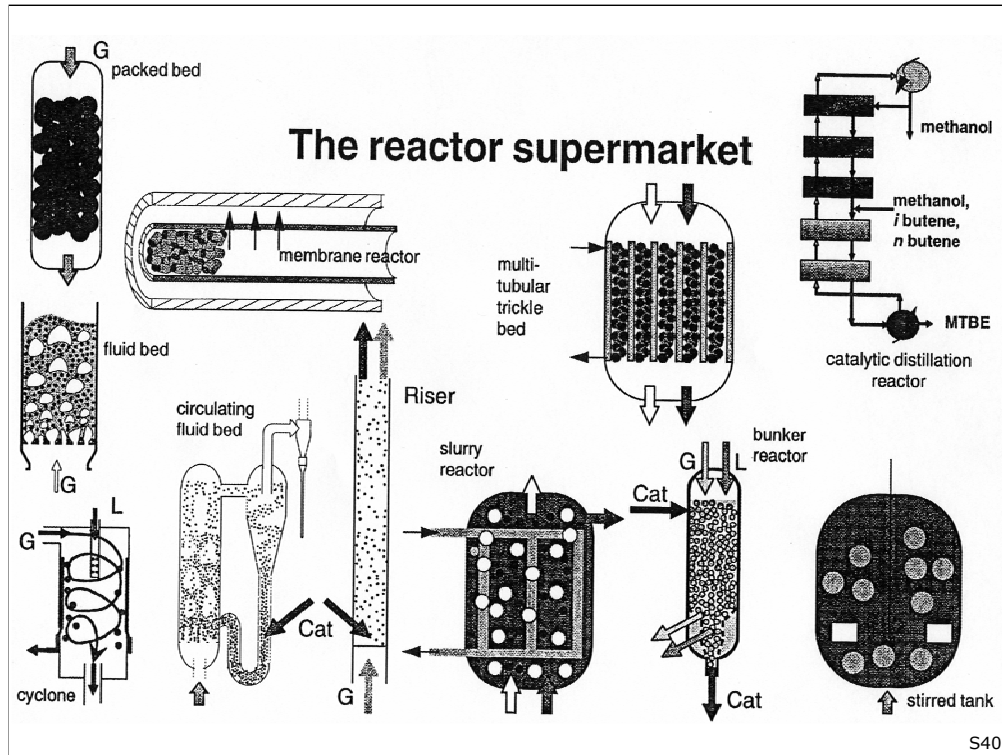
**Slide 38. In expanded solvents much faster transport rates than in liquids are achieved. Solubilities of homogeneous catalyst can be readily changed and in situ separation achieved.**

# A SYSTEMS APPROACH TO MULTIPHASE REACTOR SELECTION



S39

**Slide 39. The rest of this short introductory course will focus on reviewing the concepts that are needed to successfully implement a systems approach in multiphase reactor selection.**



**Slide 40. This is an absolute necessity to be able to make wise choices in the reactor supermarket.**



## Homework Assignments

1. What are the alternative chemistries for making carbon disulfide on the large scale? Are there more benign than the carbon-sulfur route? What solvent currently has dominant use in production of rayon fibers. If it is not carbon disulfide, is it more environmentally benign and if so, why? What is the process by which the solvent is made? How is the solvent disposed of? What chemical is likely to substitute mono-ethanol glycol as antifreeze? How is it made? Is that an environmentally benign process?

## Suggested Readings:

Anastas, P.T.; Warner, J.C., *Green Chemistry: Theory and Practice*, Oxford University Press, New York, 1998.  
Levenspiel, O., *chemical Reaction Engineering*, Third Edition, John Wiley & Sons, New York, 1999.