Chemical Reaction Engineering (CRE), Environmental Protection and Sustainable Development

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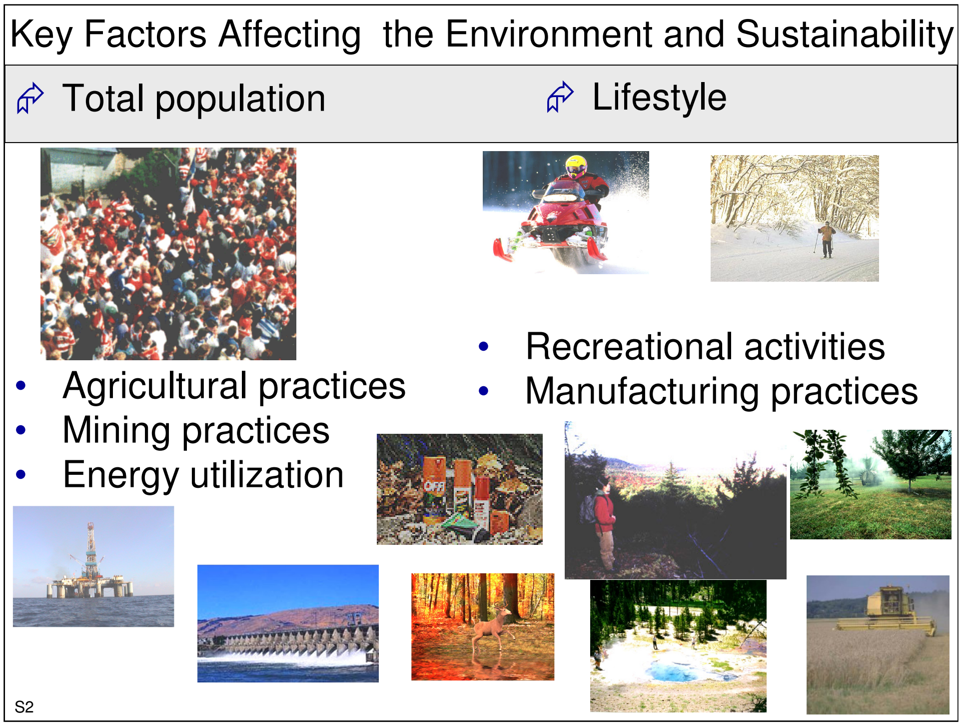
- **Introduction**
- **Role (Current and Future) of CRE**
- **Importance of Multiphase Reactors**
- **Conclusions**

http://crelonweb.che.wustl.edu

SLIDE 1. It is a special privilege to speak in the auditorium of the university I attended as an undergraduate student, in the very hall where my bother Aleksander – Sasha mesmerized students with his exciting lectures in transport and reactions.

I will try today to convey to you as to why chemical reaction engineering, which is at the heart of the chemical engineering discipline, is still very important and why advances in CRE can help us in dealing with environmental protection and development of more sustainable technologies.



SLIDE 2. The two key factors that affect the environment and sustainability of our practices is the total number of people and their life style.

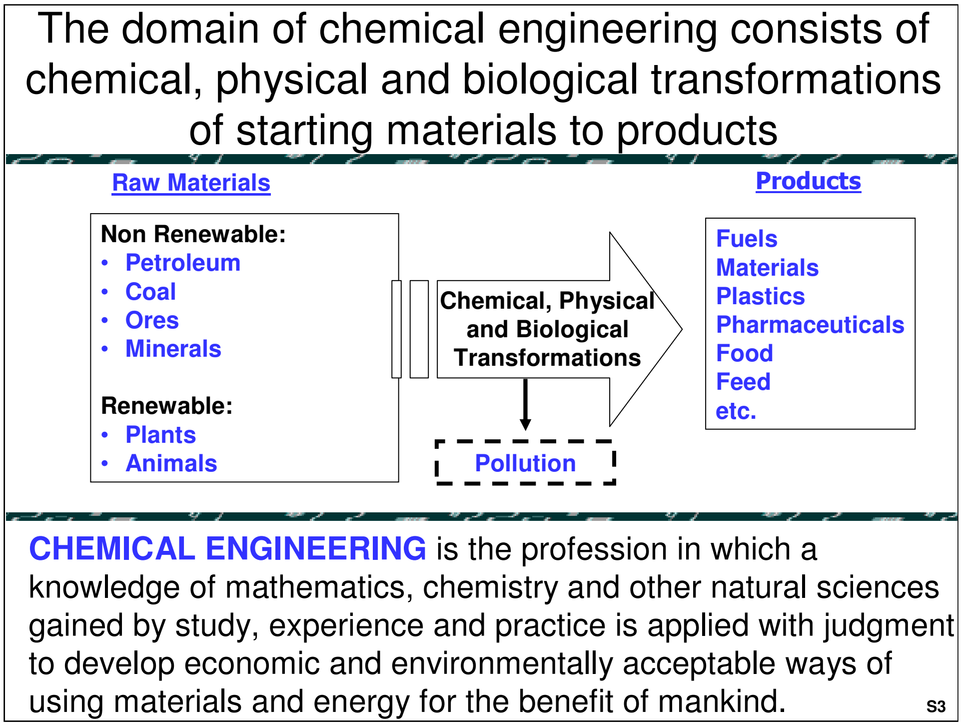
Agricultural practices, clearing of forest for arable land, irrigation of deserts, the extent of use of herbicides and pesticides, etc., obviously are important.

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, such as country skiing or driving a snow mobile, walking or using a dune buggy, have different environmental consequences.

As important as all of the above are, it is <u>the manufacture of products from fuels to chemicals, plastics, pesticides</u> that make alternate life styles possible and that is the realm of chemical and process engineering, which I wish to discuss.



SLIDE 3. 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.

$$\text{Pollution (Damage To Environment)} = \left(\frac{\text{Pollution}}{\text{Energy}}\right) \times \left(\frac{\text{Energy}}{\text{GNP}}\right) \times \left(\frac{\text{GNP}}{\text{Population}}\right) \times \text{Population}$$

$\dfrac{\text{Pollution}}{\text{Energy}}$ - Depends on level of available technology

$\dfrac{\text{Energy}}{\text{GNP}}$ - Depends on the market forces

$\dfrac{\text{GNP}}{\text{Population}}$ - Depends on economic growth

Population - Depends on population growth

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SLIDE 4. Let us take a brief global look as to the damage to the environment created by our technological activities. The total pollution generated can be, in the first approximation, expressed as a product of four factors. 1) Pollution generated per unit of energy used, which depends on the level of available technology and process efficiency, 2) energy used for GNP generation which depends on market forces, 3) GNP/per capita, which is affected by economic growth, and 4) total population.

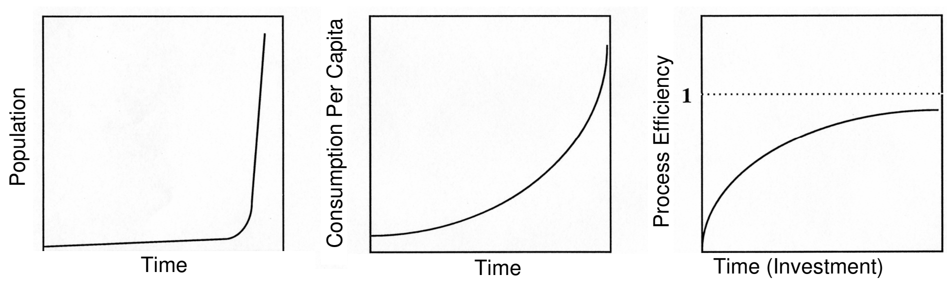
GLOBAL VIEW

Pessimistic Assessment

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

Optimistic Assessment

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



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SLIDE 5. One can further simplify this global view of the pollution problem 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.

Most Effective Ways of Pollution Prevention And Reduction

- **POPULATION GROWTH CONTROL**

  Not feasible due to political and religious opposition

- **REDUCTION IN PER CAPITA CONSUMPTION**

  Not feasible due to business interests – expansion needed to sustain the current world economic system.

  THEREFORE

- **Pollution prevention and reduction via improved technology**

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SLIDE 6. So, from the logical point of view, the best answer to preventing pollution growth is control of population growth and reduction in per capita consumption. The first approach, control of the population, is anathema to two major religions and viewed as politically incorrect! The second, reducing the consumption per capita, is anathema and heresy to the free market and dreams of economic expansions that want even the developing world to consume per capita as much as we do in the US! The only remaining viable approach left is to take the optimistic viewpoint that salvation will come via improved technology. Thus, as scientists and engineers we must work on dramatic reductions in process inefficiency. This, of course, as already stated, requires capital investment and time. As voters we should fight for mandatory increases in process efficiencies globally as this seems to be the only viable answer. Le us see now what we have done so far:

Increased Profits, Government Regulation and Public Pressure are Primary Motivators for Pollution Prevention and Reduction

- Better ‘ housekeeping’ practices in existing processes, minimizations of wastes and spills with the goal of ‘zero emission’.
- ‘End-of-the-pipe’ clean –up via installation of processes for clean-up and for recycling whenever possible with the goal of ‘total recycle’.
- Retrofitting existing processes for improved efficiency, waste reduction and enhanced recycle with the goals of ‘zero emissions’ and ‘total recycle’.
- Development of and installation of new more efficient process technologies that minimize waste and pollution.

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SLIDE 7. There are four accepted ways of pollution reduction and prevention listed in order of increased capital expenditures. 1) Better house-keeping attempts to eliminate obvious wastes, 2) end-of-the-pipe clean-up usually is the response to pubic pressure or government regulations, 3) retrofitting of existing processes introduces better process efficiency and thus reduces waste and pollution, 4) finally, it is the new technologies that offer the best hope for minimization and prevention of pollution.

We should recall that better environmental practices are the result of increased government regulations generated in response to the increased peer pressure from the consumers and general public. Too little regulation increases pollution, too much stifles business activity. Hence, a medium road must be taken. While often we hear about a company acting responsibly to protect the environment, the truth is that the motivator is always profits. Either one has to do it to stay in the business due to regulations, or to prevent even more dramatic regulations. Or due to changing markets there is value to be extracted from recycling. Or new technology expands the market.

Unfortunately, at present there is no incentive for companies to invest and take a risk with new green technologies. The profit motive, in absence of global regulations, suggests as optimal strategy to repeat the known technology at locations where labor is cheaper and regulations less strict. It is a myth that new technology in chemical processes is favored, as there are substantial risks in its implementation and no obvious rewards.

The Rich and The Poor

People	Rich	Poor
Total Population	0.97 billion	2.3 billion
Population Growth (% Annual)	0.5	1.8
Life Expectancy	78	58
Fertility Rate	1.7	3.7
Infant Mortality (Per 1000 Births)	5.4	82
Literacy	98	59
Environment		
Surface Area (Sq KM)	35 million	32 million
Energy Use Per Capita (Kg Oil EQ)	5,350	508
Electricity Per Capita (KWH)	8,340	302
Economy		
GNI Per Capita (US $)	28,550	450
Technology & Infrastructure		
Fixed & Mobile Phones (per 1000 People)	1,250	39
PCs Per 1000 People	470	6.9
Paved Roads (% of Total)	93	13

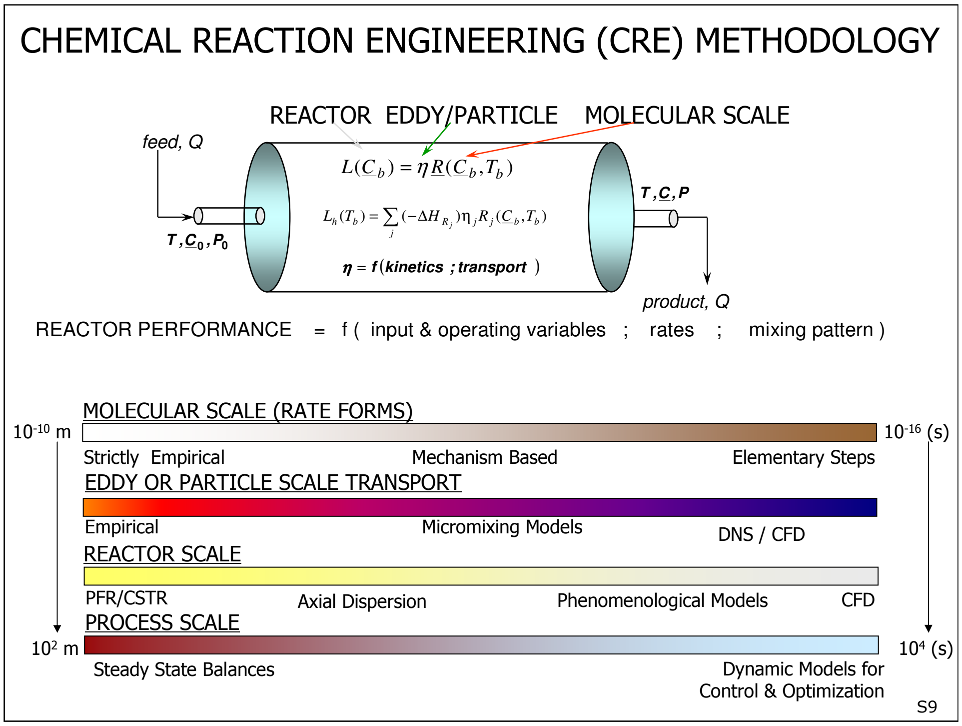
Source: The World Bank Group S8

SLIDE 8. Another reason while eventually we will have to embrace the new efficient process technologies is the fact that the enormous gap between the rich and poor nations must be bridged if we are going to avoid serious social upheavals in the future. And using the current inefficient technology will not do it since this is too wasteful in energy usage.

So to bring the standard of living of Asia and Africa to American level with current technology is clearly unsustainable.

Let us plan considering only the new technologies, that we must start to develop and implement proper understanding and application of reaction engineering principles will be essential.

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 in the development of cleaner new green processes.



SLIDE 9. 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.

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

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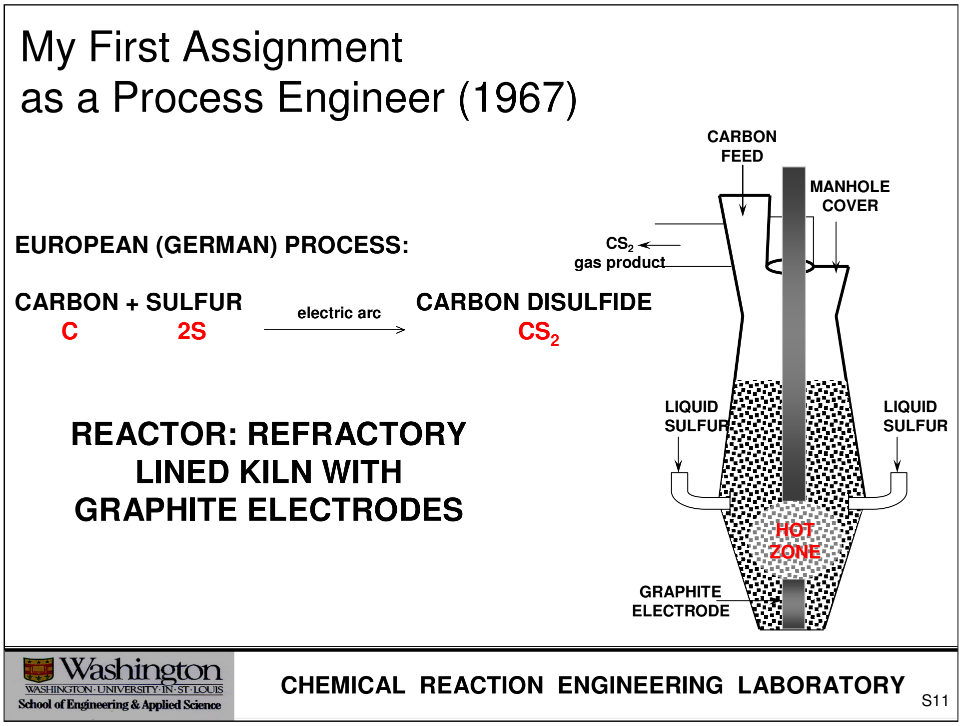
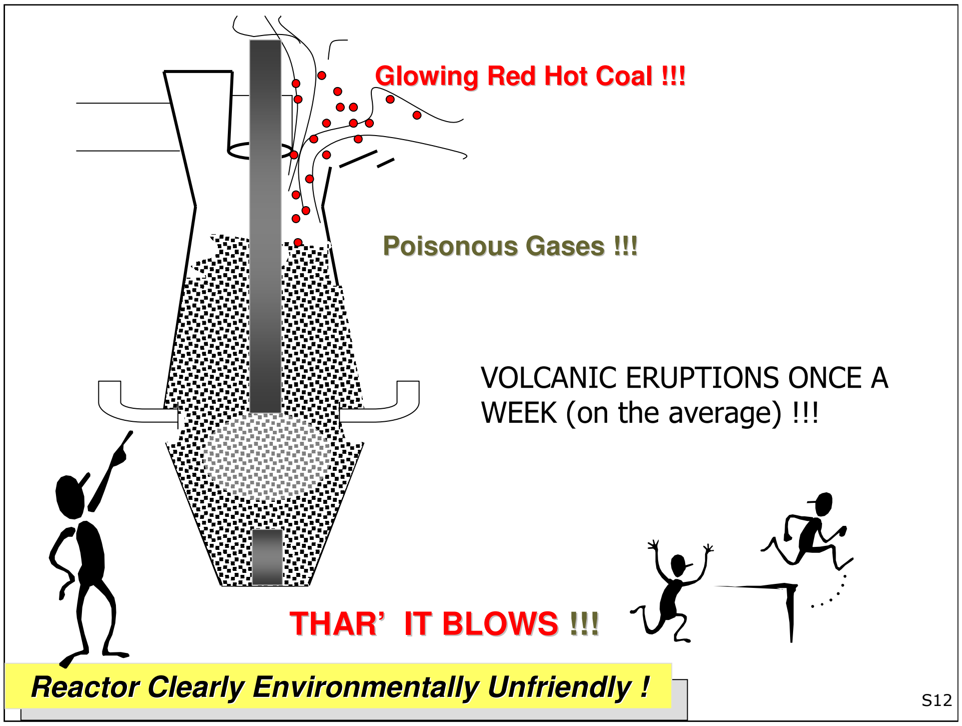
SLIDE 10. The enclosed table illustrates the so-called E factor of various industries. Clearly, those that practice CRE at the high level produce the fewest undesirable products per unit desired product. So-called high tech industries, which are really high value added industries, like the electronic 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.

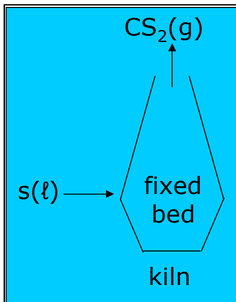
The other point that should be understood is that the so-called principles of green chemistry are just one of the prerequisites for a green process. Whether the process will be successful or not, depends on selection of proper reactor type and its proper operation. A great number of new processes is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



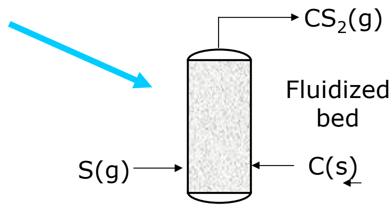
SLIDE 11. To illustrate the pivotal role of reaction engineering in pollution prevention let me use an example from personal experience. My first assignment as process engineer was to expand the capacity for production of rayon fibers which utilized carbon disulfide as a solvent. In Eastern Europe at 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 CS2. Please, note that atom efficiency is 100% so the process is from that point of view better than producing CS2 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 12. 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.

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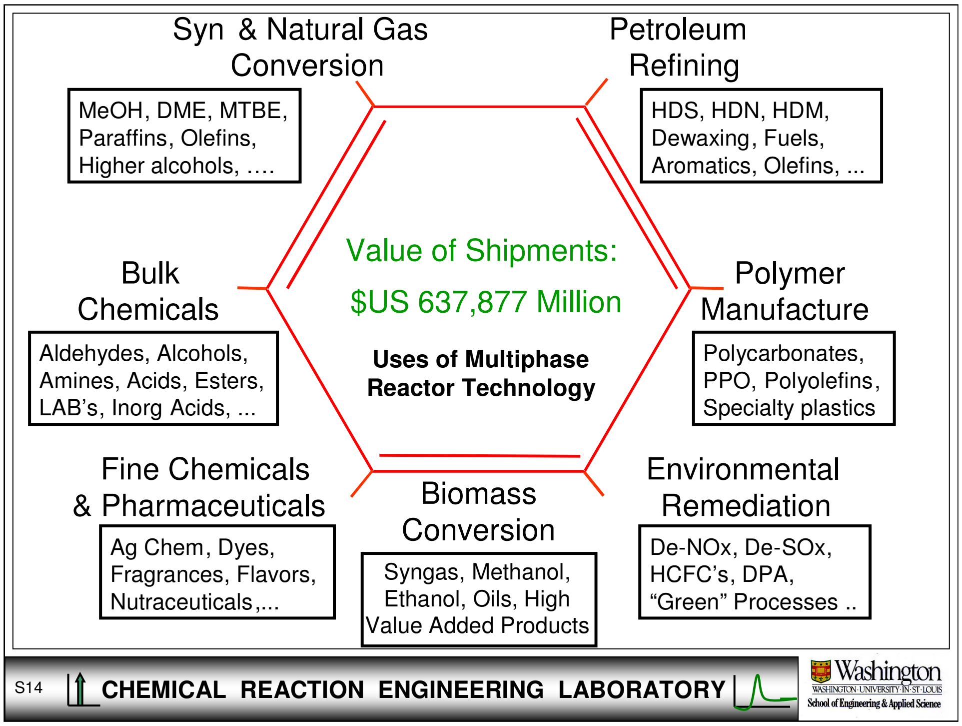
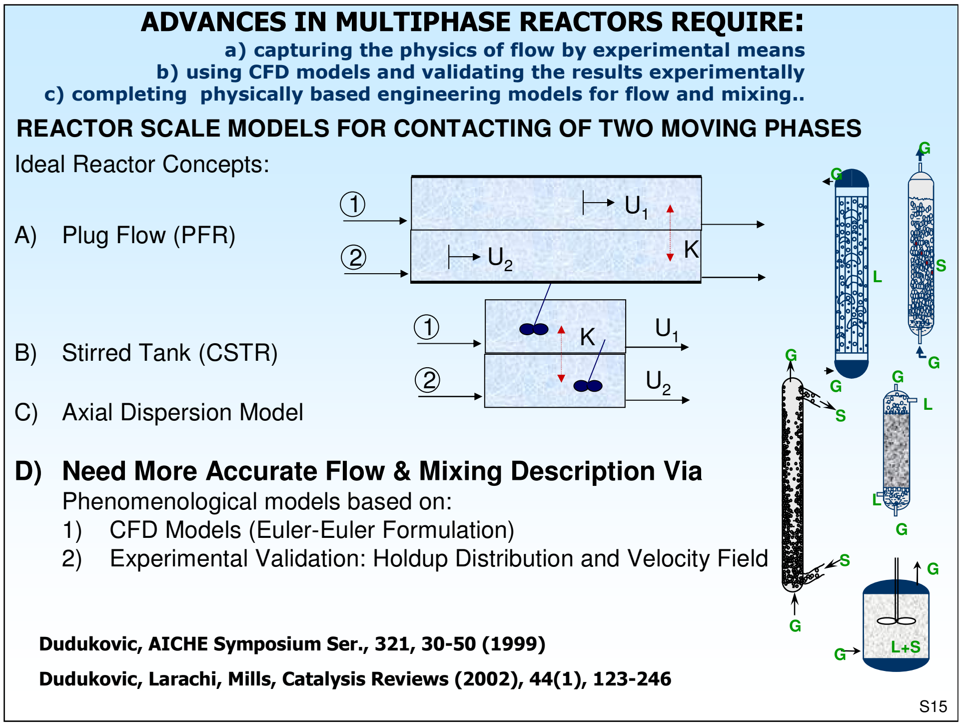
SLIDE 13. The point is that the reactor was selected poorly for the process. It was the wrong reactor. Nevertheless, when we suggested that a fluidized bed reactor with pre-volatized sulfur feed would not have a hot spot problem and would be stable and work reliably, our suggestion was dismissed as too 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.

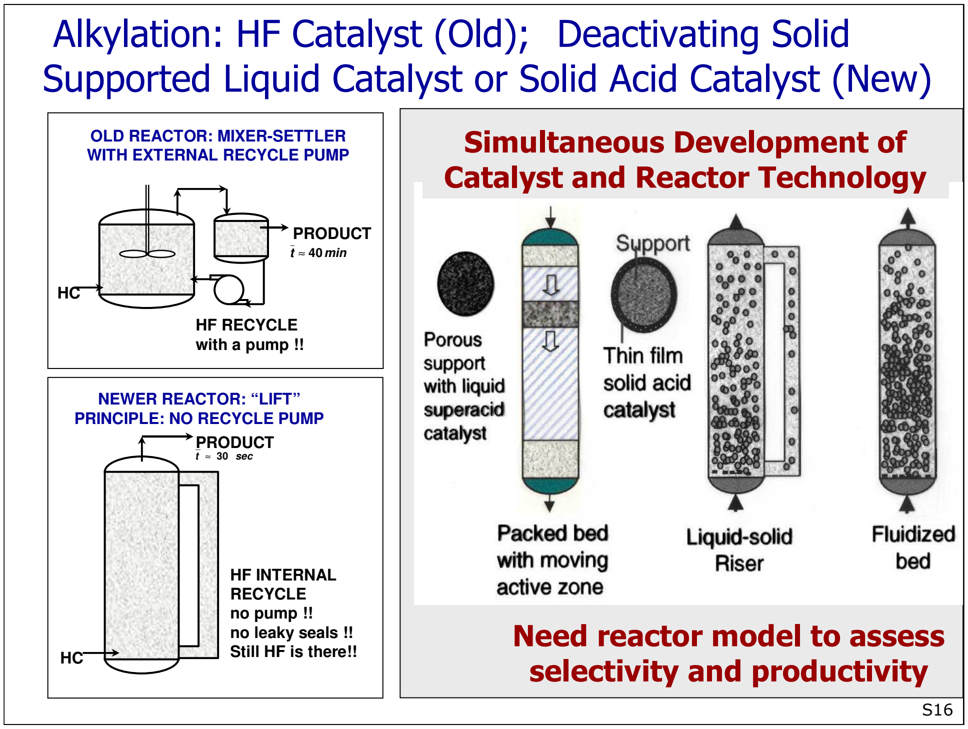


SLIDE 14. We need to recognize that the above example involved a multiphase reactor and that multiphase reactors are important in all process industries and contribute significantly to the national product. All chemical, petrochemical, pharmaceutical and other manufacturing industries use them.



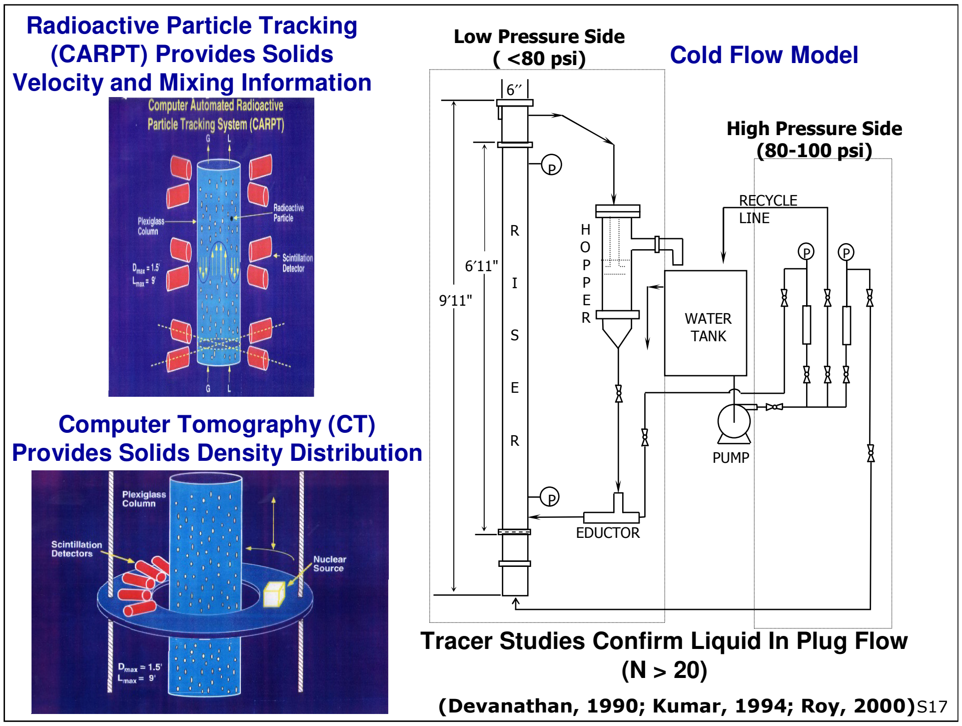
SLIDE 15. In all of these technologies it is the chemical reactor, in which chemical transformation takes place that is at the heart of the process. For proper quantitative description of reactor performance it is important to properly describe how are species brought into contact on smaller scale, by flow and mixing. For example, when we have a reactor system with two moving phases it is important to be able to describe the flow pattern of each. In the past we relied on ideal reactor assumptions of treating each phase as being either in plug flow or perfectly mixed. When reality did not conform to these assumptions the axial dispersion model is often used to match experimental observations but almost always lacked predictability.

To really advance the design, scale-up and operation of these reactors, we must be able to describe the flow pattern and phase contacting better. We need a better description via phenomenological models that capture the physics of the flow. We need such models to be based on CFD calculations which are experimentally validated. Everyone who has dealt with multiphase flows will recognize the necessity of experimental validation of the existing CFD codes due to uncertainty of closures used. The difficulty lies in the opaque character of all multiphase systems of industrial interest in which laser based diagnostic systems do not work. This can be overcome by use of radioactive source based techniques introduced in our laboratory. Thus, the modern approach to reactor modeling requires:a)capturing the physics of flow by experimental means, b)using CFD models and validating the results experimentally, c)completing physically based engineering models for flow and mixing..



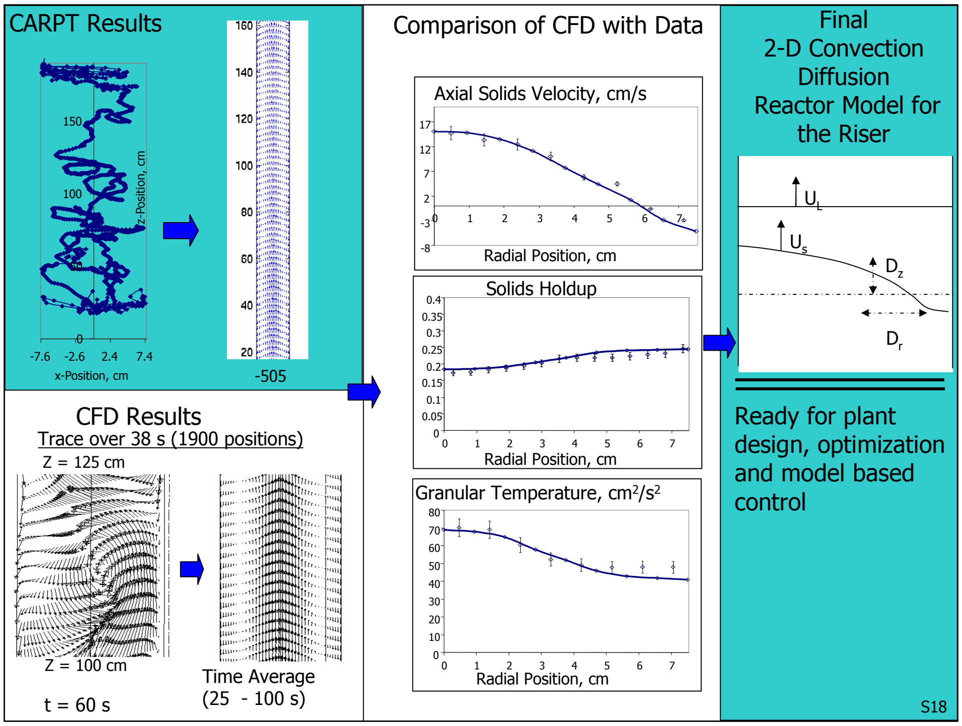
SLIDE 16. Let us consider the application of CRE to the alkylation as an example that illustrates the need for the multi scale approach to the problem. The original process used stirred tanks (mixer settlers with heat exchanger) in which HF used as the catalyst was recycled with the external pump. The hydrocarbon parafin-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 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.



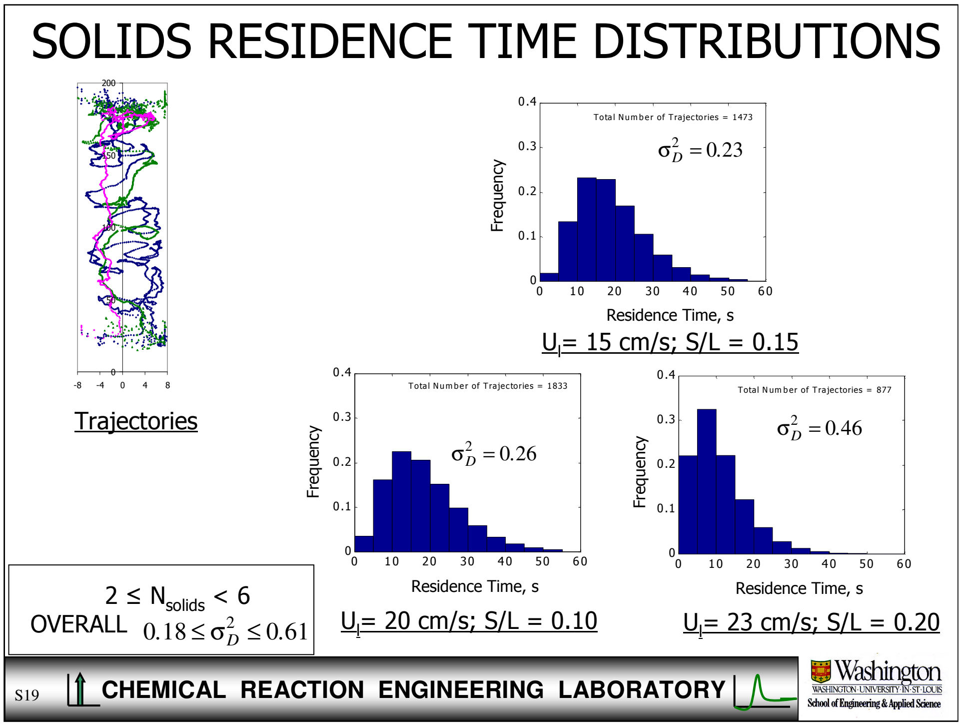
SLIDE 17. By building a prototype cold flow model of the riser, one can execute appropriate studies to obtain the needed information and validate the CFD code that can be used to predict liquid and solid mixing and holdup distribution. Liquid tracer studies (with KCl as tracer and electroconductance 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.

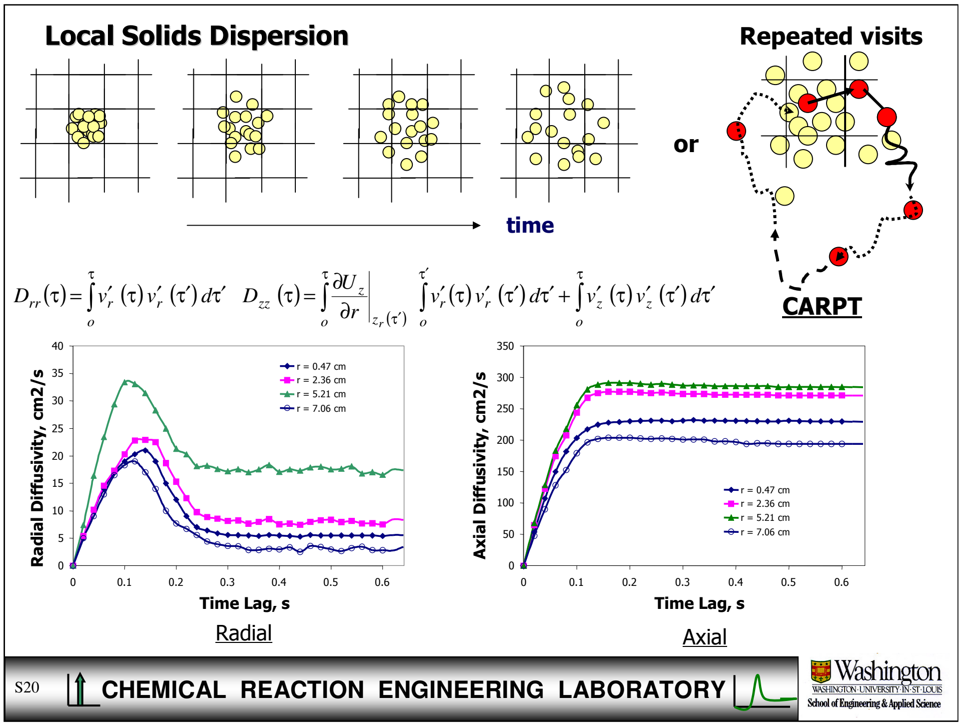


SLIDE 18. CARPT results reveal that a trajectory of a tracer particle during its single sojourn through the riser is anything but a straight line! Hence the individual particle does not experience plug flow but meanders in a helical irregular path as it travels through the riser. However, upon obtaining 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.

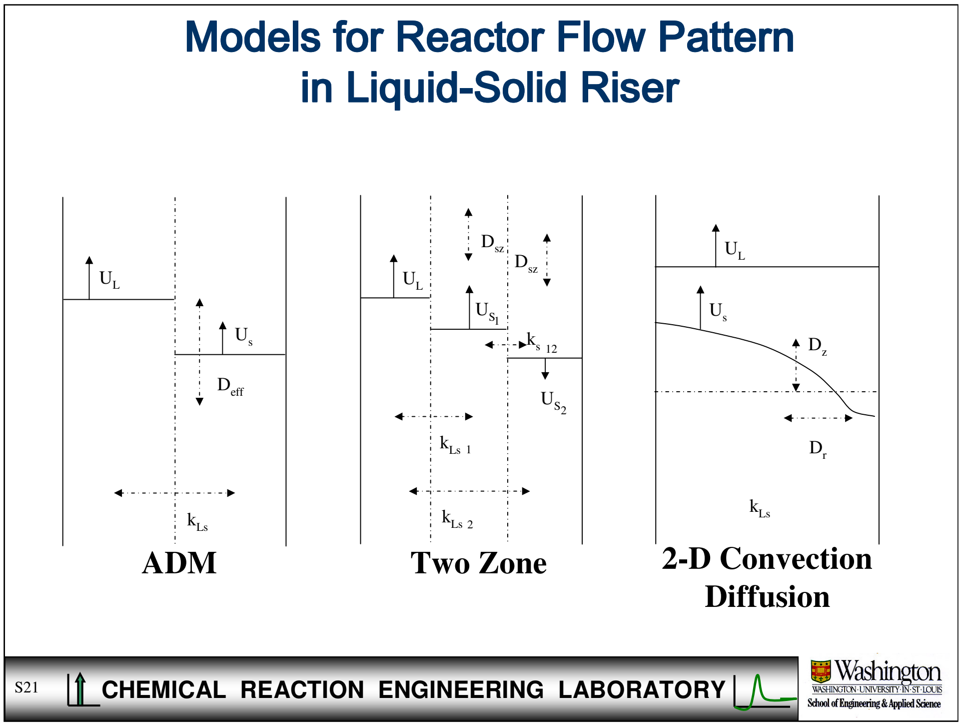
This now provides the basis for a reactor flow pattern and mixing model that can be coupled with kinetics of reactions and deactivation. The model assumes liquid in plug flow, solids with their axial velocity profile and superimposed eddy diffusivities. All parameters can be calculated from CFD and are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



SLIDE 19. As a bonus from CARPT slides in the riser we obtain the residence time distributions of solids which clearly show that solids are much more backmixed than liquid. The RTD of solids is well represented with 2-6 tanks in series, depending on the operating conditions CFD codes are able to compute the RTD even in 2D axisymmetric simulation.

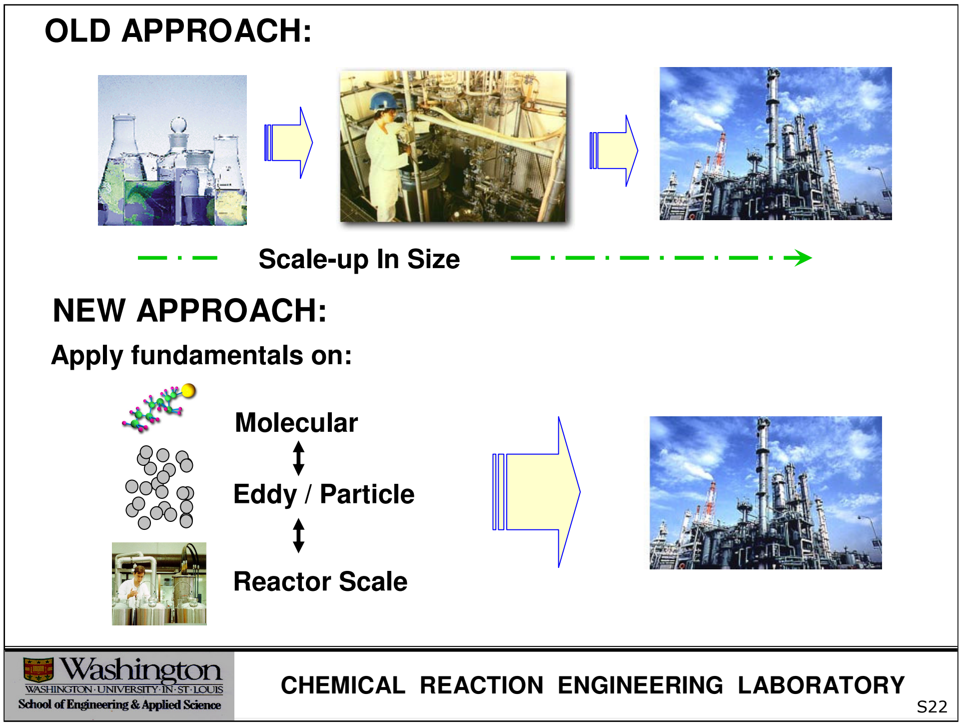


SLIDE 20. Another bonus of the CARPT technique is the direct estimation from first principles of the eddy diffusivity components. We see that axial diffusivity is an order of magnitude higher than radial.

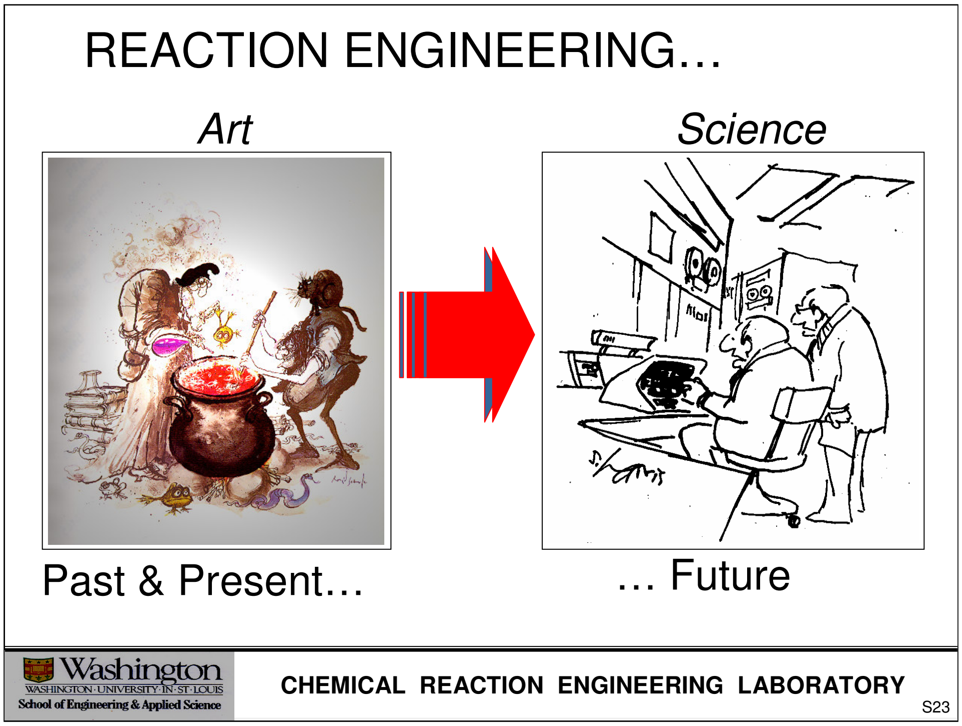


SLIDE 21. Hence, now we have all the information ready to adopt any level of reactor scale model that is needed. Moreover we have experimental validation of CFD codes for modest scale-up factors.

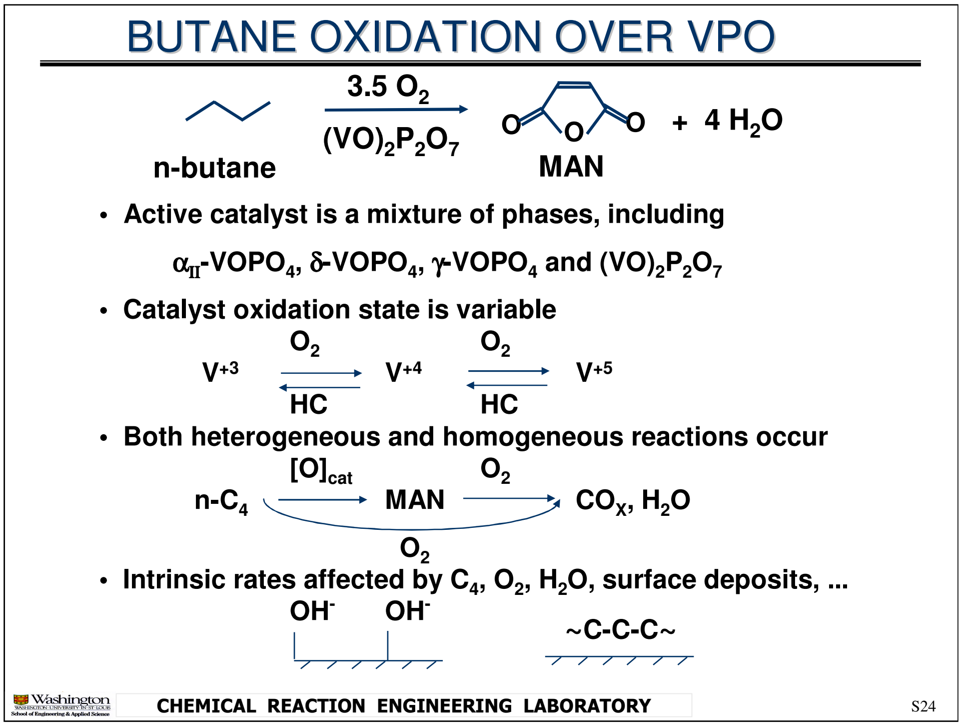
However, we should not forget that we always need to worry about phenomena on all scales. Dramatic reduction in deactivation rate is possible via use of CO2 expanded solvent which may require use of a different reactor type.



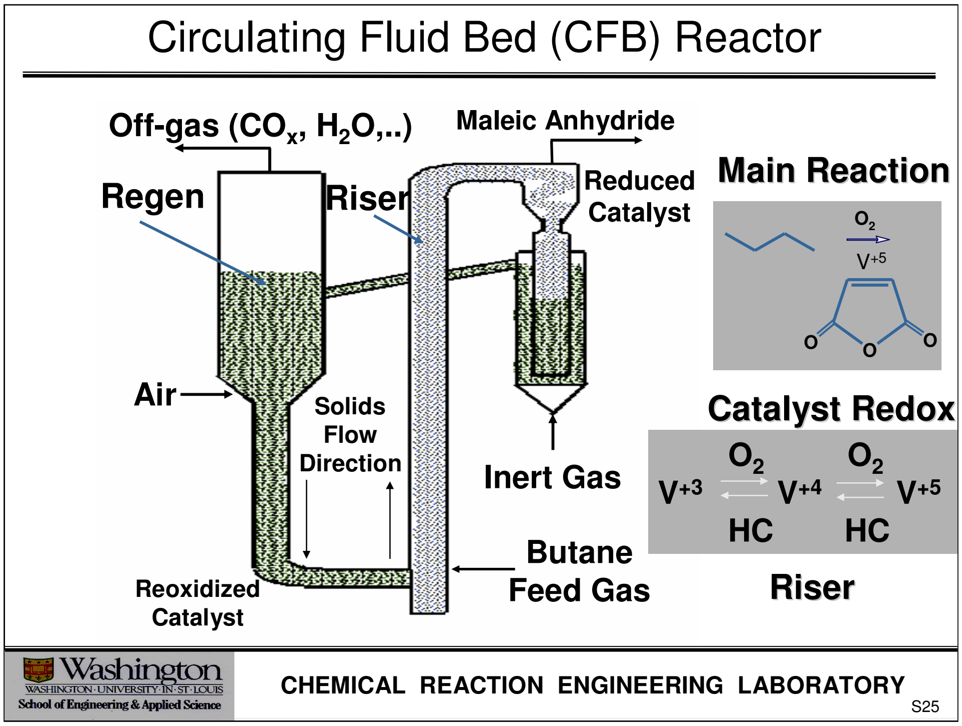
SLIDE 22. The previous example of alkylation illustrates well the reasons as to why we must replace the old approach of reproducing the invented chemistry in an ever larger equipment size (which is often unsuccessful) by a new highly interactive modeling approach on all scales coupled with needed experiments. This moves the process to commercialization faster and meets the green processing requirements inherently as they are part of the goals during process development.



SLIDE 23. Thus, if we want to have high tech processes which will be "green", we must move reaction engineering from art towards science. The days when the chemist found a magic ingredient (catalyst) for a recipe, and the chemical engineer tried in earnest to get its full flavor expressed in an available kettle, must be replaced by the coordinated effort of the chemist to select the best catalyst and chemical engineer to provide it with the best flow pattern and reactor.



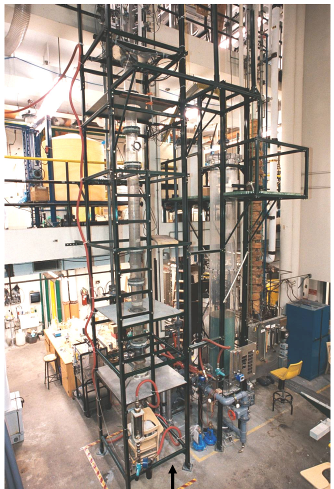
SLIDE 24. Another example of the need for better understanding of the flow pattern in multiphase reactors is the celebrated green process of butane oxidation to maleic anhydride with 100% carbon atom efficiency which replaced the old benzene oxidation route. Catalyst investigations revealed an intriguing mechanism involving variable catalyst oxidation state. Attrition resistant catalyst was successfully made.



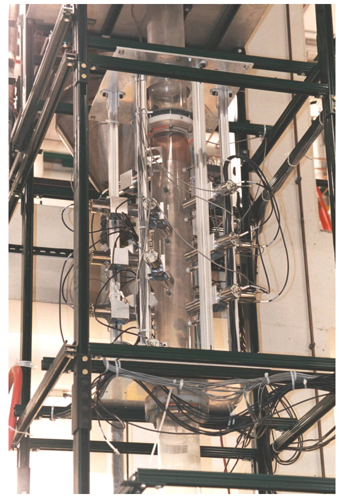
SLIDE 25. This chemistry is then executed in a fluid bed-riser combination to accommodate successive oxidation and reduction of the catalyst. Yet, large scale operations apparently are not fully matching the yield and productivity promise pointing to the importance of fully understanding the contacting pattern in a multiphase reactor and its changes with scale up.

GAS-SOLID RISER

Gas-Solid Riser



Gas-Liquid or Liquid Fluidized Bed



CARPT Detectors on Gas-Solid Riser

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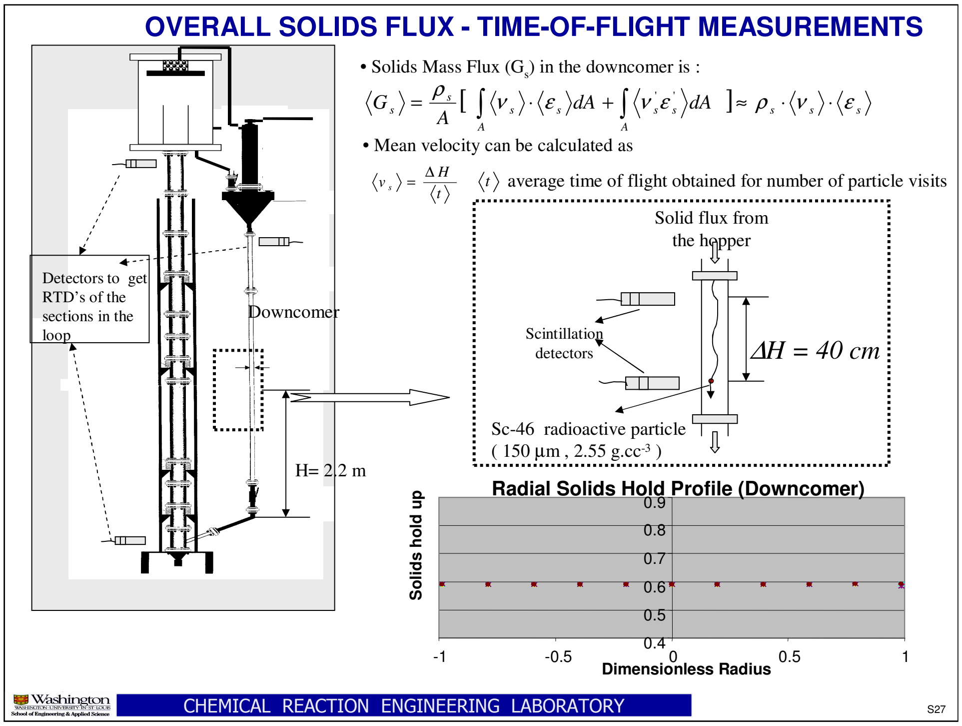
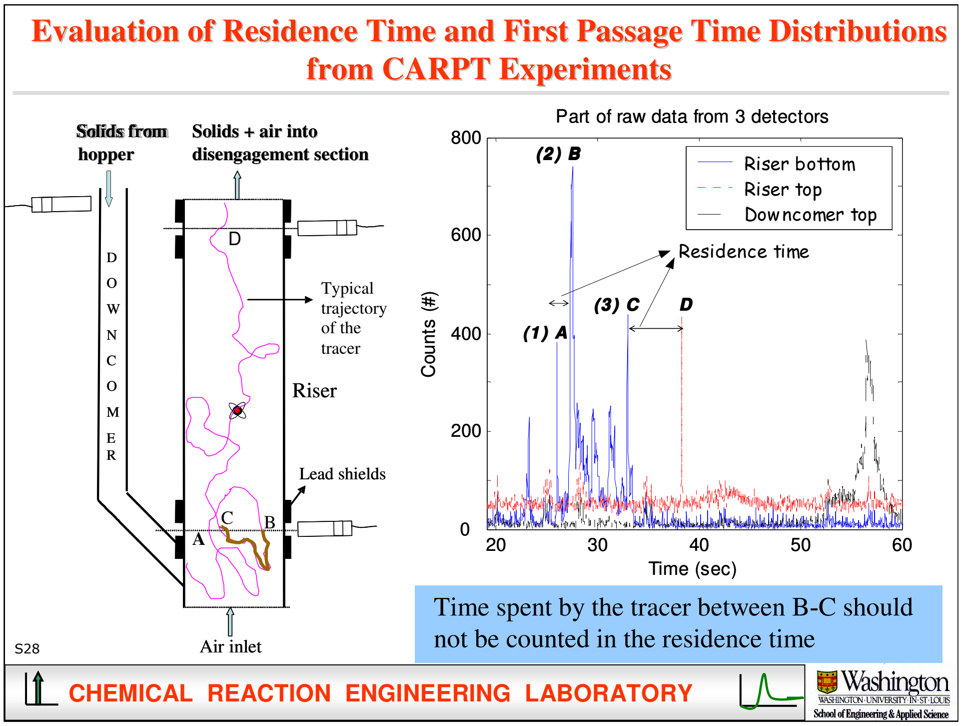
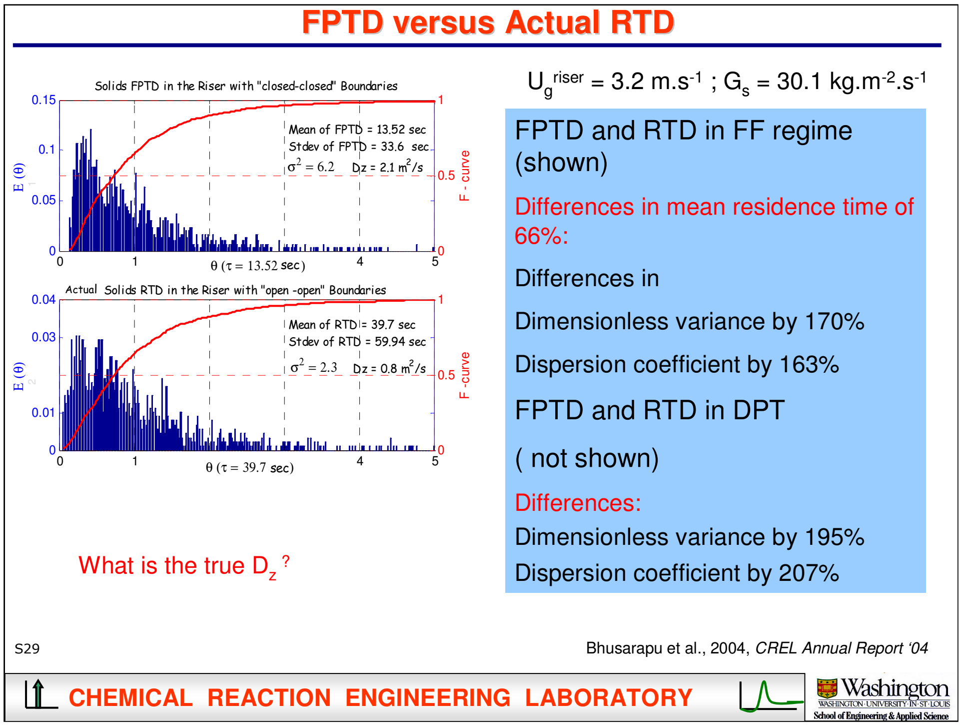
SLIDE 26. In the systems with closed recirculation of solids it is difficult to assess the solids recirculation rate and solids RTD. It is well known that impulse injection of tracer leads to nonunique results for solids recirculation rate and solids RTD. We have resolved this problem by using the CARPT-CT technique by which with time of flight measurements in the downcomer we can assess exactly the solids circulation rate. Moreover, strategically locating detectors at entrance and exit of riser we get the solids RTD and backmixing parameters. The experimental facility consisting of a 6” diameter 26 foot riser is shown here. Detectors for identification of particle trajectories in a fully developed region are also shown.



SLIDE 27. By tomography we establish that the solid holdup in the downcomer is uniform and by time of flight measurement for our radioactive particle we get the solids velocity. Thus, solids recirculation flow is obtained.



SLIDE 28: In this slide we illustrate the ability of CARPT to determine the residence time distribution time of solids in the riser. By monitoring the appearance time of our tracer particle in the inlet plane of the riser and in the exit plane of the riser, each monitored by a collimated scintillation detector, we can determine the total time that the tracer particle spends in the riser. For example, for the trajectory shown, the appearance A in the inlet plane is not followed by tracer appearance at the exit plane but rather by two additional consecutive appearances at the inlet plane B and C, followed by tracer appearance at the exit plane, D. Hence, we know that only time intervals A to B and C to D contribute to the residence time. Only the time interval C to D contributes to the first passage time. Such information is not available by conventional tracer studies where a response to a pulse injection of multiple tracer particles is monitored.



SLIDE 29: To illustrate the distinction between RTD and FPTD, and point out the confusion that may arise from impulse-response measurements when it is unclear as to what is measured, we present this slide. Clearly the mean residence time and the variance and, hence, the solids backmixing inferred from the variance is vastly different, indicating that great caution is advised when interpreting the results from the literature if people did not use CARPT. This slide presents the probability density function (pdf) for both the residence time distribution and first passage tracer distribution at one operating condition. Even during first passage times significant backmixing is detected. This information and the full blown CARPT studies in the riser will provide the needed data base for validation of riser models.

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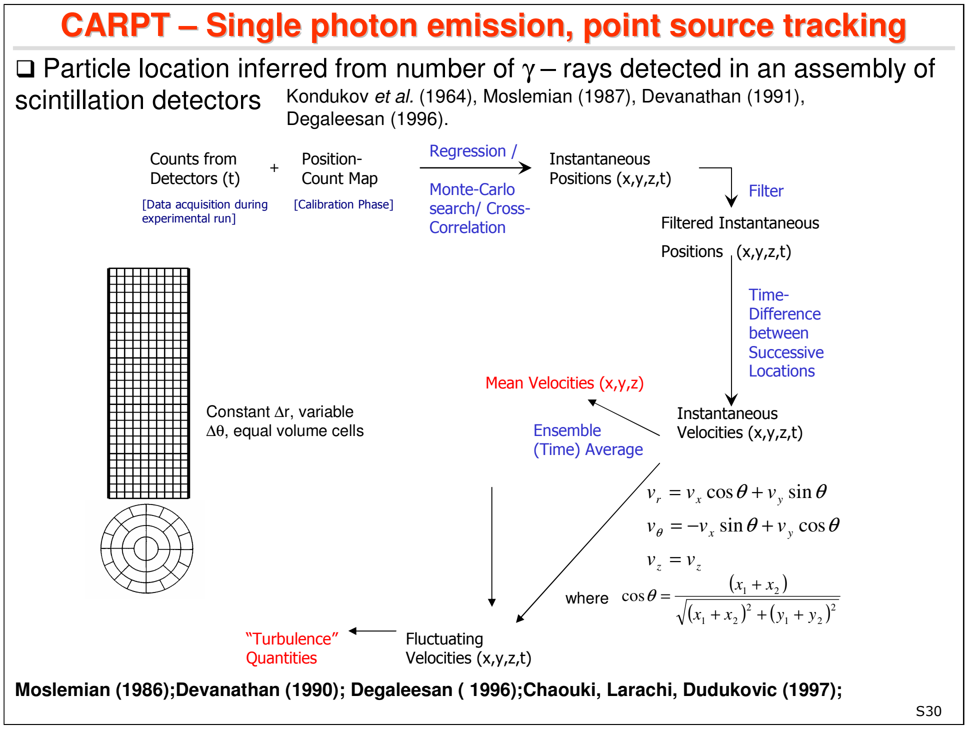
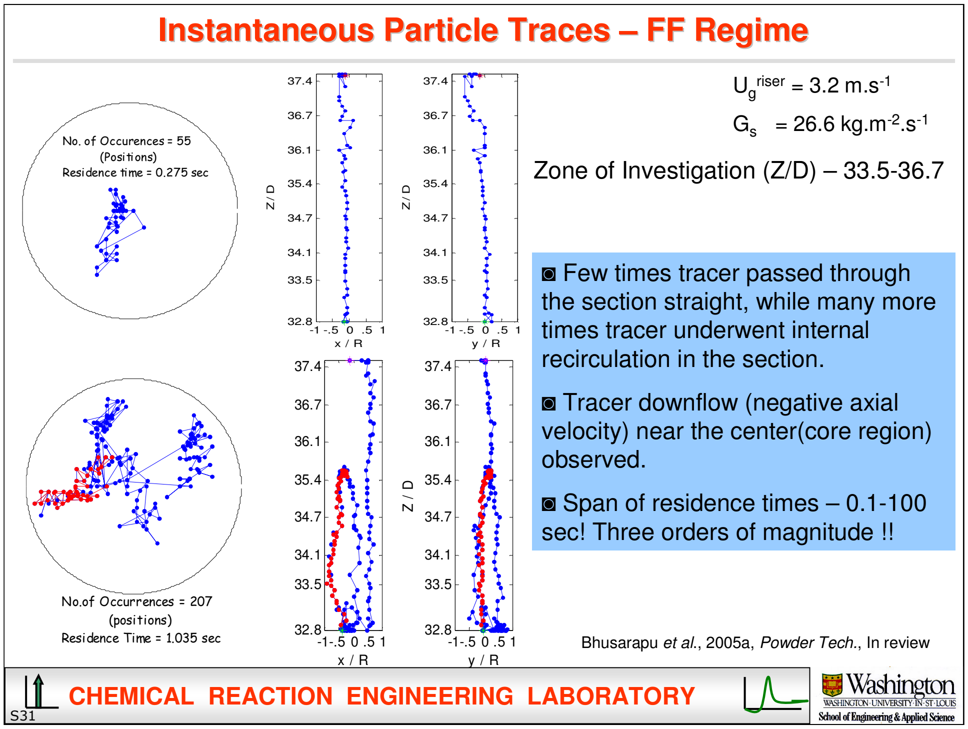
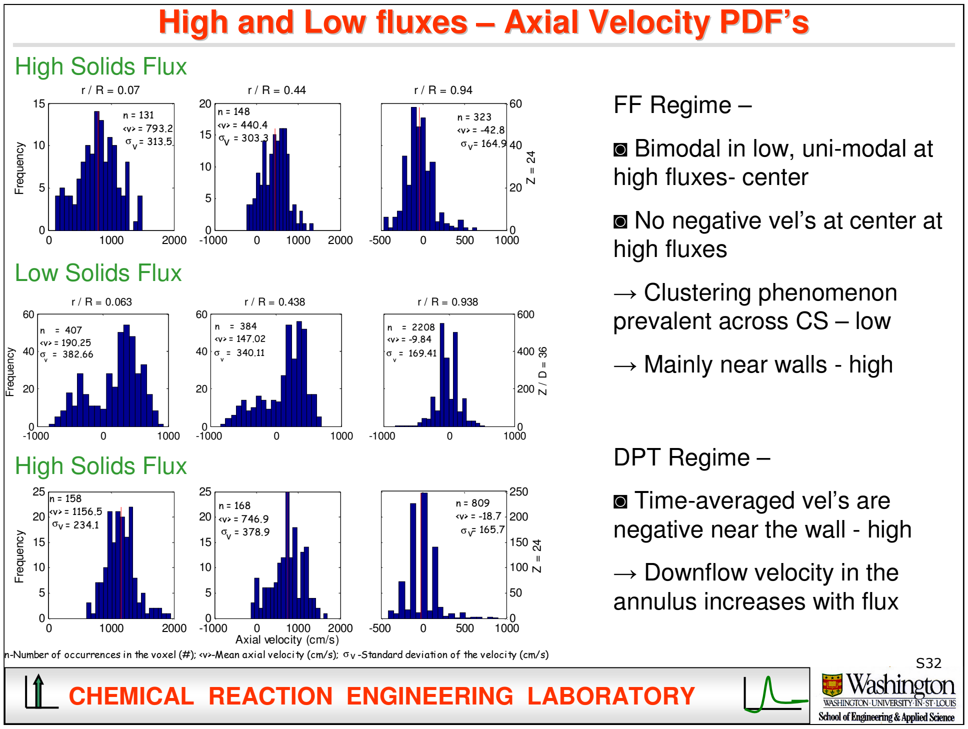


Slide 30. **Using a pre-established algorithm, based on calibrated detectors, instantaneous particle position is identified, filtered from the noise of gamma radiation, and from successive two positions instantaneous velocity is identified and assigned to the cell capturing the midpoint of two positions. Mean velocities are evaluated by ensemble averaging the instantaneous velocities assigned to the same cell. Appropriate turbulence quantities are obtained form the differences of instantaneous and mean velocities.**

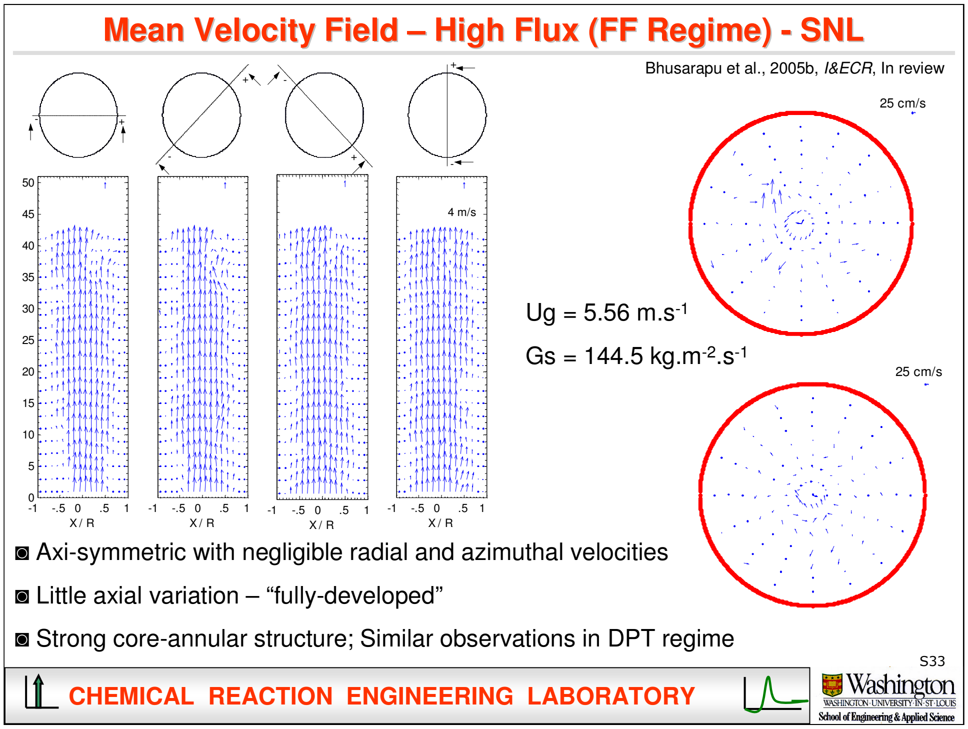


S31 Some of the typical trajectories of the tracer particle captured in the riser section between 33.5 and 36.7 Z/D in the FF regime is depicted here. A few trajectories are almost straight up and the particle travels upward at the center of the column. Many more trajectories exhibit multiple loops including strong tracer down-flow even close to the center of the column. The tracer particle residence time in this section spans three orders of magnitude!! The particle that moves straight up stays very short in the section, the one caught in numerous down drafts stays very long. Only about 20% of the particles go straight up without exhibiting downward velocities in the section of interrogation.

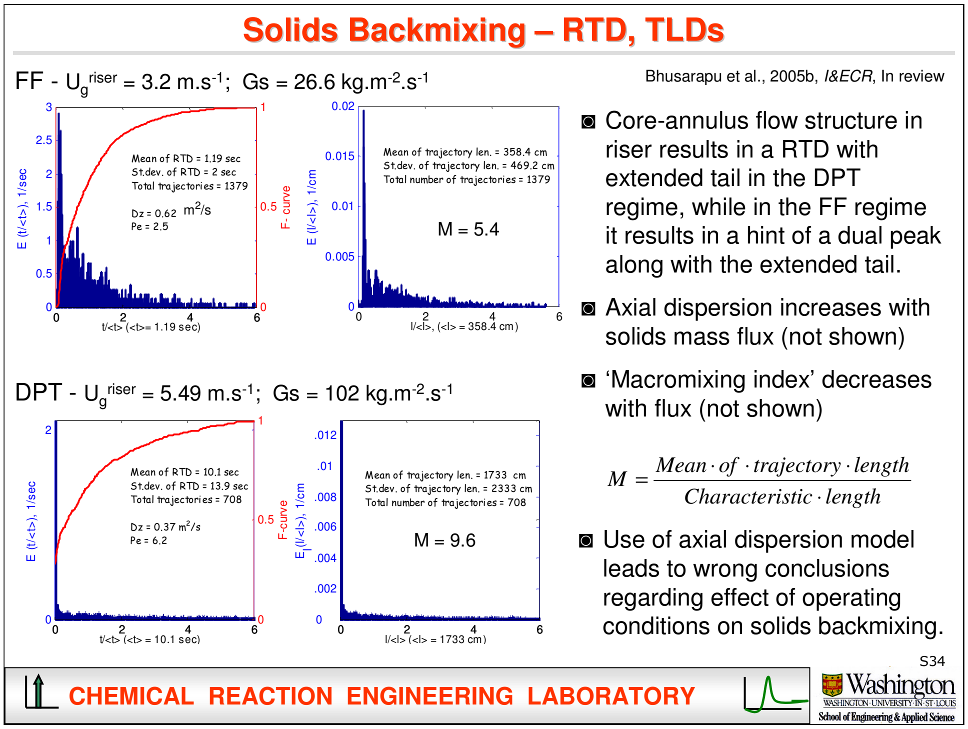


S32 **This slide shows how the p.d.f. of axial solids velocity characterize the flow dynamics. In the FF regime at high solids fluxes all solids flow up in the center of the column, some down-ward flow is observed at r/R = 0.44 and much down-ward flow at r/R = 0.94 close to the wall. In contrast, in the same FF regime at low solids fluxes, a bimodal p.d.f. is observed at the center of the column with many solid particles flowing downward even there, as well as at r/R of 0.44 and near the wall. A very slow moving solids seem to be present at the wall.**

In the DPT regime one never observes negative or even small positive velocities near the center of the column, with most of the downward flow occurring at the wall. That downward velocity increases with solids flux.



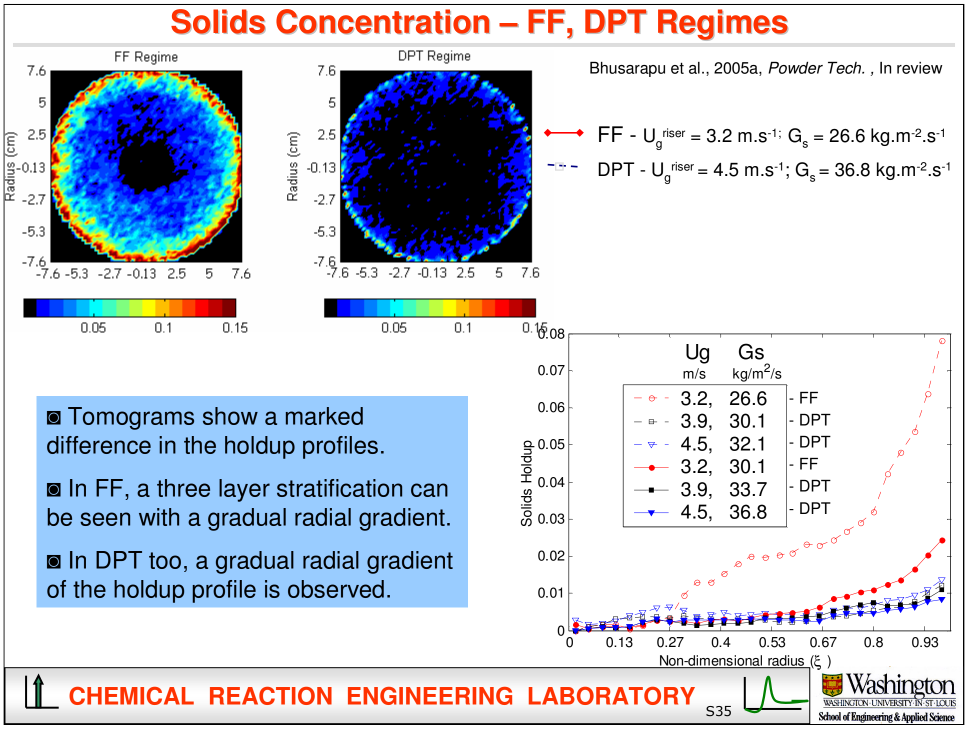
S33 **The ensemble averaged solids velocity field for the Sandia riser at high flux conditions is shown. Clearly the flow in the average sense is almost axisymmetric and one dimensional. Solids rise in the middle and fall by the wall. This is also observed at the CREL riser and at all other operating conditions.**



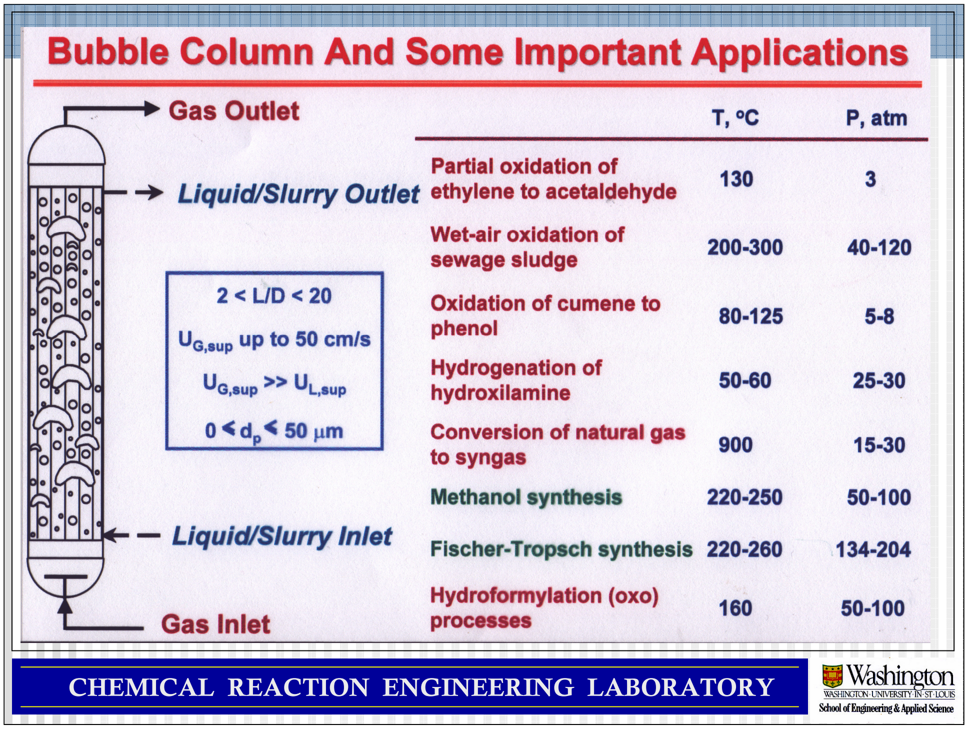
S34 **The core-annulus flow structure in the riser results in the RTD with extended tail in the DPT regime and in a hint of a dual peak in the FF regime along with the extended tail. As measure of backmixing one traditionally takes the axial dispersion coefficient, but in actuality the macromixing index, introduced by late professor Villermaux, is a much better measure of backmixing and is obrainable directly from the tracetory length distributions determined by CARPT.**

The macromixing index decreases with flux indicating approach to plug flow.

Clearly, the use of the axial dispersion model leads to the wrong conclusion regarding the effect of operating conditions on the extent of solids backmixing.

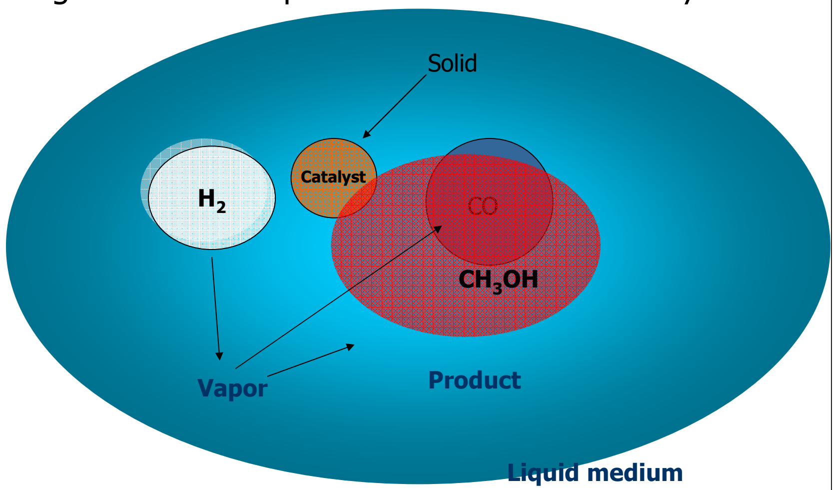


S35. **Gamma ray CT scans show a remarkable difference in solids distribution. In the FF regime a 3 layer structure is observed. In DPT regime a thin layer of solids at the wall has experimentally decreasing solids holdup as one moves inward to the center of the column.**



SL36 Let us look now at the application of CARPT-CT in developing an improved model for many of the bubble column uses. We have proven the validity of this model for FT, methanol and DME synthesis. In process industry bubble columns are operated at very high superficial velocity to increase their productivity. These are buoyancy dominated churn turbulent flows.

- These transformations require contacting of reactants and catalysts in different phases
- Successful operation and transfer of lab scale information to the industrial process requires knowledge of how the phases flow and how they mix



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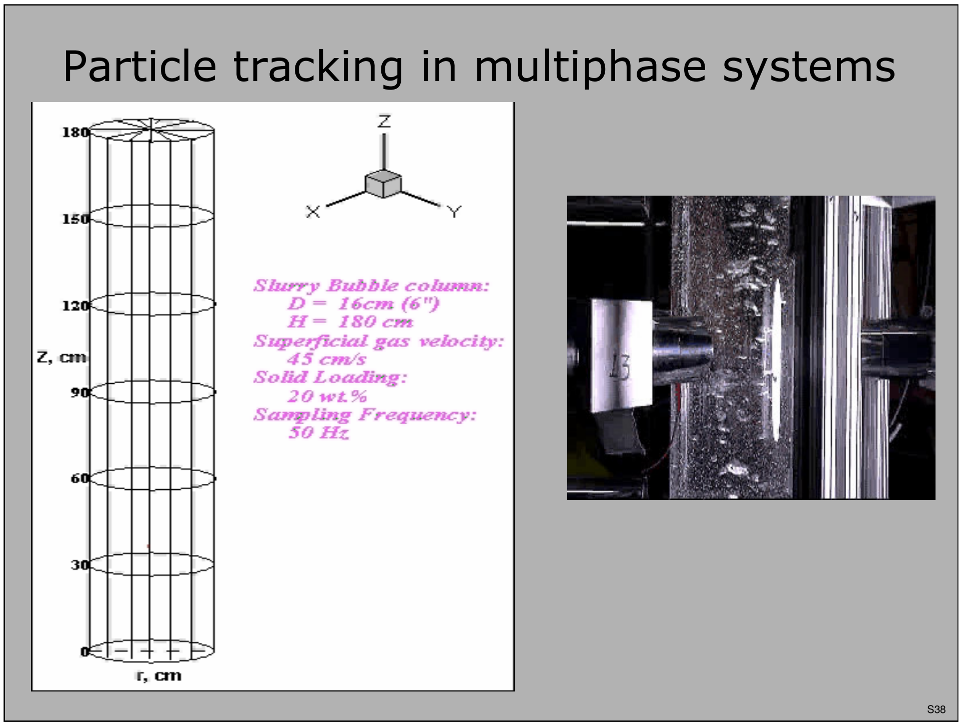
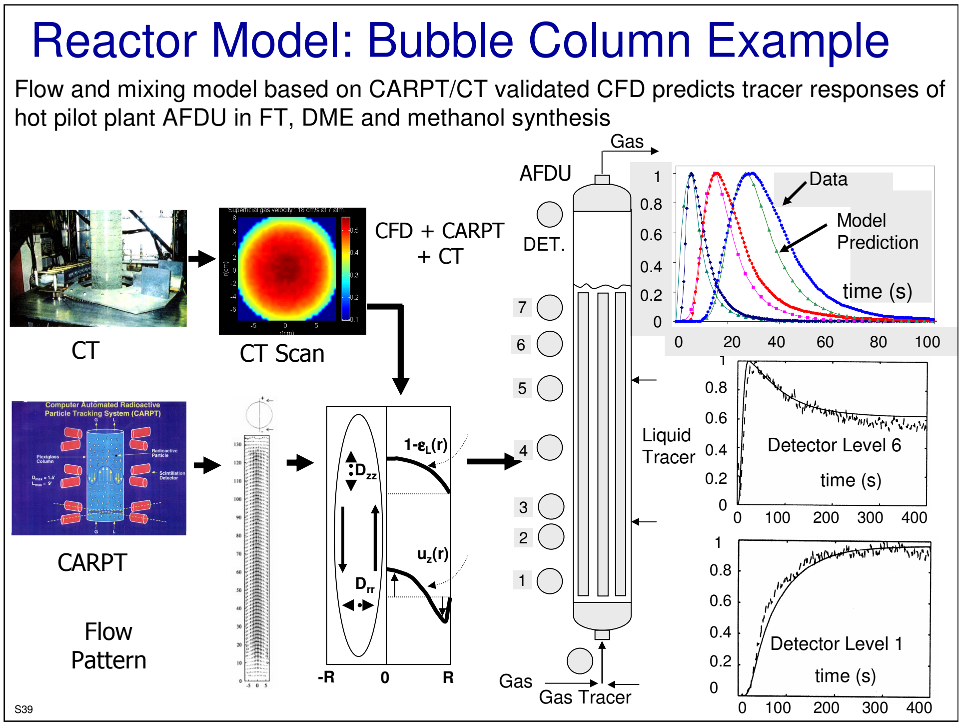
SLIDE 37. This reminds us that successful contacting of gas reactants on a solid catalyst in liquid solvent is needed. (The nice animation may not work on the web site).

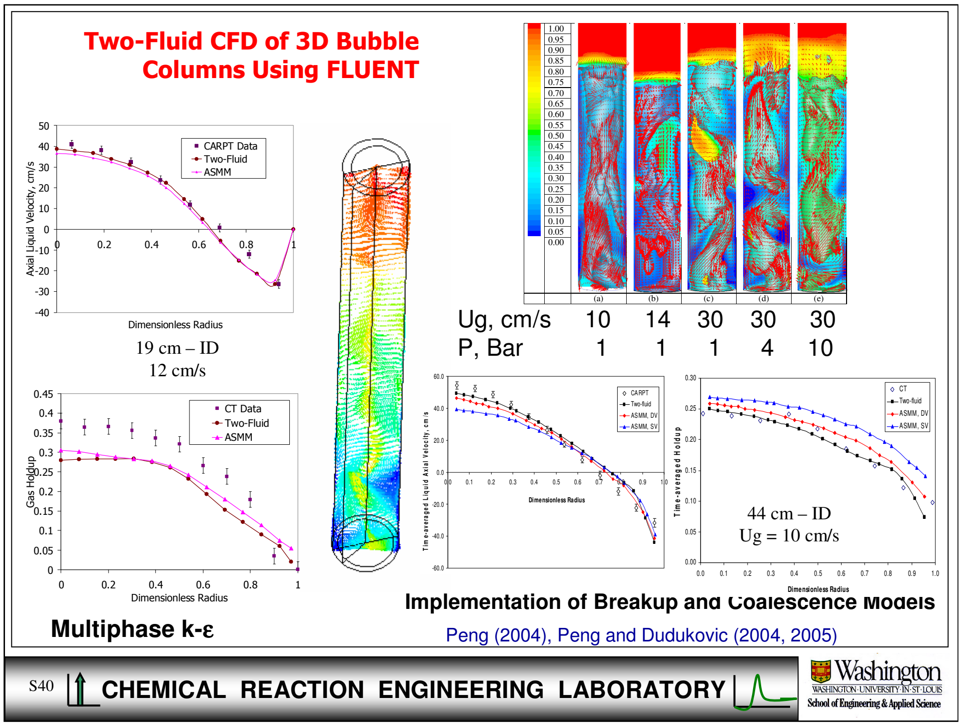


SLIDE 38. To appreciate CARPT we show this brief animation that exhibits the trajectory of the particle in a BC operated in churn turbulent flow. The column on the right is operated at much lower gas velocity. (We will repeat this separately at the end).

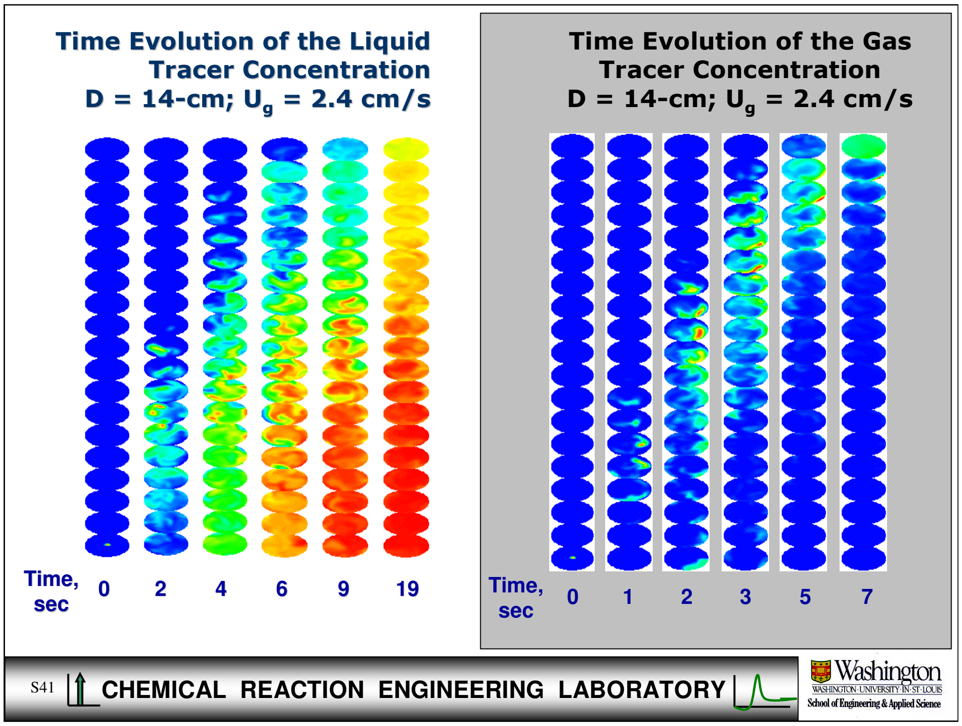


SLIDE 39. Here we illustrate the development of a predictive flow pattern model for bubble columns based on CT-CARPT data that were used for validation of CFD codes. In churn turbulent flow parabolic gas holdup profile drives the time averaged global scale liquid re-circulation in which radial and axial eddy diffusivities are superimposed. The model is able. with no adjustable parameters, to predict tracer responses for the liquid and gas tracer measured at different elevations in an operating pilot plant column at various processes.

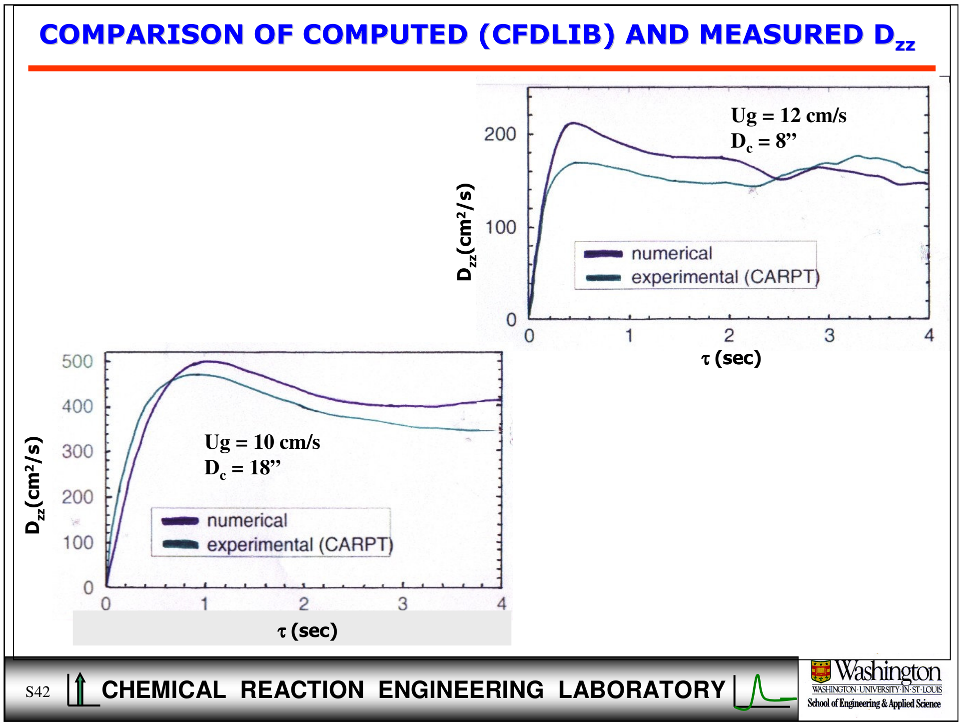
This is important for design of bubble column for FT synthesis and desulfurization of heavy fractions.



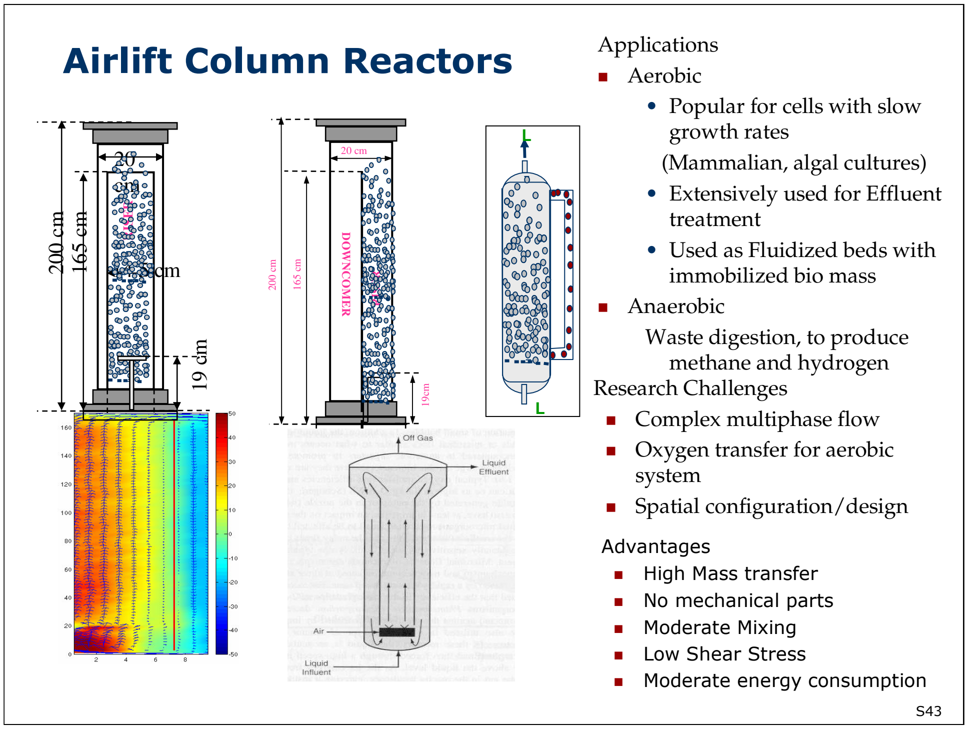
SLIDE 40. We have also obtained agreement with data in 3D churn turbulent flow based on selecting a good estimate of bubble size. We obtained a much better prediction of both liquid velocity and gas holdup distribution by incorporating the BPBE into CFD calculations.



SLIDE 41. Simulations of spreading of a tracer in the batch liquid, as well as the passage of gas tracer, can be readily simulated in 3D once the flow field is computed.



SLIDE 42. From such simulations one can compute the eddy diffusivities and compare with the CARPT data. Good agreement is obtained for axial diffusivity in bubbly flow.

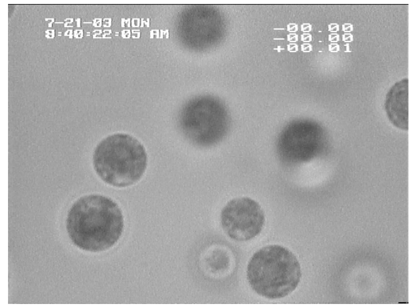


Slide 43 Airlift type of bubble columns with draft tube, split and external leg are popular in many biological applications. Optimal reactor selection may have an effect on reactor productivity.

Let us illustrate this by considering micro algae growth in such systems. This study was conducted by Professor Al-Dahhan and his graduate student, Huping Luo, in our CREL.

Interests in Microalgal/Cyanobacteria

- **High value products**
  - Pigments (food color to immunoassays)
  - Biologically active substances (antiviral, antifungal)
  - Polyunsaturated Fatty Acids (PUFA)
- **Biomass source**
  - Single Cell Protein (human, livestock)
  - Food additives (alginates, xantan gums)
- **Renewable energy**
  - Methane, biodiesel, ethanol or hydrogen
- **Wastewater and animal wastes treatment**
- **CO_2 Fixation**



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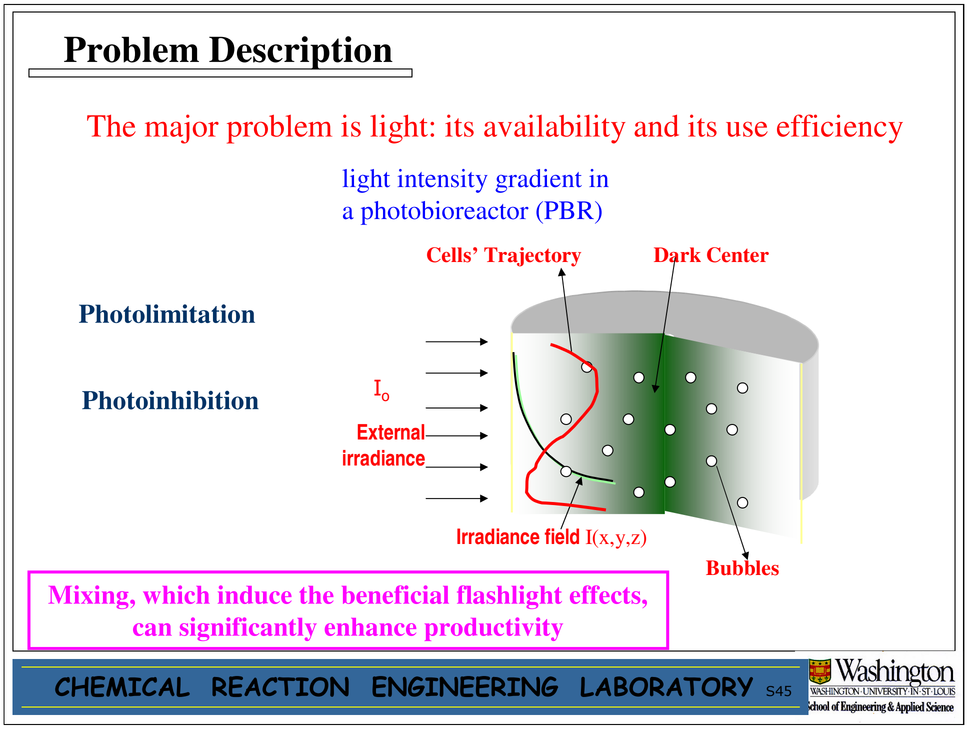
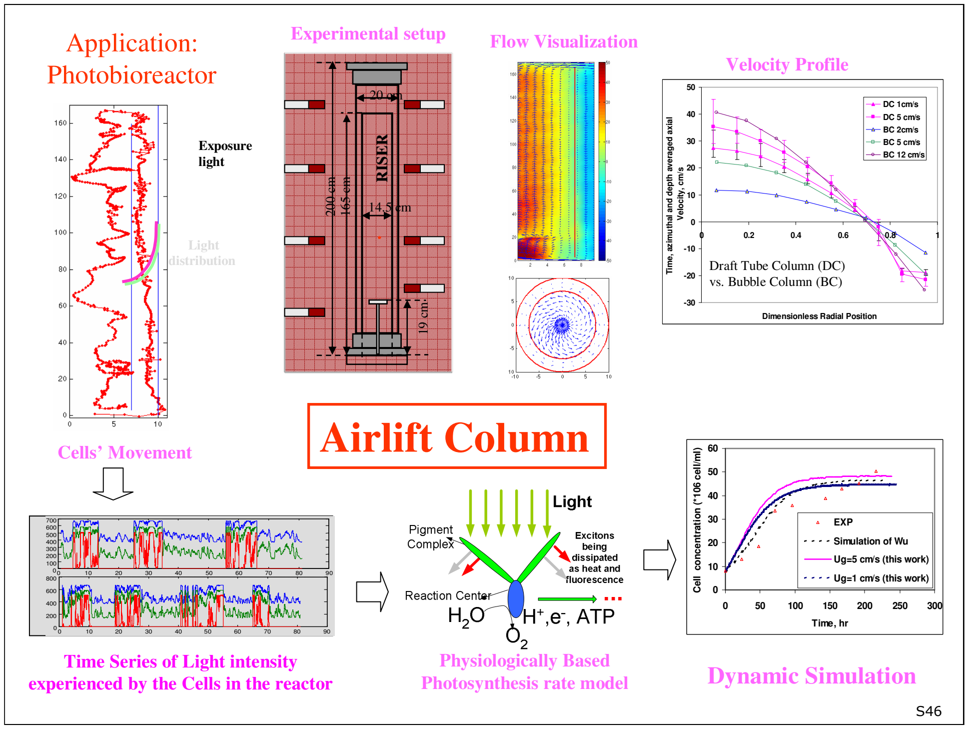
Slide 44: Micro algae /Cyano bacterial cultures can be used to produce high value added products, as biomass source for food and feed, as renewable energy source. Through the photo synthetic process they fix carbon dioxide and release oxygen. So availability of light is essential.



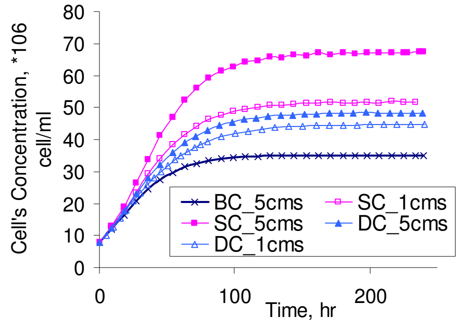
Slide 45: Cells in their passage trough the reactor get exposed to different levels of illumination. Too little light leads to photo limitation, too much light to photo inhibition. Proper mixing can significantly enhance the beneficial flashlight effect.



SL46 Using CARPT one develops the velocity flow pattern of algae in the system consisting of a riser and downer section. The ensemble averaged velocity field becomes available as a function of air superficial velocity used. The shear stress field is also developed.

In addition, for the first time, the illumination time distribution of the algae can be calculated. Tomography provides the density profiles needed for proper calculation of the Beer-Lambert effect. Coupling the illumination time history with three basic states of the algae and algae kinetics (not shown on the slide) one can predict the reactor performance.

Dynamic Model -- Results ; Luo and Al Dahhan(2003)

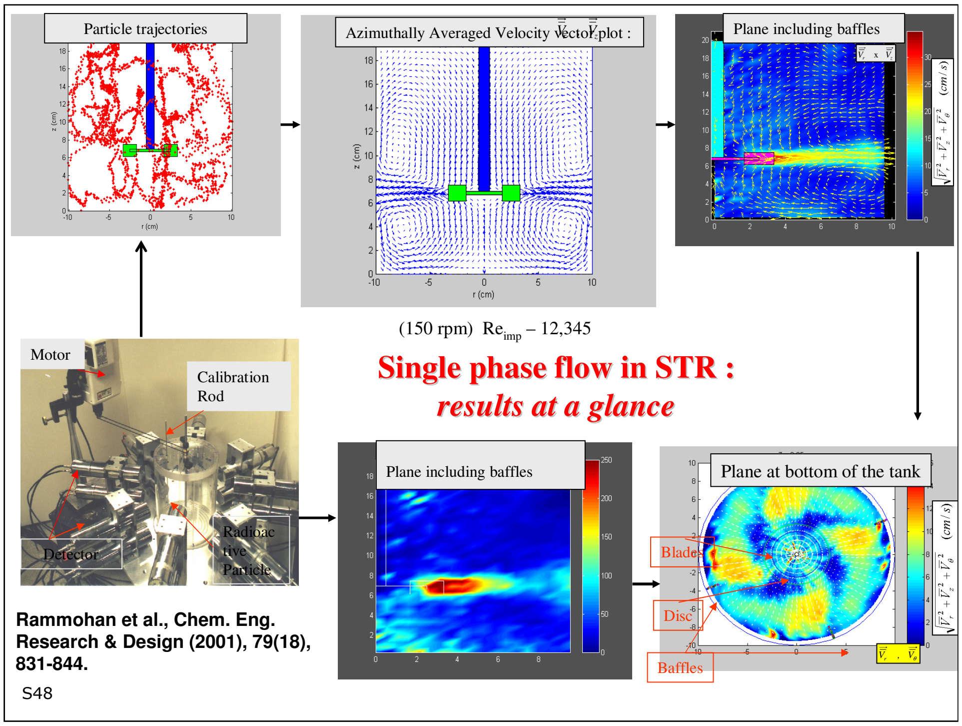


(BC: Bubble Column; SC: Split airlift column; DC: Draft tube airlift column)

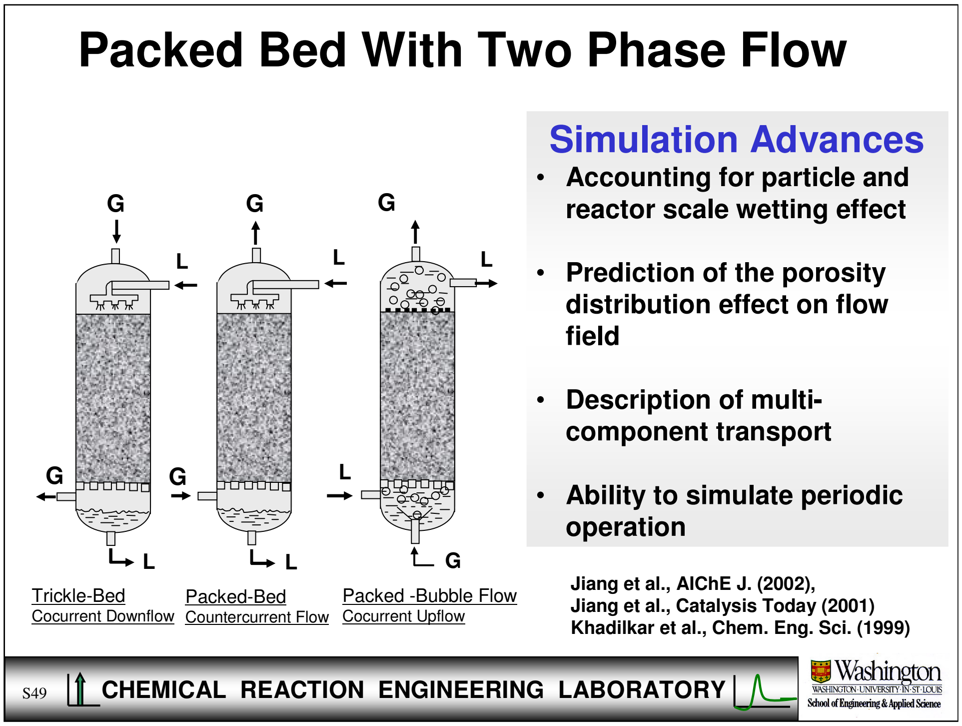
Simulation condition: External Irradiance: 250 μE m^{-2} s^{-1}; Initial Cells concentration: 8×10^{6} cells/*ml* (BC: Bubble column; SC: Split column; DC: draft tube column.)

Note: This dynamic model approach can be extended to any other physiologically based photosynthetic rate model and more reliable irradiance distribution model

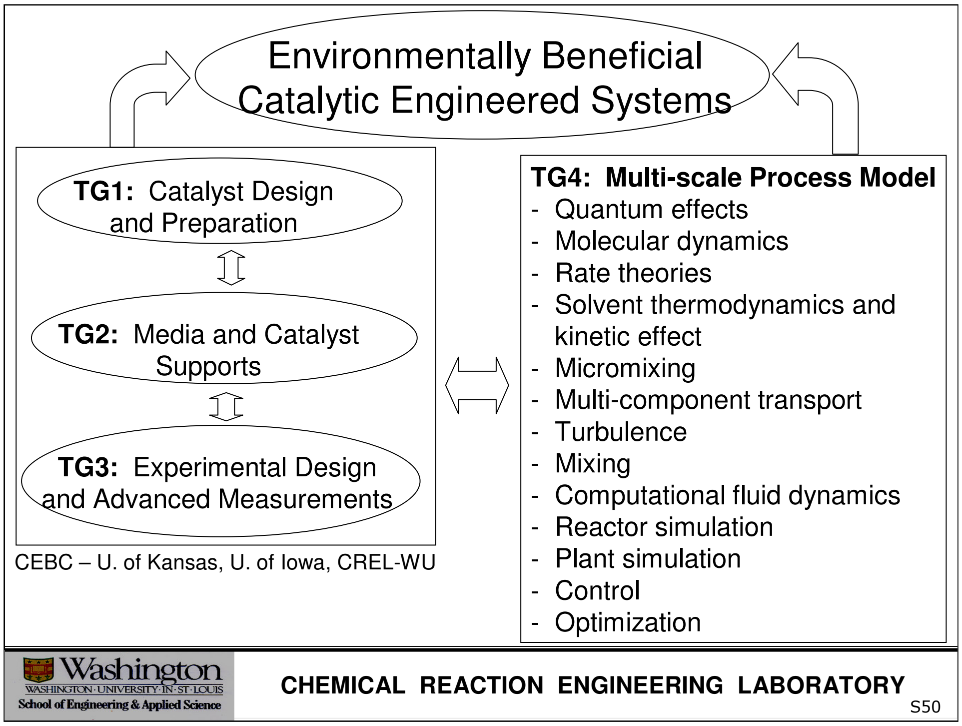
S47: Upon CFD validation, one can use the combined reactor and cell model to predict cell concentration in various reactor configurations to find out that at the same constant volumetric average irradiance a draft tube column is better than bubble column, and a split column is far the best!



SLIDE 48. Since stirred tanks are used in such a wide area of applications, we have confirmed that CARPT is capable of faithfully capturing the mean flow features, the intensity of vorticity and up to 80% of turbulent kinetic energy in single phase flow, where CARPT data is compared to LDA, PIV, etc. It takes only 16 hours for CARPT to obtain this information that takes months for other techniques to acquire. But CARPT data can be obtained in two and three phase flows where laser based techniques are useless.



SLIDE 49. Packed beds with two phase flow are also used extensively in industry. We have made advances of being able to use commercial CFD packages in modeling gas and liquid distribution in the bed given bed voidage distribution. We can account for particle and reactor wetting effects, describe multicomponent transport and simulate periodic operation. CT has proven useful here.



SLIDE 50. Based on the previously discussed concepts it is clear that systems approach is needed in development of environmentally beneficial catalytic engineered systems. We have joined the lead of the University of Kansas, and with them and U of Iowa, entered into a partnership for formation of a Center for Environmentally Beneficial Catalysis. CEBC became a reality as one of the 4 new NSF ERCs on September 1, 2003.

The idea is to implement a highly interactive multiscale approach consisting of experiments and modeling for development of new environmentally beneficial catalytic processes.

CONCLUSIONS

- The best way to protect the environment is to eliminate it or minimize production of undesired species at the source. This can only be done effectively via advances in and proper application of chemical reaction engineering (CRE).

- CRE advances require research on
  - Molecular scale (e.g., discovery of "green" processes, improved estimation of kinetic forms and constants, etc.)
  - Particle/Eddy scale (e.g., multi-component transport effects on complex kinetics, etc.)
  - Reactor scale (e.g., full description of large scale flow patterns and mixing, etc.)
- Most reactor systems involve multiphase flows and are opaque in character. Knowledge of flow patterns and phase contacting and their changes with scale-up is essential for proper prediction of reactor performance. Since CFD codes at present cannot predict with certainty the flow fields and phase distributions in such systems experimental data is needed for validation of the codes.

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SLIDE 51. In conclusion, it seems clear that the best way to prevent pollution is at the source. This requires the multiscale CRE approach consisting of molecular, particle/eddy and reactor scale considerations. Most reactor systems involve multiphase flows and we must validate CFD codes for them before we can use them in design and scale up.

CONCLUSIONS (continued)

- Gamma radiation based techniques like CT and CARPT are capable of providing data for validation of CFD codes of mechanistically based reactor models.
- The magnitude of CRE contributions to pollution prevention and reduction depends on the level of government and private funding of:
  - Fundamental CRE research
  - Generic research of various existing and new reactor types
  - Development of sustainable technologies

  (This in turn requires stable energy sources and globalization of regulations).

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SLIDE 52 Gamma radiation based techniques like CT and CARPT are capable of providing data for validating CFD codes and this gives rise to phenomenological reactor models.

The magnitude of CRE contributions to sustainable technology depends on the available funding of CRE research of various existing and new reactor types. Reactor scale research must be kept alive and on par with molecular scale discoveries.

Ultimately CRE contributions will depend on demand for it which is related to development and implementation of sustainable technology.

A major activity in this direction requires globalization of environmental regulations and solution to the energy question. Clean, stable preferably sustainable energy sources must be found. This per se is the key issue of green processing and is deserving of an Apollo type federally funded research program.

Acknowledgement of Financial Support and Effort in Advancing Multiphase Reaction Engineering and Establishing Unique CARPT/CT Technologies

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SLIDE 53. To develop experimental and modeling resources for advancing state of the art descriptions of reactor scale flow patterns and mixing requires a lot of resources. We at CREL were fortunate in the past to enjoy government and industrial support. We also had excellent students that worked with us. The future is less certain as molecular level research is exclusively emphasized, and production facilities move off shore and companies keep merging! However, as I illustrated today, reactor scale advances are needed in addition to molecular scale discoveries to convert green chemistry to green engineering and sustainable processes.

I am especially thankful to the National Science Foundation for the engineering research center grant (EEC-0310689) for the Center for Environmentally Beneficial Catalysis (CEBC) which made it possible to put some of these ideas together, hopefully in a coherent way.

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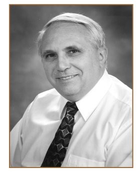
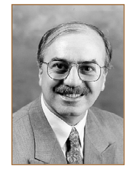


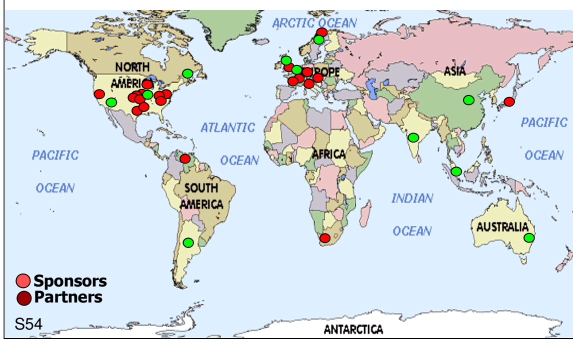
M. Dudukovic
Director



M. Al-Dahhan
Co-Director

Objectives

- Education and training of students
- Advancement of reaction engineering methodology
- Transfer of state-of-the-art reaction engineering to industrial practice



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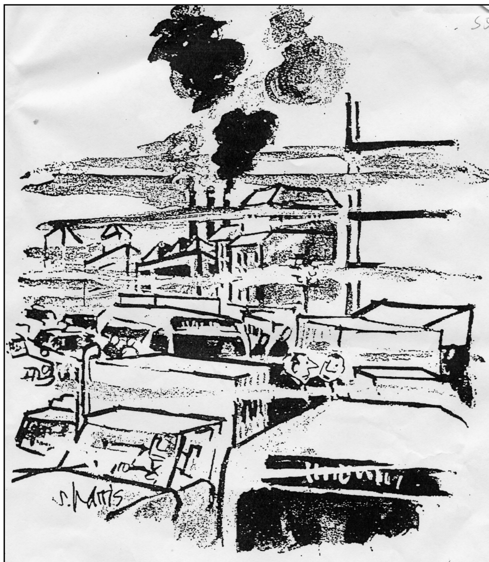
	UOP

SL54 **If you have a multiphase reactor modeling or scale up problem I invite you to work with us.**



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".

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SLIDE 55. Just to ensure that you can think outside the box let me inspire you with this cartoon. Since all research money seems to be flowing into the genome related research perhaps this unconventional idea is less far fetched than you think.